Dyes and Pigments 143 (2017) 151-164



Contents lists available at ScienceDirect

Dyes and Pigments

journal homepage: www.elsevier.com/locate/dyepig

Charged dinuclear Cu(I) complexes for solution-processed singleemitter warm white organic light-emitting devices



PIGMENTS

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ARTICLE INFO

Article history: Received 21 February 2017 Received in revised form 29 March 2017 Accepted 19 April 2017 Available online 20 April 2017

Keywords: Dinuclear Cu(I) complex Photoluminescence Single-emitter OLED

ABSTRACT

A series of charged dinuclear Cu(I) complexes were developed by functionalization of both central bipyrimidine-based ligands and organic phosphine ligands. The chemical modification of the ligands can effectively affect the absorption, emission and thermal stability properties of the Cu(I) complexes. The decomposition temperatures (T_d) are improved by using bulky ligands. Interestingly, the complexes with the triphenylamine group on the bipyrimidine ligand show higher photoluminescence quantum yield (PLQY) than the complexes bearing the triphenylphosphine oxide group, while the complexes having the triphenylamine group on the phosphine ligand display lower PLQY. The functional groups also show an obvious influence on the redox behaviors of these complexes. Most importantly, the organic lightemitting diodes (OLEDs) based on selected dinuclear Cu(I) complexes show impressive EL features. The best performance is achieved by the device based on complex Cu-MD-1 with the maximum external quantum efficiency (EQE) of 6.09%, current efficiency (CE) of 12.78 cd A⁻¹ and power efficiency (PE) of 5.93 lm W⁻¹, representing the state-of-the-art EL efficiencies reported for the charged Cu(I) complexes. In addition, the OLEDs based on these Cu(I) complexes can emit warm white light with Color Rendering Index (CRI) as high as 88 and Commission Internationale Ed I'eclairage (CIE) coordinates close to (0.40, 0.46), showing the great potential of these Cu(I) complexes in fabricating single-emitter warm WOLEDs. © 2017 Published by Elsevier Ltd.

1. Introduction

The long-lived emission properties of Cu(I) complexes with N^N type ligands have attracted the attention of the researchers since 1978 [1]. These Cu(I) complexes can show great potential in several fields, including luminescence-based sensing, solar-energy conversion and as bio-probes, etc. [2–4] However, the tetrahedral Cu(I) complexes tend to show weak emission with metal-to-ligand charge transfer (MLCT) character due to structural distortions in their excited states, which will enhance the non-radiative decay rate constant (k_{nr}) to give low photoluminescence quantum yields (PLQYs) [5,6]. Fortunately, the optimized Cu(I) complexes with both bulky N^N ligand and bidental P^P ligand can show greatly enhanced PLQYs in solution [7-10]. In addition, the emission of the Cu(I) complexes can be enhanced in the solid state due to the absence of the exciplex with the solvent molecules [10,11]. Generally, the emissions of these Cu(I) complexes mainly originate from triplet MLCT states (³MLCT) [12], which are very similar to those of cyclometalated phosphorescent Ir(III) and Pt(II) complexes [13–16]. However, considering the high cost of using Ir(III) and Pt(II) complexes to fabricate OLEDs, the emissive Cu(I) complexes with low cost and abundant supply are very competitive candidate as highperformance phosphorescent emitters for making low-cost OLEDs.

Since the first OLED fabricated using the Cu(I) complex Cu-1

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(Scheme 1) as emitter by Ma et al. [17], the EL efficiency of OLEDs using phenanthroline-based Cu(I) complex Cu-2 with bis[2-(diphenylphosphino)phenyl]ether has been improved to ca. 11 cd A^{-1} by Wang and Li, respectively [12,18]. Recently, novel phosphine-based Cu(I)X (X = Cl, Br, I) complexes can show outstanding electroluminescence (EL) performance [19,20]. For example, the three-coordinate Cu(I) complex Cu-3 prepared by Osawa et al. gave the EL efficiencies over 65 cd A^{-1} and 21% in vacuum-deposited devices, which are among the highest EL efficiencies ever achieved by the Cu(I) complexes [19]. In addition, Liu et al. have reported that the emissive Cu(I) complex Cu-4 can be formed in-situ by vacuum co-deposition to show high EL efficiencies in simple EL devices, providing an important outlet to construct high performance devices based on Cu(I) complexes [21]. Some high performance neutral dinuclear Cu(I) complexes have also been developed as emitters for OLEDs. Bian et al. reported that the μ -iodino-bridged dinuclear Cu(I) complex Cu-5 could show high EL efficiencies of 51.6 cd A^{-1} and 15.7% [22]. Baumann et al. demonstrated that the fully bridged dinuclear Cu(I) complex Cu-6 achieved an extremely high current efficiency (CE) of 76 cd A^{-1} and external quantum efficiency (EQE) of 23% [23]. However, although the charged dinuclear Cu(I) complexes (e.g. Cu-7 and Cu-8) have also been synthesized to investigate their structural and emissive features, they are rarely employed in OLEDs [24-26]. Therefore, we synthesized a series of charged dinuclear Cu(I) complexes bearing functional groups to explore not only their structure-property relationship, but also assess their potential in the field of OLEDs. The experimental results show that the thermally stable, photophysical and redox properties of these dinuclear Cu(I) complexes can be conveniently tuned by adjusting or modifying the ligands. Furthermore, solution-processed OLEDs based on selected dinuclear Cu(I) complexes can display satisfactory EL performance with the highest EQE of 6.09%, current efficiency (CE) of 12.78 cd A^{-1} and power efficiency (PE) of 5.93 Im W^{-1} , setting a benchmark of EL efficiencies for the charged Cu(I) complexes. More encouragingly, devices based on these charged Cu(I) complexes can emit intense warm white light with high CRI of 88. Generally, white light can be generated by mixing the red, green and blue (RGB) colors or by



Scheme 1. The molecular structures of some Cu(I) complexes.

ratiometric fine-tuning of two complementary colors of light. However, these two approaches require an elaborate design of device structures as well as the delicate balance between each emitting material, which will not favor the practical application at low cost. Therefore, the development of WOLEDs based on a single emitter becomes more attractive [27,28]. Our new Cu(I) complexes nicely show the great potential in fabricating single-emitter warm WOLEDs.

2. Experimentals

2.1. Methods

All reactions were conducted under a nitrogen atmosphere and no special precautions were required during the workup. Solvents were carefully dried and distilled from appropriate drying agents prior to use. Commercially available reagents were used without further purification unless otherwise stated. All reactions for the preparation of the organic compounds were monitored by TLC with Merck pre-coated aluminum plates. Flash column chromatography was carried out using silica gel from Shenghai Qingdao (200-300 mesh). UV-vis spectra were recorded on a Shimadzu UV-2250 spectrophotometer. Emission spectra and lifetimes of these compounds were recorded on an Edinburgh Instruments Ltd (FLSP920) fluorescence spectrophotometer using the software package provided by Edinburgh Instruments. The PLOYs of these dinuclear Cu(I) complexes in doped PMMA film on guartz substrate with ca. 10 wt % doping level were measured in an integration sphere associated with FLSP920 fluorescence spectrophotometer. The lifetimes were measured by a single photon counting spectrometer from Edinburgh Instruments FLS920 with a nano-LED as the excitation source. The data analysis was conducted by iterative convolution of the luminescence decay profile with the instrument response function using the software package provided by Edinburgh Instruments. Fast atom bombardment (FAB) mass spectra were collected with Finnigan MAT SSQ710 system. The thermal gravimetric analysis (TGA) was conducted on a NETZSCH STA 409C instrument under nitrogen with a heating rate of 20 K min⁻¹. Electrochemical measurements were measured using a Princeton Applied Research model 2273A potentiostat with a scan rate of 100 mV s⁻¹. A conventional three-electrode configuration consisting of a glassy carbon working electrode, a Pt-sheet counter electrode, and a Pt-wire reference electrode was used. The supporting electrolyte was 0.1 M [Bu₄N]PF₆ in MeCN. Ferrocene was added as a calibrant after each set of measurements, and all potentials reported are quoted with reference to the ferrocene-ferrocenium (Fc/Fc^+) couple.

