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PAPER

Copper(I) complexes with bipyridyl and phosphine ligands: a systematic study

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Phosphorescent copper(I) complexes carrying 2,2′-bipyridyl derivatives and phosphine ligands have been prepared and fully characterised. The role of the bipyridyl as well as the phosphine ligands in defining the optical, as well as the chemical properties of the complexes, are discussed. The light emission of these complexes is investigated as a function of the molecular geometry: rigid complexes with restricted freedom to rearrange in the excited state are found to show a quantum yield of phosphorescence one order of magnitude higher than those complexes with no steric constraint. The complexes have been extruded in a polymer matrix as a proof of principle of their processability.

Introduction

Copper(I) coordination complexes bearing arylphosphine ligands are gathering tremendous interest as phosphorescent active materials for organic light emitting devices (OLEDs),[1,2] polymer light emitting devices (PLEDs)[3,4] and organic light emitting electrochemical cells (OLECs).[5,6]

While the first generation of Cu(I) light emitting devices did not compare in performance with OLEDs manufactured with Ir(III) cyclometalated coordination complexes, recent reports suggest Cu(I) complexes provide an efficient alternative to the expensive and rare iridium metal.[7,8] Challenges still need to be overcome for copper to enter the OLED market: in particular the emission needs to cover the full RGB colour gamut and active materials need to prove stable in operation. While the rules governing the emission in heavy metals such as iridium(III) and platinum(II) are generally understood, literature reports on structurally similar copper(I) compounds appear to show inconsistent optical properties.[9] From previous publications, it seems clear that geometrical issues play a major role in determining the optical properties of the complexes, over the electronic structure of the ligand.[10–13]

We recently reported on trinuclear copper complexes, whose emission wavelengths extend across the range of the visible spectrum and show efficient phosphorescence at room temperature in degassed solutions.[14] Although the alkynyl trinuclear copper(I) complexes show unique optical features, in our hands they were unstable. In particular, the electrochemistry led to fast degradation of the complexes even in the absence of oxygen. Thermal characterisation further confirmed the poor stability of those complexes, probably due to a weak bond between the alkynyl ligand and the trinuclear copper(I) cluster.

In this work, we present novel tetra-coordinated copper(I) complexes based on phosphine ligands and 2,2′-bipyridyl derivatives.

Synthesis of the complexes

The synthetic protocol to prepare complexes **1–3(a–c)** involves room temperature reaction of $(CH_3CN)_4CuBF_4$ with stoichiometric amounts of the bidentate phosphine ligands (bis(2-diphenylphosphino)phenyl ether (**1**) or 9,9-dimethyl-4,5-bis-(diphenylphosphino)xanthene (**2**), or a double molar amount of triphenylphosphine (**3**), and 2,2′-bipyridyl. Purification of the yellow, air stable Cu^{1+} complexes by precipitation in diethyl ether–hexane mixtures affords the complexes in excellent yield (see Fig. 1). In all cases, the complexes were obtained as BF_4 salts, as shown in the ^{19}F NMR, which show a strong signal at *ca.* −150 ppm, consistent with the presence of a BF_4^- group.[14]

Phosphine ligands play a crucial role in securing the stability of the complexes. Attempts to prepare analogous complexes carrying solely 2,2′-bipyridyl ligands failed, due to disproportionation of the Cu(I) ion to Cu(II) and metallic copper deposited at the bottom of the vessel. Cu(I) complexes carrying solely phosphine ligands and showing poor emission were reported elsewhere and were therefore not investigated in this work.[15–17]

The complexes discussed here showed excellent shelf life at room temperature in air and no sign of degradation or oxidation was detected upon several months of storage in the solid state, by comparison of elemental analyses before and after storage.

Complex **3c** could not be isolated in satisfactory purity. NMR and mass analysis do show the presence of the complex, but attempts to purify it resulted in significant amounts of free ligand

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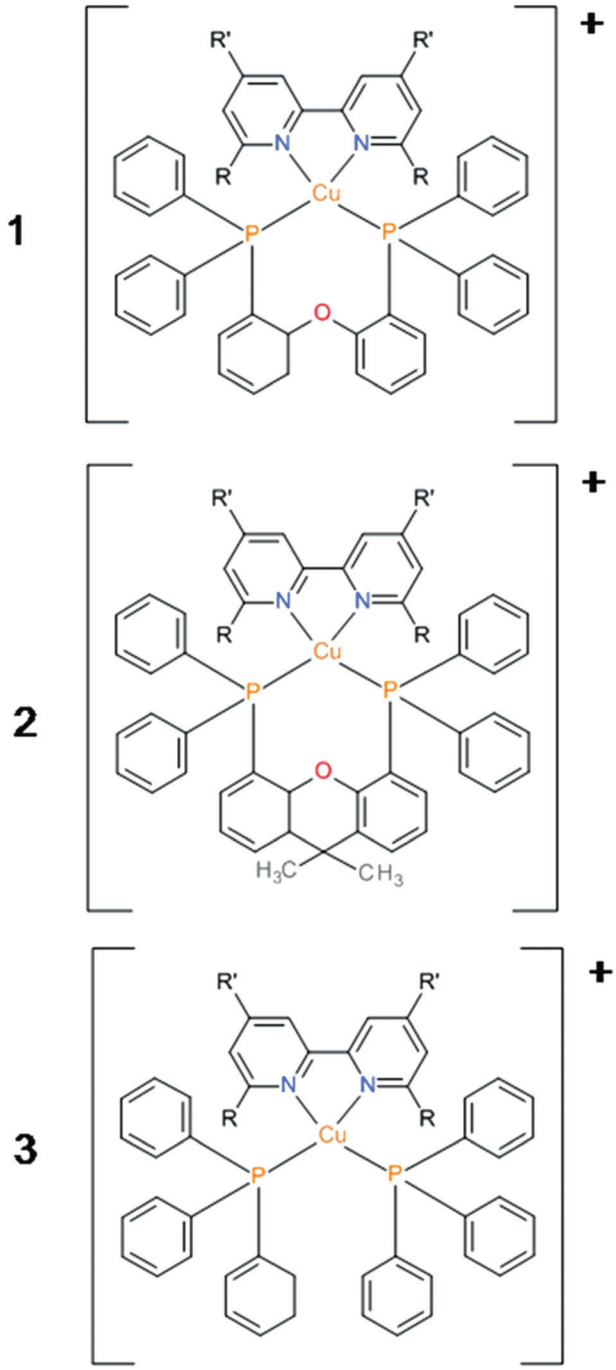

Fig. 1 Chemical structure of complexes **1–3**. *a*: R = R′ = H; *b*: R = H, R′ = CH_3; *c*: R = CH_3, R′ = H. BF_4^- is the counter ion in all complexes.

and discolouration, as a sign of oxidation. It is likely that the combined effect of steric hindrance of the bipyridyl ligand and the weak Cu–P bond in the case of triphenylphosphine result in an unstable complex.

Processing of the complexes and thermal analysis

Complexes **1–3(a–c)** were obtained as amorphous powders by precipitation. The solubility of these complexes is excellent in halogenated solvents, as well as polar solvents such as acetonitrile and dimethylformamide. Thin films for optical measurements of absorption and emission spectra were prepared by spin coating 2% w/v PMMA solutions in dichloromethane, containing 0.16% w/v of the desired complex as dopant.

Fig. 2 Extruded phosphorescent polypropylene doped with complex **2c** (green) and **2a** (orange).

The complexes can also be extruded as dopants in a polymer matrix. PMMA doped with 1% w/w of the complexes was processed in a Haake MiniLab co-rotating twin screws extruder at 200 °C and the extruded material was manually drawn into a fibre of *ca.* 1 mm thickness. The resulting fibres showed bright luminescence under UV excitation at 360 nm as proof of stability at high temperature. PMMA fibres are transparent but very brittle, therefore, using the same method, polypropylene was extruded with complexes **1–3(a–c)** and even in this case flexible luminescent extruded polymer fibres were obtained (see Fig. 2).

Thermogravimetric analysis (TGA) of complexes **1–3(a–c)** showed the stability to be dependent upon the coordinating phosphine ligand (see Fig. 3). Triphenylphosphine coordinated complexes **3a–b** show far lower thermal stability than complexes **1–2(a–c)**. The increased rigidity of the ligand, combined with the availability of the oxygen's electron pairs in **1** and **2** type structures, results in exceptional thermal stability. In the case of triphenylphosphine bound complexes **3(a–b)**, the weight loss occurring at temperatures in excess of 200 °C is not accompanied by any endothermic signal detectable by scanning differential calorimetry, suggesting the process is degradation rather than evaporation of the complex (see Fig. 4).