2.2. Computational details

Density functional theory (DFT) calculations using the B3LYP were performed for all the Cu(I) complexes and their geometries were obtained by theoretical optimization during the computation. The basis set used for C, H, N and O atoms was 6-31G while effective core potentials with a LanL2DZ basis set were employed for P and Cu atom [29,30]. The energies of the excited states of the complexes were computed by time-dependent (TD) DFT (TD-DFT) based on all the ground-state geometries. All calculations were carried out using the Gaussian 09 program [31]. Mulliken population analyses were performed using MullPop [32]. Frontier molecular orbitals obtained from the DFT calculations were plotted using the Molden 3.7 program [33].

2.3. OLED fabrication and measurements

The pre-cleaned ITO glass substrates were treated with ozone for 20 min. Then, a 35 nm thick PEDOT:PSS was deposited on the ITO glass substrates by spin-coating. After drying 30 min at 100 °C, the emission layer of 50 nm was constructed by spin-coating the solution of the mixture of TCTA and Cu(I) complex in 1,2dichloroethane. After drying 20 min at 50 °C, TPBI, LiF and Al were evaporated successively at a base pressure of less than 10^{-6} Torr. The EL spectra and CIE coordinates were measured with a PR650 Spectra colorimeter. The *J*–*V*–*L* curves of the devices were recorded using a Keithley 2400/2000 source meter and the luminance was measured using a PR650 SpectraScan spectrometer. All of the experiments and measurements were carried out at room temperature under ambient conditions.

2.4. Synthesis

The synthesis of [(CH₃CN)₄Cu]BF₄ [34], 4-(diphenylamino)phenylboronic, **PPO-Br** and (4-bromophenyl)diphenylphosphine were prepared by the literature methods [35]. **DEPHOS** and **XANTPHOS** were purchased from Acros. The dinuclear Cu(I) complexes have been prepared by referring to the synthetic method employed for the preparation of mononuclear analogs [36].

2.4.1. Synthesis of MD-Br

2,2'-Bipyrimidine (0.5 g, 3.16 mmol), Br₂ (3 mL) and nitrobenzene (1.5 mL) were charged into a sealed reaction tube. The reaction mixture was heated to 160 °C for 24 h. Then, the reaction mixture was poured into 1 M Na₂S₂O₃ (30 mL) and the pH of the aqueous phase was adjusted to *ca*. 10. Then, the mixture was extracted with CH₂Cl₂ (3 × 30 mL). The organic phase was collected and dried over Mg₂SO₄. The crude product was purified by column chromatography on silica gel with a mixture of ethyl acetate (EA) and methanol (MeOH) (V_{EA}/V_{MeOH} = 5:1) as eluent to give the product as an off-white solid (0.19 g, Yield: 25%). ¹H NMR (400 MHz, CDCl₃): δ (ppm) 9.03 (s, 2H), 9.00 (d, *J* = 4.8 Hz, 2H), 7.44 (t, *J* = 4.8 Hz, 1H); ¹³C NMR (100 MHz, CDCl₃): δ (ppm) 161.61, 160.24, 158.70, 158.08, 121.66, 121.59; FAB-MS (*m*/*z*): 236, 238 [M]⁺; Anal. Calcd. for C₈H₅BrN₄: C, 40.53; H, 2.13; N, 23.63; found: C, 40.28; H, 2.38; N, 23.47.

2.4.2. Synthesis of PPO-B

PPO-Br (0.36 g, 1.0 mmol), bis(pinacolato)diboron (0.31 g, 1.2 mmol) potassium acetate (0.49 g, 5.0 mmol) were added to dioxane (15 mL) in an inert atmosphere and stirred at 100 °C for 18 h. After cooling to room temperature, water (20 mL) was added. The mixture was extracted with CH₂Cl₂ (3 × 20 mL). The collected organic phase was dried over anhydrous MgSO₄ and the solvent was removed under reduced pressure. The residue was chromatographed on a silica column using CH₂Cl₂ (DCM) and petroleum ether (PE) (5:1 v/v) as eluent to afford the product as a white solid (0.34 g, 83%). ¹H NMR (400 MHz, CDCl₃): δ (ppm) 7.89–7.87 (m, 2H), 7.70–7.62 (m, 6H), 7.55–7.51 (m, 2H), 7.46–7.42 (m, 4H). ¹³C NMR (100 MHz, CDCl₃): δ (ppm) 134.56, 134.44, 132.11, 132.01, 131.93, 131.91, 131.21, 131.11, 128.51, 128.39, 84.17, 24.82. ³¹P NMR (162 MHz, CDCl₃): δ (ppm) 29.15; FAB-MS (*m/z*): 404 [M] ⁺. Anal. calcd. for C₂₄H₂₆BO₃P: C, 71.31; H, 6.48; found: C, 71.19; H, 6.53.

2.4.3. Synthesis of MD-TPA

Under a N_2 atmosphere, 4-(diphenylamino)phenylboronic (0.094 g, 0.325 mmol), **MD-Br** (0.0516 g, 2.17 mmol) and Pd(PPh₃)₄ (0.025 g, 0.021 mmol) were added to the mixture of THF (5 mL) and 2 M K₂CO₃ (3 mL). The reaction mixture was stirred at 110 °C for 16 h. After cooling to room temperature, water (20 mL) was added and the mixture was extracted with CH₂Cl₂ (3 × 20 mL). The organic phase was collected and dried over Mg₂SO₄. After removing the solvent, the residue was purified by column chromatography on silica gel with a mixture of ethyl acetate (EA) and methanol (MeOH) (V_{EA}/V_{MeOH} = 3:1) as eluent to give the product as a white solid (0.071 g, Yield: 81%). ¹H NMR (400 MHz, CDCl₃): δ (ppm) 9.18 (s, 2H), 9.04 (d, *J* = 4.8 Hz, 2H), 7.55 (d, *J* = 8.8 Hz, 2H), 7.44 (t, *J* = 4.4 Hz, 1H), 7.33–7.29 (m, 4H), 7.21–7.15 (m, 6H), 7.10 (t, *J* = 4.4 Hz, 2H); ¹³C NMR (100 MHz, CDCl₃): δ (ppm) 158.07, 155.20, 149.26, 147.04, 129.50, 127.78, 125.12, 123.86, 122.99; FAB-MS (*m/z*): 401 [M]⁺; Anal. Calcd. for C₂₆H₁₉N₅: C, 77.79; H, 4.77; N, 17.44; found: C, 77.58; H, 4.53; N, 17.23.

2.4.4. Synthesis of MD-PPO

Under a N₂ atmosphere, **PPO-B** (0.14 g, 0.35 mmol), **MD-Br** (0.07 g, 0.30 mmol) and Pd(PPh₃)₄ (0.035 g, 0.03 mmol) were added to the mixture of THF (10 mL) and 2 M K₂CO₃ (3 mL). The reaction mixture was stirred at 110 °C for 16 h. After cooling to room temperature, water (20 mL) was added and the mixture was extracted with CH_2Cl_2 (3 \times 30 mL). The organic phase was collected and dried over Mg₂SO₄. After removing the solvent, the residue was purified by column chromatography on silica gel with a mixture of ethyl acetate (EA) and methanol (MeOH) ($V_{EA}/V_{MeOH} = 5:1$) as eluent to give the product as a white solid (0.10 g, Yield: 80%). ¹H NMR (400 MHz, CDCl₃): δ (ppm) 9.23 (s, 2H), 9.05 (d, J = 4.8 Hz, 2H), 7.90-7.85 (m, 2H), 7.79-7.77 (m, 2H), 7.73-7.68 (m, 4H), 7.60-7.56 (m, 2H), 7.52–7.45 (m, 5H); ¹³C NMR (100 MHz, CDCl₃): δ (ppm) 162.04, 161.58, 158.14, 156.10, 137.24, 134.53, 133.51, 133.29, 133.19, 132.58, 132.23, 132.20, 132.10, 132.00, 131.54, 128.72, 128.60, 127.25, 127.13, 121.63; ³¹P NMR (162 MHz, CDCl₃): δ (ppm) 28.43 (s); FAB-MS (*m*/*z*): 434 [M]⁺; Anal. Calcd. for C₂₆H₁₉N₄OP: C, 71.88; H, 4.41; N, 12.90; found: C, 71.76; H, 4.48; N, 12.79.