This observation is further confirmed by the multi-step nature of the TGA trace for complex **3a**. Complexes **1a–c** show melting points in excess of 230 °C, characterised by large sharp endothermic signals in the DSC traces. In the case of complex **1c** the melting point is significantly lower, possibly induced by a distorted geometry. No recrystallisation peak was detected in the cooling step, as a sign of irreversible thermal behaviour.

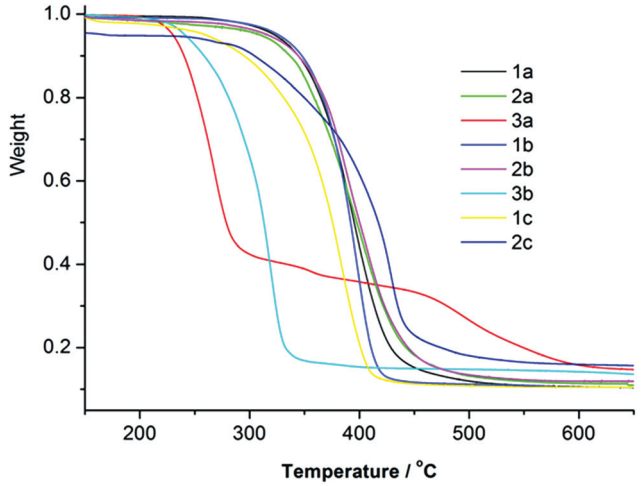

Fig. 3 TGA traces of complexes **1–3(a–c)**.

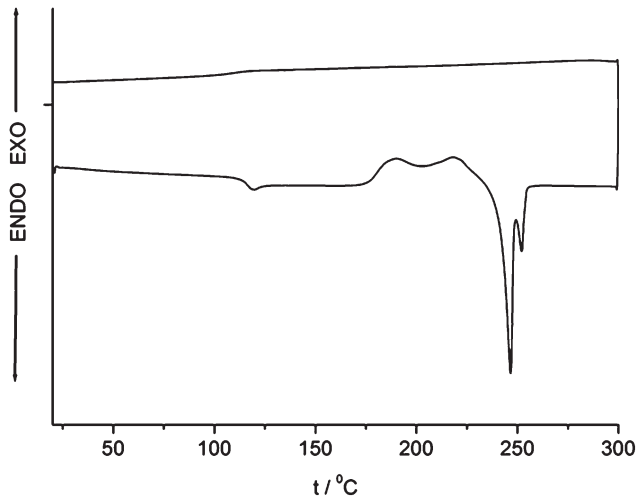

Fig. 4 DSC trace of complex **1a**.

Complexes with triphenylphosphine and 9,9-dimethyl-4,5-bis-(diphenylphosphino)xanthene as ligands do not show any significant thermal process up to 300 °C. In summary, the thermal analysis suggests all complexes are stable within a sensible range and suitable for applications such as OLEDs and OLECs. However, complexes containing triphenylphosphine as the ligand can only be processed from solution as they show thermal decomposition above 200 °C, rather than a clean evaporation (Fig. 3).

Optical spectroscopy

UV-vis absorption spectroscopy of complexes **1–3(a–c)** in dichloromethane solutions reveals two sets of features. Broad absorption features centred around 370 nm with a molar extinction coefficient ε in the region of 1–5000, characteristic of metal-to-ligand-charge-transitions (MLCT) are observed. A second set of features of higher intensity (ε = 10 000–50 000) centred around 280 nm are assigned to π–π^* transitions centred

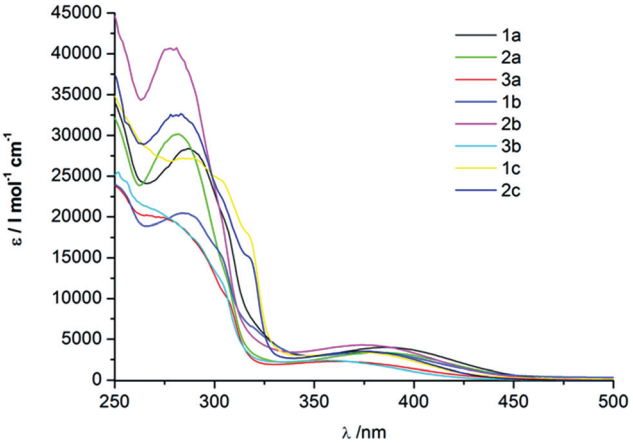

Fig. 5 Absorption spectra of complexes **1–3(a–c)**.

on the aromatic ligands (see Fig. 5). The absorption maxima are consistent across the structures, suggesting that the geometrical and electronic structure of these complexes in the ground state is very similar. The absorption spectra recorded in PMMA thin films show analogous maxima, although in this case the molar extinction coefficients could not be reproducibly measured. The absorption spectra were found to be in agreement with those published by Rader *et al.* for similar compounds.[18]

Complexes **1–3(a–b)** do not show phosphorescence at room temperature in organic solvents, either in the presence of oxygen or in degassed solutions. However, they do emit at 77 K in a glass, indicating that the flexibility of the system and possible solvent quenching are the cause of the lack of emission observed in solution. Conversely, complexes **1–2c** are phosphorescent in solution in the absence of oxygen, thus confirming a rigid structure is necessary for a radiative path to compete with non radiative relaxation. The solution quantum yields of **1–2c** are 5.2% and 1.6%, respectively.

When complexes **1–3(a–c)** are processed as 5% w/w dopants in a polymethylmethacrylate (PMMA) film, emission is observed at room temperature, even in the presence of air (see Fig. 6). This result reflects the previous observations in tetra-coordinated Cu(I) complexes, where the rigidity of the complex is key to efficient phosphorescence.[10]

Tetra coordinated Cu(I) complexes with phosphine and pyridine type ligands are reported to have a moderate distortion from the ideal tetrahedral geometry.[19–21] During this work, we were unable to isolate single crystals of the size required for X-ray diffraction based structure refinement and we therefore assume the structures of complexes **1–3(a–c)** to be similarly distorted from an ideal tetrahedral geometry.

When the excited state is not locked in a rigid configuration, alternatives to a radiative decay path can be found, involving geometrical rearrangement. Extensive structural rearrangements occurring in the excited state are confirmed by the relatively large Stokes shifts observed in copper(I) complexes, often exceeding a 150 nm gap between the emission and absorption maxima.

The quantum yield of photoluminescence was measured in 5% doped PMMA films spin coated from a dichloromethane solution, using an integrating sphere, following the method

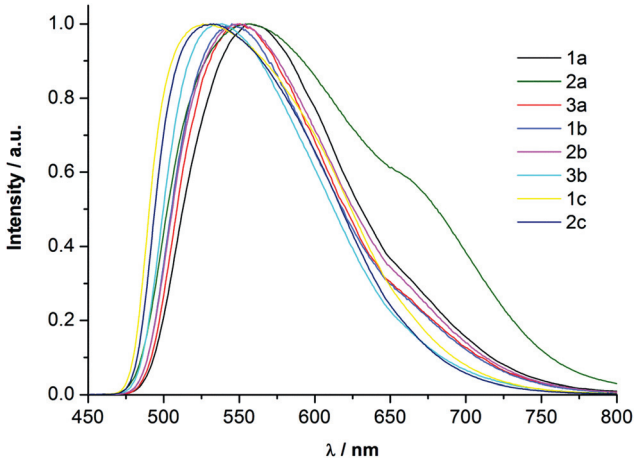

Fig. 6 Emission spectra of complexes **1–3(a–c)** in PMMA films.