2.4.5. Synthesis of TPA-PPP

Under a N₂ atmosphere, 4-(diphenylamino)phenylboronic (0.82 g, 2.84 mmol), (4-bromophenyl)diphenylphosphine (0.80 g, 2.35 mmol) and Pd(PPh₃)₄ (0.15 g, 0.13 mmol) were added to the mixture of THF (20 mL) and 2 M K₂CO₃ (6 mL). The reaction mixture was stirred at 110 °C for 16 h. After cooling to room temperature, water (30 mL) was added and the mixture was extracted with CH_2Cl_2 (3 × 60 mL). The organic phase was collected and dried over Mg₂SO₄. After removal of the solvent, the residue was purified by column chromatography on silica gel with a mixture of CH₂Cl₂ (DCM) and petroleum ether (PE) (bp 60–90 °C) ($V_{DCM}/V_{PE} = 1:4$) as eluent to give the product as a white solid (0.98 g, Yield: 85%). ¹H NMR (400 MHz, CDCl₃): δ (ppm) 7.54 (dd, J = 1.4, 8.0 Hz, 2H), 7.47 (d, J = 8.8 Hz, 2H), 7.37–7.33 (m, 10H), 7.29–7.25 (m, 6H), 7.14–7.11 (m, 6H), 7.05-7.17 (m, 2H); ³¹P NMR (162 MHz, CDCl₃): δ (ppm) -6.19 (s); FAB-MS (m/z): 505 [M]⁺; Anal. Calcd. for C₃₆H₂₈NP: C, 85.52; H, 5.58; N, 2.77; found: C, 85.47; H, 5.49; N, 2.79.

2.4.6. General procedure for the synthesis of the dinuclear Cu(1) complexes

Under a N₂ atmosphere, $[(CH_3CN)_4Cu]BF_4$ (1.0 equiv) and the organic phosphine ligand (2.0 equiv for PPh₃ and **TPA-PPP**; 1.0 equiv for **DPEPHOS** and **XANTPHOS**) were mixed in CH₂Cl₂. After stirring for 2 h at room temperature, the corresponding 2,2'-bipyrimidine-based ligand (0.5 equiv) was added. The reaction was allowed to proceed at room temperature for 4 h. The solvent was removed under reduced pressure. The colored residue was dissolved in CH₂Cl₂ (2 mL) and precipitated in diethyl ether. The precipitation was collected by filtration and washed with diethyl ether three times. The title Cu(I) complexes were obtained as colored solids in high yields.

2.4.6.1. **Cu-MD-1** [24](yield: 94%) ¹H NMR (400 MHz, CDCl₃). δ (ppm) 8.74 (d, J = 5.2 Hz, 4H), 7.91 (t, J = 5.2 Hz, 2H), 7.31 (t, J = 7.2 Hz, 12H), 7.15 (t, J = 7.2 Hz, 24H), 7.06 (br, 24H); ³¹P NMR (162 MHz, CDCl₃): δ (ppm) 3.81 (s); FAB-MS (*m*/*z*): 1332 [M-2BF₄]⁺; Anal. Calcd. for C₈₀H₆₆B₂Cu₂F₈N₄P₄: C, 63.72; H, 4.41; N, 3.72; found: C, 63.53; H, 4.48; N, 3.63.

2.4.6.2. **Cu-MD-2** [37](yield: 91%) ¹H NMR (400 MHz, CDCl₃). δ (ppm) 8.91 (d, J = 4.8 Hz, 4H), 7.95 (t, J = 5.2 Hz, 2H), 7.29–7.22 (m, 12H), 7.17 (t, J = 7.2 Hz, 16H), 7.00–6.95 (m, 24H), 6.71 (m, 4H); ¹³C NMR (100 MHz, CDCl₃): δ (ppm) 158.26, 134.41, 132.80, 132.34, 130.72, 129.28, 125.42; ³¹P NMR (162 MHz, CDCl₃): δ (ppm) –10.65 (s); FAB-MS (m/z): 1360 [M-2BF₄]⁺; Anal. Calcd. for C₈₀H₆₂B₂Cu₂F₈N₄O₂P₄: C, 62.56; H, 4.07; N, 3.65; found: C, 62.37; H, 3.89; N, 3.47.

2.4.6.3. **Cu-MD-3** (yield: 90%) ¹H NMR (400 MHz, CDCl₃). δ (ppm) 8.54 (d, J = 5.2 Hz, 4H), 7.86 (t, J = 5.2 Hz, 2H), 7.68 (d, J = 7.6 Hz, 4H), 7.22 (t, J = 7.6 Hz, 8H), 7.18 (t, J = 7.6 Hz, 4H), 7.07 (t, J = 7.2 Hz, 16H), 6.90 (m, 16H), 6.61 (m, 4H); 1.77 (s, 12H); ¹³C NMR (100 MHz, CDCl₃): δ (ppm) 158.05, 155.03, 134.06, 132.40, 131.48, 130.50, 130.29, 130.11, 129.93, 129.25, 129.20, 129.16, 128.05, 126.77, 125.37, 124.57, 118.62, 118.47, 118.31 36.11, 28.27; ³¹P NMR (162 MHz, CDCl₃): δ (ppm) –13.13 (s); FAB-MS (*m*/*z*): 1440 [M-2BF₄]⁺; Anal. Calcd. for C₈₆H₇₀B₂Cu₂F₈N₄O₂P₄: C, 63.91; H, 4.37; N, 3.47; found: C, 63.79; H, 4.50; N, 3.35.

2.4.6.4. **Cu-MD-4** (yield: 91%) ¹H NMR (400 MHz, CDCl₃). δ (ppm) 8.85 (d, J = 5.2 Hz, 4H), 7.97 (t, J = 5.2 Hz, 2H), 7.40 (d, J = 8.0 Hz, 8H), 7.34 (d, J = 8.4 Hz, 8H), 7.27–7.23 (m, 24H), 7.15–7.03 (m, 72H); ¹³C NMR (100 MHz, CDCl₃): δ (ppm) 158.31, 148.08, 147.34, 143.15, 133.61, 132.65, 132.46, 131.03, 130.80, 129.35, 128.07, 127.75, 127.22, 126.92, 124.76, 123.32, 123.22; ³¹F NMR (162 MHz, CDCl₃): δ (ppm) 2.91 (s); FAB-MS (m/z): 2304 [M-2BF₄]⁺; Anal. Calcd. for C₁₅₂H₁₁₈B₂Cu₂F₈N₈P₄: C, 73.58; H, 4.79; N, 4.52; found: C, 73.63; H, 4.84; N, 4.35.

2.4.6.5. **Cu-MD-5** (yield: 90%) ¹H NMR (400 MHz, CDCl₃). δ (ppm) 8.60 (br, 4H), 7.72 (br, 1H), 7.37 (t, J = 8.0 Hz, 4H), 7.30–7.27 (m, 10H), 7.21–7.14 (m, 60H); ¹³C NMR (100 MHz, CDCl₃): δ (ppm) 158.09, 153.15, 150.85, 148.04, 147.36, 146.29, 142.95, 133.58, 132.99, 130.79, 129.74, 129.40, 129.26, 128.36, 127.73, 127.17, 125.99, 124.80, 123.39, 123.13, 121.37; ³¹P NMR (162 MHz, CDCl₃): δ (ppm) 4.48 (s); FAB-MS (*m/z*): 1575 [M-2BF₄]⁺; Anal. Calcd. for C₉₈H₇₉B₂Cu₂F₈N₅P₄: C, 67.21; H, 4.55; N, 4.00; found: C, 67.05; H, 4.39; N, 3.82.

2.4.6.6. **Cu-MD-6** (yield: 92%) ¹H NMR (400 MHz, CDCl₃). δ (ppm) 8.72 (br, 4H), 7.82 (br, 1H), 7.34–7.02 (m, 126H); ¹³C NMR (100 MHz, CDCl₃): δ (ppm) 147.96, 147.34, 132.95, 130.71, 129.68, 129.35, 129.22, 127.70, 127.09, 125.88, 124.73, 123.31, 123.14; ³¹P NMR (162 MHz, CDCl₃): δ (ppm) 3.49 (s); FAB-MS (*m*/*z*): 2548 [M-2BF₄]⁺; Anal. Calcd. for C₁₇₀H₁₃₁B₂Cu₂F₈N₉P₄: C, 74.94; H, 4.85; N, 4.63; found: C, 74.69; H, 4.58; N, 4.37.

2.4.6.7. **Cu-MD-7** (yield: 93%) ¹H NMR (400 MHz, CDCl₃). δ (ppm) 8.69 (d, J = 29.6 Hz, 4H), 7.95 (t, J = 4.8 Hz, 2H), 7.79–7.74 (m, 4H), 7.59–7.52 (m, 8H), 7.33–7.13 (m, 61H); ¹³C NMR (100 MHz, CDCl₃): δ (ppm) 158.12, 154.84, 137.07, 133.48, 133.38, 132.97, 132.30, 132.12, 132.02, 130.79, 129.24, 128.88, 128.76, 127.94, 127.82, 126.56; ³¹P NMR (162 MHz, CDCl₃): δ (ppm) 28.81, 4.61 (s); FAB-MS (m/z): 1608 [M-2BF4]⁺; Anal. Calcd. for C₉₈H₇₉B₂Cu₂F₈N₄OP₅: C, 65.97; H, 4.46; N, 3.14; found: C, 65.79; H, 4.32; N, 2.89.

2.4.6.8. **Cu-MD-8** (yield: 88%) ¹H NMR (400 MHz, CDCl₃). δ (ppm) 8.80 (d, J = 16.0 Hz, 4H), 7.88 (br, 2H), 7.77–7.86 (m, 4H), 7.43–7.36

(m, 24H), 7.28–6.99 (m, 97H); 13 C NMR (100 MHz, CDCl₃): δ (ppm) 147.96, 147.32, 142.96, 133.63, 133.41, 132.79, 132.06, 131.96, 130.71, 129.34, 128.84, 128.72, 127.99, 127.87, 127.67, 127.10, 126.62, 124.71, 123.28, 123.18; 31 P NMR (162 MHz, CDCl₃): δ (ppm) 28.58, 3.61 (s); FAB-MS (*m*/*z*): 2582 [M-2BF₄]⁺; Anal. Calcd. for C₁₇₀H₁₃₁B₂Cu₂F₈-N₈OP₅: C, 74.05; H, 4.79; N, 4.06; found: C, 73.93; H, 4.68; N, 3.98.

3. Results and discussion

3.1. Synthesis

The synthetic route for these complexes are shown in Scheme 2 and Scheme 3. The ligands, i.e., **MD-TPA**, **MD-PPO** and **TPA-PPP**, were prepared through Suzuki cross-coupling reaction in high yields. In the ³¹P NMR spectra, the single resonance peak at *ca*. 28.43 ppm and -6.19 ppm can be assigned to the $-POPh_3$ unit in **MD-PPO** and $-PPh_3$ unit in **TPA-PPP**, respectively.

The bipyrimidine-based dinuclear Cu(I) complexes can be easily prepared in high yields by firstly treating the precursor Cu(I) complex [(CH₃CN)₄Cu]BF₄ with the corresponding organic phosphine ligand, and then adding the 2,2'-bipyrimidine-based ligand at room temperature. The target bipyrimidine-based dinuclear Cu(I) complexes can be purified by precipitation in diethyl ether. In the ¹H NMR spectra of the dinuclear Cu(I) complexes, the two resonance sets with peaks at 9.0 ppm and 8.0 ppm indicate the protons on the bipyrimidine core of the central ligands. The single resonance peak located at *ca.* 3.0–4.0 ppm in the ³¹P NMR spectra can be assigned to the phosphine moieties in either **PPh₃** or **TPA-PPP** from **Cu-MD-1**, **Cu-MD-4**, **Cu-MD-5** and **Cu-MD-6**. Owing to the influence of the ether bond in the bis(2-diphenylphosphinophenyl)ether (**DPE-PHOS**) and 4,5-bis(diphenylphosphino)-9,9-dimethylxanthene (**XANTPHOS**), the chemical shifts for the phosphine moiety in **Cu-MD-2** (–10.65 ppm) and **Cu-MD-3** (–13.13 ppm) are in the negative region. In the ³¹P NMR spectra for both **Cu-MD-7** and **Cu-MD-8**, there are two singlet peaks which can be assigned to the –POPh₂ (29.0 ppm) and –PPh₂ (4.0 ppm), respectively.

3.2. Thermal stability

The thermal stability of these bipyrimidine-based dinuclear Cu(I) complexes was characterized by thermogravimetric analysis (TGA) (Table 1). For the complexes bearing small-size phosphine ligand PPh₃, **Cu-MD-1**, **Cu-MD-5** and **Cu-MD-7** exhibit noticeably lower decomposition temperature ($T_d < 290 \,^{\circ}$ C) than the complexes bearing either bidentate phosphine ligand **DPEPHOS** and **XANTPHOS** (**Cu-MD-2** $T_d = 380 \,^{\circ}$ C and **Cu-MD-3** $T_d = 385 \,^{\circ}$ C) or





Scheme 3. Synthesis of the dinuclear Cu(I) complexes.

Table 1Decomposition temperatures (T_d) for these dinuclear Cu(I) complexes.

Complex	Cu-MD-1	Cu-MD-2	Cu-MD-3	Cu-MD-4	Cu-MD-5	Cu-MD-6	Cu-MD-7	Cu-MD-8
<i>T</i> _d (°C)	285	380	385	359	282	366	260	366

large-size phosphine ligand **TPA-PPP** (**Cu-MD-4** $T_d = 359 \degree$ C, **Cu-MD-6** $T_d = 366 \degree$ C and **Cu-MD-8** $T_d = 366 \degree$ C) (Table 1). It seems that chemical tailoring of the central bipyrimidine ligand might not exert a sound influence on the thermal stability of these complexes. Hence, these TGA results clearly indicate that the thermal stability of these dinuclear Cu(I) complexes is mainly decided by the nature of the phosphine ligands. According to their structural features, the decomposition of these dinuclear Cu(I) complexes should be induced by the cleavage of the phosphine ligands. Reasonably, the large-size and bidentate phosphine ligands are difficult to cleave from the Cu(I) centers, in line with the aforementioned TGA results.