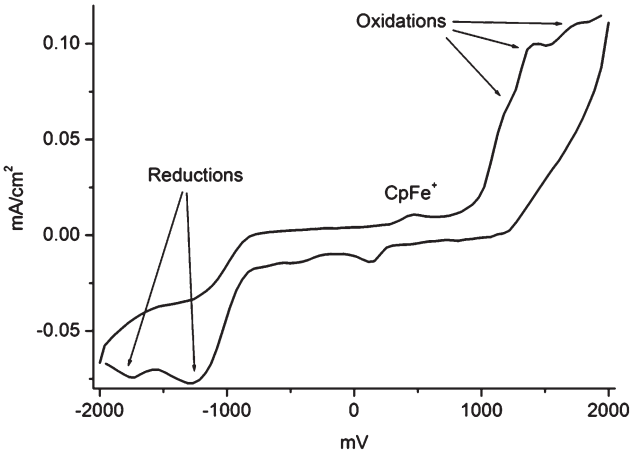

Fig. 7 Cyclic voltammetry of complex **1b** in degassed, anhydrous acetonitrile.

Table 1 Optical UV-vis absorption maxima at room temperature in dichloromethane

	Abs. λ_{max}/nm	E_m λ_{max}/nm	Φ/%	τ/μs	$E_{1/2\ ox}$/V	$E_{1/2\ red}$/V
1a	385; 287	559	3.3	9.0	0.72	−1.73
2a	382; 281	560	0.1	11.5	0.67	−1.54
3a	357; 270	550	0.4	10.0	0.83	−1.93
1b	377; 284	544	0.3	11.2	0.66	−1.66
2b	375; 280	558	1.1	10.7	0.74	−1.71
3b	354; 264	537	0.2	10.7	0.81	−1.64
1c	372; 286	528	14.5	15.7	0.82	−1.58
2c	375; 282	530	33.3	15.1	0.81	−1.56

Emission maxima in 5% PMMA films. Quantum yields and lifetimes of photoluminescence in 5% PMMA films. Redox potentials in anhydrous, degassed acetonitrile *vs.* Cp_2Fe/Cp_2Fe^+ used as internal reference.

published by Porres *et al.*[22] Whilst complexes of the **a** and **b** series show low to very low quantum yields, complexes of the **c** series are surprisingly efficient (see Table 1). In this work the effect of substituents of the bipyridyl ligand is striking clear: the steric hindrance of methyl groups on position 6 and 6′ results in better shielding of the copper core of the complexes and in enhanced emission. In the same complexes, the optical band gap is significantly narrower than in complexes without methyl groups on the bipyridyl ligand or where the methyl groups sit outside the core of the complex. Complexes **1–2c** show blue shifted emission and narrower band shape as a result of a lesser degree of distortion in the excited state, although no appreciable shift is observed in the absorption spectrum. This is a clear sign that the restrictive geometrical effect of the methyl groups, rather than the electronic effect, is responsible for the difference in optical behaviour among these complexes. The metal-to-ligand charge transfer nature of the excited state results in a partially oxidised copper ion, which prefers a flattened geometry.[23–27] The presence of the methyl groups prevents the rearrangement to a certain degree, resulting in blue shifted and enhanced emission. The lifetime of the emitting species is in the region of 10 μs, consistent with the assignment as a MLCT excited state. The featureless emission spectra are in contrast with those observed by Rader *et al.*[18] at 77 K and single exponential decay was observed in all cases in PMMA films as a sign of single, rather than multiple emissions at room temperature.

Conversely, the effect of the phosphine ligand in tuning the emission properties is negligible.

Electrochemistry

Cyclic voltammetry was performed on complexes **1–3(a–c)** in CH_3CN, using the redox couple Cp_2Fe/Cp_2Fe^+ as the internal reference. All complexes show a first oxidation wave at 0.6–0.8 V *vs.* Cp_2Fe/Cp_2Fe^+, which, by comparison to similar complexes, can be assigned to metal centred oxidation to Cu(II).[1,3] Oxidation on the metal is likely to result in significant geometrical rearrangement, as divalent copper ions prefer a flatter geometry. In solution, the complexes are likely to be unstable upon oxidation, as indicated by an irreversible wave. Further oxidations are detected at higher voltages (see Fig. 6), which are likely to be localised on the phosphine ligands, by comparison with the cyclic voltammetry signals of the corresponding free ligands in solution. These signals are also irreversible. All complexes show a reduction wave centred at −(1.7–1.9 V) *vs.* Cp_2Fe/Cp_2Fe^+. In phosphorescent metal complexes, this signal is typically assigned to a reduction centred on the bipyridyl ligand. The reduction wave is only partially reversible, in solution, as is often the case in transition metal complexes (Fig. 7).[28]