3.3. Photophysical properties and theoretical calculations

The UV–Vis absorption spectra of these dinuclear Cu(I) complexes in CH₂Cl₂ are shown in Fig. 1. All these dinuclear Cu(I) complexes typically exhibit two sets of absorption bands. The intense UV absorption bands before *ca*. 350 nm can be ascribed to the π - π * transition processes from both bridging bipyrimidinebased ligands and the organic phosphine ligands. For **Cu-MD-4**, **Cu-MD-6** and **Cu-MD-8**, there is an intense absorption band located at *ca*. 360 nm (Fig. 1 and Table 2), which can be assigned to the π - π * transition associated with the triphenylamine unit. This result has



Fig. 1. UV–Vis absorption spectra of the bipyrimidine-based dinuclear Cu(I) complexes.

also been observed in other complexes bearing triphenylamine or similar units [38,39]. Besides the intense absorption bands in the UV region, the weak and broad absorption bands located in the long wavelength region have been detected except for Cu-MD-4. Cu-MD-6 and Cu-MD-8 (Fig. 1). According to the reported results for Cu(I) complexes, these weak absorption bands can be ascribed to the charge transfer (CT) transitions. The indiscernible absorptions of Cu-MD-4, Cu-MD-6 and Cu-MD-8 in the long wavelength region may be caused by the overlap between the weak absorption bands and the strong π - π ^{*} transition bands from the triphenylamine unit. Fig. 1 also indicates that the MLCT absorption bands of these Cu(I) complexes can be red-shifted with an enhanced intensity by introducing an electron-donating triphenylamine moiety to the bridging bipyrimidine ligand. However, it seems that the electronwithdrawing triphenylphosphine oxide unit shows an inappreciable influence on the CT absorption bands of these Cu(I) complexes as indicated by the similar CT absorption features of Cu-MD-7 and Cu-MD-8 with respect to that of the reference complex Cu-MD-1.

In order to gain insight of the absorption behaviors of these Cu(I) complexes, the transition features of the representative complexes have been obtained theoretically by the time-dependent density functional theory (TD-DFT) calculations (Table 3). Due to its large contribution (>90%) to the lowest singlet excited states (S₁), the HOMO \rightarrow LUMO transition (H \rightarrow L) features can represent the character of the S₀ \rightarrow S₁ transition in these dinuclear Cu(I) complexes. As shown in Fig. 2, the HOMOs are mainly located on the Cu(I) center

and the Cu–P σ -bonding orbital, while the LUMOs are contributed by the π -antibonding orbital of the central bipyrimidine-based ligands in Cu-MD-1, Cu-MD-2, Cu-MD-3 and Cu-MD-7. Hence, their S₁ states exhibit obvious metal-to-ligand charge transfer (MLCT) character. Accordingly, the low-energy weak CT absorption bands in Cu-MD-1, Cu-MD-2, Cu-MD-3 and Cu-MD-7 should be induced by the MLCT transition. Differently, the $H \rightarrow L$ transition in Cu-MD-5 displays inter-ligand charge transfer (ILCT, *i.e.* from the triphenylamine unit to the bipyrimidine segment) property with very minor involvement from the Cu(I) centers. Thus, the S₁ states from Cu-MD-5 possess ILCT feature and its weak CT absorption band is mainly assigned to ILCT as well. From the TD-DFT results (Table 3), the oscillator strength (*f*) of the $S_0 \rightarrow S_1$ transition in **Cu-MD-5** (*ca.* 0.6619) is nearly ten times higher than that for **Cu-MD-1** (ca. 0.0699), Cu-MD-2 (ca. 0.0839), Cu-MD-3 (ca. 0.0549) and Cu-MD-7 (ca. 0.0664). The upshot is that **Cu-MD-5** should show much stronger CT absorption bands, which is in good agreement with the experimental results in Fig. 1. These results also indicate the validity of the theoretical computational results in interpreting the absorption behavior of these dinuclear Cu(I) complexes. As for Cu-**MD-4** and **Cu-MD-8**, they have similar $H \rightarrow L$ transition patterns (Fig. 2), indicating that their $S_0 \rightarrow S_1$ transitions are dominated by the ILCT character. Therefore, it is reasonable that Cu-MD-4 and Cu-**MD-8** show similar absorption spectra (Fig. 1).

The photoluminescence (PL) properties of these Cu(I) complexes were characterized in doped PMMA film with 10 wt % doping level. Fig. 3 shows the effect of the organic phosphine ligands on the emission properties of the Cu(I) complexes. Compared with the reference complex **Cu-MD-1** displaying emission maximum at *ca*. 619 nm, both Cu-MD-2 bearing DPEPHOS and Cu-MD-3 bearing XANTPHOS show red-shifted emissions with peaks at ca. 622 and 650 nm, respectively. Considering their large Stokes shift (>100 nm), the shape of the decay curve and long lifetime in the order of microsecond (µs), these emissions were common phosphorescence. According to the TD-DFT results (Table 3), the character of the T₁ states in Cu-MD-1, Cu-MD-2 and Cu-MD-3 can be reflected by the features of the $H \rightarrow L$ transitions due to their high contribution (>80%) to the T_1 states. Hence, the frontier molecular orbital (MO) patterns of Cu-MD-1, Cu-MD-2 and Cu-MD-3 can be employed to rationalize the phosphorescent characters. The HO-MOs of Cu-MD-1, Cu-MD-2 and Cu-MD-3 are mainly located on the Cu(I) centers and the organic phosphine units. Clearly, the electrondonating ether unit in both Cu-MD-2 and Cu-MD-3 will elevate their HOMO level to facilitate the $H \rightarrow L$ transition and hence lower the energy level of the T₁ states. As a result, the phosphorescent peaks of Cu-MD-2 and Cu-MD-3 are located in the longer wavelength region compared with that of the reference complex Cu-MD-1 (Fig. 3). Besides the ether linker, the phosphine ligands in Cu-**MD-3** contain another electron-donating C(CH₃)₂ linker, which will

 Table 2

 Photophysical data for bipyrimidine-based dinuclear Cu(I) complexes.

Complex	Absorption λ_{abs}^{a} (nm)	Emission λ_{em}^{b} (nm)	$\tau_{\rm p}{}^{\rm b}$ (µs)	PLQY ^c
Cu-MD-1	248 (4.89), 285 (4.48), 362 (3.71)	619	1.1	0.45
Cu-MD-2	246 (4.78), 288 (4.47), 376 (3.79), 505 (3.48)	622	3.6	0.10
Cu-MD-3	248 (4.80), 286 (4.50), 376 (3.53), 505 (3.16)	650	4.5	0.19
Cu-MD-4	248 (5.04), 293 (4.85), 358 (5.07)	421	d	_d
Cu-MD-5	258 (4.74), 296 (4.51), 460 (4.17), 545 (3.82)	671	5.7	0.15
Cu-MD-6	260 (5.27), 296 (5.06), 357 (5.03), 463 (4.16), 550 (3.83)	676	5.4	0.06
Cu-MD-7	258 (4.76), 325 (4.22), 365 (3.66)	662	3.2	0.01
Cu-MD-8	246 (5.10), 295 (4.95), 357 (5.11)	422	d	_d

 $^a\,$ Measured in CH_2Cl_2 at a concentration of $10^{-5}\,M$ and $log\epsilon$ values are shown in parentheses.

^b Measured in doped PMMA film with the thickness of ca. 200 nm on quartz and the doping-level of 10-wt%.

^c Measured in an integrating sphere with 10-wt% doped PMMA film on quartz as sample and the excitation wavelength was set at 360 nm.

^d Cannot be detected properly.

Table 3	
Theoretical calculation results for the selected dinuclear Cu(I) complex	xes.ª

Complex Contribution of d_{π}	Contribution of d_π	Calculated energy of T ₁	Contribution of $H \rightarrow L$. Calculated energy of S_1	Contribution of $H \rightarrow I$. f
orbitals to HOMO ^D	orbitals to LUMO ^D	state (in wavelength)	to the T ₁ state	state (in wavelength)	to the S_1 state	$(S_0 \rightarrow S_1)$
Cu-MD- 29.21%	1.77%	618.06 nm	83.3%	563.09 nm	97.0%	0.0699
1 Cu-MD- 28.25%	2.04%	661.00 nm	83.1%	599.48 nm	95.2%	0.0839
2						
Cu-MD- 28.18%	1.50%	678.48 nm	82.2%	532.81 nm	93.2%	0.0549
Cu-MD- 0.32%	1.37%	887.67 nm	93.6%	623.32 nm	97.5%	0.6619
5						
Cu-MD- 29.06% 7	1.57%	607.78 nm	84.5%	556.95 nm	96.9%	0.0664

^a The TD-DFT results cannot be obtained properly for Cu-MD-4, Cu-MD-6 and Cu-MD-8 due to their large molecular size.

^b The data have been obtained by exporting DFT results with the software AOMix.

further rise the HOMO level of **Cu-MD-3**, leading to the more redshifted phosphorescent emission of **Cu-MD-3** (Fig. 3).

However, only very weak emission band located at ca. 420 nm was detected for Cu-MD-4 using TPA-PPP as the organic phosphine ligand. The PLQY and lifetime cannot be determined properly. We tentatively assign this emission to the ligand-centered fluorescence because a similar emission is apparent in **TPA-PPP**, which means that the TPA-PPP ligand should disfavor the phosphorescent emission from Cu(I) complexes. This conclusion is properly supported by the emission properties of **Cu-MD-6** and **Cu-MD-8** which also contain TPA-PPP ligand. For Cu-MD-8, nearly no phosphorescent emission can be observed as well (Fig. 4). Despite its phosphorescent emission, Cu-MD-6 still shows much lower PLQY of *ca*. 0.06 with respect to its analogue **Cu-MD-5** (PLQY = *ca*. 0.15) without TPA-PPP ligand (Table 2). As the theoretical calculation results indicated (see Table S1 in Supporting Information), the complexes bearing **TPA-PPP** possess much narrower energy gaps $(E_{\sigma} < 0.7 \text{ eV})$, which implies that the potential-energy profile of S₀ state will get much closer to that of the S₁ state in Cu-MD-4, Cu-MD-6 and Cu-MD-8. This might provide the chance to form a crosspoint between the potential-energy profiles of S_0 and T_1 states (Fig. 5a), which greatly increases the opportunity for the nonradiative decay process from the T₁ states to the S₀ states through the cross-point (Fig. 5a). The non-radiative decay process will definitely weaken the phosphorescent emission. Therefore, Cu-MD-4, Cu-MD-6 and Cu-MD-8 just exhibit weak or even no phosphorescence (Fig. 4). Different from Cu-MD-4, Cu-MD-6 and Cu-**MD-8**, the other complexes possess wider band gap in the range from 2.28 to 2.98 eV (Table S1) and hence there should be no crosspoint between the potential-energy profiles of their T₁ and S₀ states (Fig. 5b). Therefore, their T_1 states can effectively decay to the S_0 states radiatively to induce phosphorescent emission (Figs. 3 and 5). What should be noted is that introducing **TPA-PPP** ligand can effectively confine the transitions of Cu-MD-4, Cu-MD-6 and Cu-MD-8 on their organic ligands, which will greatly weaken the spinorbital coupling effect to reduce the quantum yield of T₁ states. This might be another reason for the low phosphorescent ability of Cu-MD-4. Cu-MD-6 and Cu-MD-8.

The effect of tuning the structure of the bridging bipyrimidine ligand on the PL behavior of these dinuclear Cu(I) complexes can be seen clearly from Fig. 6. Compared with that of their reference complex **Cu-MD-1** ($\lambda_{em} = 619$ nm), the emission maxima for **Cu-MD-5** (*ca.* 671 nm) and **Cu-MD-6** (*ca.* 676 nm) show an obvious bathochromic effect due to the introduction of an electron-donating triphenylamine unit to the bipyrimidine ligand. As aforementioned, the H \rightarrow L transition in **Cu-MD-5** displays ILCT (*i.e.* from triphenylamine to bipyrimidine) features. The strong electron-donating ability of triphenylamine unit together with the

strong electron-accepting capacity associated with the bipyrimidine segment will definitely facilitate the $H \rightarrow L$ transition in Cu-**MD-5** to lower the energy-level of its T₁ states. Hence, its phosphorescent emission from the T₁ states is located in the longer wavelength region (Fig. 6). The complex **Cu-MD-6** shows the $H \rightarrow L$ transition with inter-ligand charge transfer from the triphenylamine unit in TPA-PPP to the bipyrimidine segment. However, the HOMO-4 of Cu-MD-6 is still located on the triphenylamine unit attached to the bipyrimidine (Fig. S1). The theoretical results indicate that the HOMO-4 of Cu-MD-6 also contributes to the features of its S_1 and T_1 states. From this point of view, it is reasonable that Cu-MD-5 and Cu-MD-6 should show similar absorption and emission properties, which have been supported by the results in Figs. 1 and 6. Indicated by the very low PLQY of ca. 0.01 for **Cu-MD-7**, introduction of an electron-withdrawing triphenylphosphine oxide to the bipyrimidine segment will seriously weaken the phosphorescent ability of these Cu(I) complexes. According to the MO patterns of **Cu-MD-7** (Fig. 2), the LUMO is mainly located on the bipyrimidine unit because the triphenylphosphine oxide group can enhance electron-withdrawing ability of the bipyrimidine unit. It will lower the LUMO level of Cu-MD-7 to narrow the band gap to facilitate the aforementioned non-radiative decay process of the T₁ states (Fig. 5a). Hence, Cu-MD-7 only emits very weak phosphorescence with a red-shifted peak at 662 nm (Fig. 6). The locations of these experimental emission peaks are in good agreement with the trend of the calculated phosphorescent wavelengths (Table 3).

3.4. Electrochemical properties

The electrochemical properties of these bipyrimidine-based dinuclear Cu(I) complexes were characterized by cyclic voltammetry (CV) using ferrocene/ferrocenium (Fc/Fc⁺) redox couple as an internal reference under a nitrogen atmosphere. The results are summarized in Table 4. Except for Cu-MD-1 and Cu-MD-7, all the other complexes show two anodic potentials (E_a) . For the complexes Cu-MD-4, Cu-MD-5, Cu-MD-6 and Cu-MD-8, the first E_a located in the low potential region from ca. 0.40 V to 0.46 V should be assigned to the reversible oxidation process of the triphenylamine group according to our previous results for the Ir^{III} complexes [35,40]. The first E_a for **Cu-MD-5** (*ca.* 0.46 V) is slightly more positive with respect to that for Cu-MD-4, Cu-MD-6 and Cu-MD-8. This result can be ascribed to the fact that the electronwithdrawing bipyrimidine will make the attached triphenylamine group in **Cu-MD-5** more reluctant to be oxidized. However, as the analogue of Cu-MD-5, Cu-MD-6 exhibits the smaller value (ca. 0.4 V) for its first E_a . According to what aforementioned, the triphenylamine group attached to the bipyrimidine in Cu-MD-6



Fig. 2. HOMO (down) and LUMO (up) patterns for these dinuclear Cu(I) complexes.

should be more difficult to be oxidized compared with the ones with strong electron-donating triphenylphosphine in the ligand **TPA-PPP**. Hence, the first oxidation process in the CV measurement of **Cu-MD-6** should be induced by the four triphenylamine blocks from the **TPA-PPP** ligands. Reasonably, the strong electron-donating triphenylphosphine unit will greatly facilitate oxidation of the triphenylamine unit of the ligand **TPA-PPP** in **Cu-MD-6**. In addition, different from **Cu-MD-4** and **Cu-MD-8**, the electron-donating triphenylamine unit attached to the central ligand of **Cu-MD-6** will weaken the electron-accepting ability of bipyrimidine from Cu(I) centers and the triphenylphosphine unit in **TPA**-

PPP ligands. Therefore, the triphenylphosphine units in **TPA-PPP** ligands of **Cu-MD-6** can exhibit stronger electron-donating ability to the attached triphenylamine units than those in **Cu-MD-4** (*ca.* 0.42 V) and **Cu-MD-8** (*ca.* 0.45 V). Hence, **Cu-MD-6** exhibits the lowest potential for its first E_a (Table 4). On this basis, it is also easy to understand the order for the first E_a of **Cu-MD-8** > **Cu-MD-4** + > **Cu-MD-6**. Without triphenylamine units, both **Cu-MD-2** and **Cu-MD-3** can show an oxidation process at a lower potential region as well (Table 4). It might be induced by the ether-linked units showing electron-donating and conjugation features.