Conclusions

This systematic study of bipyridyl Cu(I) complexes with diphosphine ligands shows that the structure of the ligand is important in defining the optical as well as chemical and physical properties of mono valent copper complexes. Efficient radiative decay from the triplet excited state is detected only when a bipyridyl ligand is carrying bulky methyl groups facing the copper nucleus. The methyl groups act as a shield towards external quenching, as well as preventing extensive geometrical rearrangement in the excited state. The effect is enhanced, as well as blue shifted emission, by virtue of a more rigid configuration. Complexes where the methyl groups are facing the outer

side of the complex, as well as complexes without methyl groups, show a mainly non radiative decay path, both in solution and in the solid state.

The phosphine ligands play a crucial role in stabilising the complexes, as shown in thermal analysis. Triphenylphosphine is the weakest among the ligands involved in this study and complexes **3a–b** are less stable as a consequence.

The combined effects of a sterically hindered bipyridyl ligand and a rigid, strong coordinating diphosphine ligand results in complexes with exceptional stability and a good quantum yield of photoluminescence in the solid state. Such complexes are particularly interesting for OLED and OLEC applications.

Experimental

Absorption spectra were recorded with a Perkin Elmer Lambda 650S UV-vis spectrophotometer. Emission spectra and lifetimes were recorded with a Horiba Jobin Ivon Fluorolog 4 fluorimeter. NMR spectra were recorded with a JEOL 400 MHz spectrometer using the resonance peak of the solvent as an internal reference. Luminescent quantum yields were measured in a 4 inch Labsphere integrating sphere used in a Horiba Jobin Ivon Fluoromax 2 spectrophotometer, using the procedure described.[22]

Chemicals were purchased from Aldrich, with the highest purity commercially available and used without further purification. The complexes were prepared following the method published by Min *et al.*[1] A dichloromethane solution (10 mL) of the bipyridyl ligand, (1 mmol) and the diphosphine ligand (1 mmol; triphenylphosphine 2 mmol), was added drop-wise to a dichloromethane solution (10 mL) of tetrakis (acetonitrile) copper(I) tetrafluoroborate (0.314 g; 1 mmol). The reaction was stirred for one hour in air at room temperature. The reaction mixture was filtered, concentrated to 5 mL and precipitated in diethyl ether–hexanes mixtures. The process was repeated twice. The products were filtered and allowed to dry in air. Yields: **1a** = 95%, **1b** = 84.5%, **1c** = 74.0%, **2a** = 66.3%, **2b** = 88.3%, **2c** = 53.0%, **3a** = 33.6%, **3b** = 61.2%.

Complex **1a**: ^{1}H NMR in $CDCl_3$: 8.42 (d, 2H, J = 3.9 Hz, pyr.); 8.33 (d, 2H, J = 8.0 Hz, pyr.); 8.00 (t, 2H, J = 7.8 Hz, pyr.); 7.20–7.31 (m, 8H, arom.); 7.16 (t, 8H, J = 7.3 Hz, arom.); 7.02 (d, 2H, J = 7.7 Hz, pyr.); 6.90–6.99 (m, 10H, arom.); 6.69–6.75 ppm (m, 2H, arom.). ^{13}C NMR in $CDCl_3$: 158.30; 151.71; 149.22; 138.97; 134.39; 133.06; 132.08; 130.08; 130.22; 128.89; 125.98; 125.23; 122.94; 120.51 ppm. ESI-MS: 757.1 M^+. 601.0 $Cu(P\hat{}P)^+$. Elem. anal. %: C: 65.56 (calc. 65.38) H: 3.92 (calc. 4.29).

Complex **2a**: ^{1}H NMR in $CDCl_3$: 8.54 (d, 2H, J = 8.0 Hz, pyr.); 8.09 (d, 2H, J = 7.8, pyr.); 8.02 (d, 2H, J = 7.8 Hz, pyr.); 7.62 (t, 2H, J = 7.5 Hz, arom.); 7.26 (t, 6H, J = 7.7 Hz, arom.); 7.12 (t, 10H, arom.); 6.79–6.95 (m, 8H, arom.); 6.50 (d, 2H, J = 7.9 Hz, pyr.); 1.76 ppm (s, 6H, CH_3). ^{13}C NMR in $CDCl_3$: 154.91; 151.74; 148.65; 139.60; 133.80; 132.78; 131.20; 130.08; 128.93; 127.18; 123.53; 119.90; 36.26; 28.12 ppm. ESI-MS: 796.9 M^+. 641.0 $Cu(P\hat{}P)^+$. Elem. anal. %: C: 66.79 (calc. 66.49; H: 4.47 (calc. 4.55); N: 3.13 (calc. 3.16).