Besides the oxidation wave at a low potential, all the dinuclear



Fig. 3. PL spectra for Cu-MD-1, Cu-MD-2, Cu-MD-3 and Cu-MD-4 in doped PMMA film with 10 wt % doping level at 298 K.



Fig. 4. PL spectra for $Cu-MD-4,\ Cu-MD-6$ and Cu-MD-8 in doped PMMA film with 10 wt % doping level at 298 K.



Fig. 6. PL spectra for Cu-MD-1, Cu-MD-5, Cu-MD-6 and Cu-MD-7 in doped PMMA film with 10 wt % doping level at 298 K.

Cu(I) complexes can show irreversible oxidation process with much higher *E*_a in the range from *ca*. 0.58 V to 0.88 V (Table 4), which can be assigned to the oxidation of the Cu(I) centers. The second E_a located at the much more positive potential region for Cu-MD-1 and Cu-MD-7 suggests that introducing electron-donating unit to either central or phosphine ligands can effectively reduce the oxidation potential of the Cu(I) centers. However, it seems that introducing electron-donating unit to the phosphine ligands is more effective in promoting the oxidation of the Cu(I) centers, since **Cu-MD-4**, **Cu-MD-6** and **Cu-MD-8** show the second E_a (<0.64 V) with much lower value with respect to other complexes. Even with relatively weaker electron-donating ether linker, Cu-MD-2 and Cu-**MD-3** still possess lower E_a (*ca.* 0.71 V and 0.69 V, respectively) than that of the reference complex **Cu-MD-1** (ca. 0.85 V). Among all the complexes, **Cu-MD-7** possesses the highest E_a for the Cu(I) centers (ca. 0.88 V) due to the fact that the electron-withdrawing triphenylphosphine oxide unit can reduce the electron density on the Cu(I) centers to make them more difficult to be oxidized.

According to the MO patterns of these dinuclear Cu(I) complexes (Fig. 2), their reduction process should be induced by the



Fig. 5. Different patterns for the potential-energy profiles involved in these dinuclear Cu(I) complexes. (a) With cross-point between potential-energy profiles of T₁ and S₀ states; (b) Without cross-point between potential-energy profiles of T₁ and S₀ states.

Complex	$E_{\rm a}\left({\sf V}\right)$	$E_{\rm c}$ (V)	$E_{\rm HOMO}^{\rm c} (\rm eV)$	E_{LUMO}^{c} (eV)
Cu-MD-1	0.85 ^a	-1.79^{a} , -2.04^{b} , -2.35^{b}	-5.45	-3.81
Cu-MD-2	0.47 ^b , 0.71 ^a	-2.47^{a}	-5.27	-2.64
Cu-MD-3	0.46 ^b , 0.69 ^a	-2.49^{a}	-5.26	-2.63
Cu-MD-4	0.42 ^b , 0.61 ^a	-2.47^{a}	-5.22	-3.22
Cu-MD-5	0.46 ^b , 0.66 ^a	-2.51^{a} , -2.69^{a}	-5.26	-3.11
Cu-MD-6	0.40 ^b , 0.58 ^a	-2.52^{a}	-5.20	-3.16
Cu-MD-7	0.88 ^a	-1.33^{a} , -1.70^{a} , -2.14^{a} , -2.99^{a}	-5.64	-3.76
Cu-MD-8	0.45 ^b , 0.63 ^a	-1.35^{a} , -1.72^{a} , -2.15^{b} , -3.12^{b}	-5.25	-3.91

 Table 4

 Redox properties of the bipyrimidine-based dinuclear Cu(I) complexes.

^a Irreversible or quasi-reversible. The value was derived from the anodic or cathodic peak potential.

^b Reversible. The value was set as $E_{1/2}$.

^c HOMO levels are calculated according to the $E_{1/2}$ of the first reversible oxidation wave or the onset potential of the first irreversible oxidation wave, respectively. LUMO levels are derived from the onset potential of the first irreversible reduction wave.

bipyrimidine unit. Compared with the reference complex Cu-MD-1 with the first cathodic potential (E_c) at ca. -1.79 V, the complexes Cu-MD-2 – Cu-MD-6 exhibit the E_c in a more negative potential region (from ca. -2.47 V to -2.52 V) due to the presence of electron-donating ligands which make the bipyrimidine units more difficult to be reduced. Bonded directly with strong electrondonating triphenylamine group, the bipyrimidine units in Cu-MD-5 and Cu-MD-6 are even more difficult to be reduced. Hence, their first *E*_c is located after *ca*. –2.50 V. For **Cu-MD-7** and **Cu-MD-8**, they possess a reduction process at ca. -1.3 V, which can be assigned to the reduction of the triphenylphosphine oxide units. Owing to the electron-withdrawing triphenylphosphine oxide units attached to the bipvrimidine units, the second *E_c* of **Cu-MD-7** and **Cu-MD-8** is located in a less negative potential region (ca. -1.72 V) with reference to that of the reference complex Cu-MD-1.

3.5. Electroluminescence properties

In order to characterize the electroluminescence properties of these bipyrimidine-based dinuclear Cu(I) complexes, the OLEDs have been constructed using **Cu-MD-1**, **Cu-MD-3** and **Cu-MD-5** as

dopants by solution processing approach due to their higher PLQYs. The devices based on the Cu(I) phosphorescent emitters possess the configuration of ITO/PEDOT:PSS (35 nm)/TCTA: Cu(I) complex (x wt %, 50 nm)/TPBI (40 nm)/LiF (1 nm)/Al (100 nm) (Fig. 7). In these OLEDs, 4,4',4"-tri(*N*-carbazolyl)triphenylamine (TCTA) is the host material and 1,3,5-tris (*N*-phenylbenzimidazole-2-yl)benzene (TPBI) serves the function of electron-transporting and holeblocking because of its relatively low HOMO level. With the aim to optimize their EL performances, these phosphorescent emitters have been doped at different doping levels (Fig. 7). Table 5 summarizes the important EL performance data for these devices.

After applying a proper voltage, these OLEDs exhibit intense electroluminescence. As shown in Fig. 8, the EL spectral profile of each optimized device is very similar to the PL spectrum of the corresponding Cu(I) complex, suggesting that the EL emission is indeed originated from the triplet excited state of the Cu(I) complex. Additionally, no residual emission from TCTA is observed in these devices, implying the efficient forward energy transfer from the host excitons to the phosphorescent Cu(I) complexes.

As listed in Table 5, the OLEDs with the doping level at 10 wt %, *i.e.*, devices **A2**, **B2** and **C2**, show the highest EL efficiencies. The current density–voltage–luminance (J-V-L) characteristics and EL



Fig. 7. Configuration of the OLEDs and chemical structures for the materials involved.

Table 5
The EL performance of these dinuclear Cu(I) complexes

Device	Dopant	$V_{\text{turn-on}}$ (V)	$L_{\rm max}^{a}$ (cd m ⁻²)	EQE (%)	$CE (cd A^{-1})$	PE ($lm W^{-1}$)	$\lambda_{\max}^{d}(nm)$	CRI/CCT ^e
A1	Cu-MD-1 (8 wt %)	4.9	3318 (13.6)	1.84 (8.6) ^a	3.90 (8.6)	1.53 (7.7)	572	75/3541 K
				1.11 ^b	2.31	1.30	(0.43, 0.47)	
				1.79 ^c	2.80	1.52		
A2	Cu-MD-1 (10 wt %)	4.3	5379 (11.3)	6.09 (6.8)	12.78 (6.8)	5.93 (6.5)	574	75/3524 K
				3.95	7.85	4.51	(0.44, 0.47)	
				6.06	12.74	5.79		
A3	Cu-MD-1 (12 wt %)	4.8	943 (11.5)	2.87 (6.7)	6.15 (6.7)	2.94 (6.5)	574	75/3674 K
				2.24	4.79	2.56	(0.43, 0.47)	
				2.71	5.81	2.50		
B1	Cu-MD-3 (8 wt %)	4.6	3131 (13.6)	2.34 (6.3)	4.96 (6.3)	2.52 (6.0)	558	78/4039 K
				2.16	4.51	2.45	(0.40, 0.46)	
				2.12	4.43	1.80		
B2	Cu-MD-3 (10 wt %)	4.3	3697 (10.8)	4.03 (6.6)	8.78 (6.6)	4.27 (6.3)	558	77/4037 K
				3.00	6.56	3.59	(0.40, 0.47)	
				3.80	8.27	3.38		
B3	Cu-MD-3 (12 wt %)	4.7	1248 (11.2)	1.54 (6.9)	3.33 (6.9)	1.56 (6.7)	558	76/4042 K
				1.50	3.17	1.55	(0.40, 0.46)	
				1.43	3.11	1.25		
C1	Cu-MD-5 (8 wt %)	4.8	462 (12.1)	1.00 (7.9)	1.55 (7.9)	0.68 (6.4)	634	80/2518 K
				0.98	1.54	0.64	(0.50, 0.46)	
				0.95	1.47	0.50		
C2	Cu-MD-5 (10 wt %)	4.3	2466 (11.1)	2.17 (6.9)	3.22 (6.9)	1.53 (6.4)	637	82/2439 K
				2.01	3.09	1.50	(0.50, 0.45)	
				2.12	3.14	1.30		
C3	Cu-MD-5 (12 wt %)	4.5	670 (11.0)	1.32 (6.5)	1.72 (6.5)	0.85 (6.2)	652	88/2342 K
				1.23	1.58	0.62	(0.50, 0.44)	
				1.02	1.33	0.44		

^a Maximum values of the devices. Values in parentheses are the voltages at which they were obtained.

 $^{\rm b}$ Values were collected at 20 cd m $^{-2}$.

^c Values collected at 100 cd m⁻².

^d Values were collected at 8 V and CIE coordinates (x, y) are shown in parentheses.

^e Color Rendering Index (CRI) and Correlated Color Temperature (CCT) obtained at 8 V.



Fig. 8. EL spectra for the optimized devices based on these dinuclear phosphorescent Cu(I) complexes at about 8 V.

efficiency–luminance curves for the optimized OLEDs are shown in Fig. 9 and Fig. 10. The optimized device (device **A2**) doped with **Cu-MD-1** can exhibit the best EL performance with a turn-on voltage ($V_{turn-on}$) of 4.3 V, and the maximum luminance (L_{max}) of 5379 cd m⁻² at 11.3 V, the peak current efficiency (CE) of 12.78 cd A⁻¹, power efficiency (PE) of 5.93 lm W⁻¹ and external quantum efficiency (EQE) of 6.09% (Table 5 and Fig. 10), representing impressive EL efficiencies for the OLEDs based on charged dinuclear phosphorescent Cu(I) complexes. The device **B2** with **Cu-MD-3** as emitter can also give decent EL performances with L_{max} of 3697 cd m⁻² at 10.8 V, CE of 8.78 cd A⁻¹, PE of 4.27 lm W⁻¹ and EQE of 4.03%. According to the energy gap law, long-wavelength

Fig. 9. The current density–voltage–luminance (J-V-L) curves for the optimized OLEDs.

emitters typically show low EL efficiencies. However, device **C2** with the EL maximum at *ca*. 640 can still show good EL efficiencies with CE of 3.22 cd A^{-1} , PE of 1.53 lm W^{-1} and EQE of 2.17%. Although these charged dinuclear Cu(I) complexes exhibit inferior EL performance with respect to some neutral dinuclear Cu(I) analogues [23,41], complex **Cu-MD-1** can still outperform the advanced charged mononuclear Cu(I) counterparts [42,43]. The charged green-emitting mononuclear Cu(I) complex bearing 1,10-phenanthroline-type ligand can show high CE of 11.0 cd A^{-1} [12], while the analogue with quinoline-based ligand can show CE of 5.58 cd A^{-1} [42]. The impressive EL performances achieved by these dinuclear Cu(I) emitters should be ascribed to the enhanced charge-trapping ability afforded by both bipyrimidine ligand and

Fig. 10. The relationship between the EL efficiency and luminance for the optimized OLEDs. (a) Device **A2**, (b) device **B2** and (c) device **C2**.

the functional groups as indicated by the CV results (Table 4). Interestingly, the OLEDs based on these charged dinuclear Cu(I) complexes can show very broad EL spectra with CRI > 75 and maximum at 88 (Fig. 8 and Table 5). As a result, the CIE coordinates for the devices based on **Cu-MD-1** and **Cu-MD-3** are very close to that of some warm WOLEDs based on complementary-color strategy with CIE of (0.395, 0.452) or (0.376, 0.467) [44]. These results demonstrate that the bipyrimidine-based dinuclear Cu(I) complexes are very promising for fabricating single-emitter warm WOLEDs, which can greatly reduce the complexity of the fabrication process as well as the cost.

4. Conclusion

Through introduction of the functional moieties with different electronic features to the bipyrimidine unit, a series of charged bipyrimidine-based dinuclear Cu(I) complexes bearing different phosphine ligands have been developed. The chemical structures of both central bipyrimidine ligands and organic phosphine ligands of the dinuclear Cu(I) complexes can exert a great influence on their thermal stability as well as photophysical properties. In addition, the functional groups can also promote the charge-trapping of these dinuclear Cu(I) complexes to benefit their EL ability. Hence, these bipyrimidine-based dinuclear Cu(I) complexes can exhibit impressive EL performances with L_{max} of 5379 cd m⁻², EQE of 6.09%, CE of 12.78 cd A^{-1} , and PE of 5.93 lm W^{-1} , representing the top-ranking EL efficiencies ever achieved by the charged Cu(I) complexes. More importantly, the OLEDs based on these dinuclear Cu(I) complexes can emit intense warm white light with CRI as high as 88, showing the great potential of these dinuclear Cu(I) complexes in achieving single-emitter WOLEDs. All these results will not only establish the structure-property relationship of these dinuclear Cu(I) complexes, but also provide valuable information for developing highly efficient Cu(I) phosphorescent emitters for improving the EL performance of the OLEDs based on charged Cu(I) complexes.

Acknowledgments

This work was supported by the National Natural Science Foundation of China (Nos. 20902072, 1572176 and 21602170), the Natural Science Foundation of Shaanxi Province (No. 2016JQ2011), Fundamental Research Funds for the Central Universities (Nos. cxtd2015003 and 01091191320074), the China Postdoctoral Science Foundation (Nos. 20130201110034 and 2015M580831), Creative Scientific Research Team for Yulin City in Shannxi Province. W.-Y.W. acknowledges the financial support from the National Basic Research Program of China (973 Program, grant no. 2013CB834702), the Areas of Excellence Scheme, University Grants Committee of HKSAR, China (AoE/P-03/08), Hong Kong Research Grants Council (HKBU 12304715), Hong Kong Baptist University (FRG1/14-15/084) and the Hong Kong Polytechnic University.

Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.dyepig.2017.04.036.

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