Complex **3a**: ^{1}H NMR in $CDCl_3$: 8.50 (d, 2H, J = 3.9 Hz, pyr.); 8.28 (d, 2H, J = 8.0 Hz, pyr.); 8.08 (t, 2H, J = 7.8 Hz, pyr.); 7.34 (t, 6H, J = 7.7 Hz, arom.); 7.18 (t, 12H, arom); 6.94–7.10 ppm (m, 12H, arom.). ^{13}C NMR in $CDCl_3$: 151.90; 149.23; 139.47; 133.05; 132.02; 130.37; 129.01; 126.18; 123.55 ppm. ESI-MS: 481.0 $N\hat{}NCuPPh_3^+$; 219.0 $N\hat{}NCu^+$. Elem. anal. %: C: 66.33 (calc. 66.48) H: 4.20 (calc. 4.61).

Complex **1b**: ^{1}H NMR in $CDCl_3$: 8.26 (d, 2H, J = 7.9 Hz, pyr.); 8.15 (d, 2H, J = 8.0 Hz, pyr.); 7.20–7.30 (m, 8H, arom.); 7.16 (t, 8H, J = 7.3 Hz, arom.); 7.00 (d, 2H, J = 7.7 Hz, pyr.); 6.90–6.99 (m, 10H, arom.); 6.69–6.75 ppm (m, 2H, arom.). ^{13}C NMR in $CDCl_3$: 158.32; 151.75; 150.85; 148.71; 134.39; 133.17; 133.05; 130.14; 128.86; 123.54; 21.44 ppm. ESI-MS: 784.9 M^+; 600.9 $Cu(P\hat{}P)^+$. Elem. anal. %: C: 65.61 (calc. 66.03); H: 4.11 (calc. 4.62); N: 3.21 (calc. 3.21).

Complex **2b**: ^{1}H NMR in $CDCl_3$: 8.42 (d, 2H, J = 7.9 Hz, pyr.); 7.79 (d, 2H, J = 7.8 Hz, pyr.); 7.62 (d, 2H, J = 7.9 Hz, pyr.); 7.26 (t, 6H, J = 7.7 Hz, arom.); 7.12 (t, 10H, arom.); 6.82–6.94 (m, 8H, arom.); 6.45 (m, 2H, arom.); 2.55 (s, 6H, CH_3); 1.79 ppm (s, 6H, CH_3). ^{13}C NMR in $CDCl_3$: 155.04; 151.79; 151.32; 148.08; 132.90; 129.99; 128.86; 126.98; 124.90; 124.12; 120.04; 36.25; 28.06; 21.44 ppm. ESI-MS: 824.9 M^+; 640.9 $Cu(P\hat{}P)^+$. Elem. anal. %: C: 67.68 (calc. 67.08); H: 4.40 (calc. 4.86); N 2.65 (calc. 3.07).

Complex **3b**. ^{1}H NMR in $CDCl_3$: 8.37 (d, 2H, J = 8.0 Hz, pyr.); 8.09 (d, 2H, J = 7.9 Hz, pyr.); 7.34 (t, 6H, J = 7.7 Hz, arom.); 7.18 (t, 12H, J = 7.5 Hz, arom.); 7.11 (m, 2H, pyr.); 7.03 (m, 12H, arom.); 2.54 ppm (s, 6H, CH_3). ^{13}C NMR in $CDCl_3$: 151.97; 151.47; 148.68; 133.15; 132.33; 130.24; 128.94; 126.84; 124.21; 21.45 ppm. ESI-MS: 509.12 $N\hat{}NCuPPh_3^+$. Elem. anal. %: C 66.96 (calc. 67.10); H: 4.46 (calc. 4.93); N: 3.33 (calc. 3.26).

Complex **1c**. ^{1}H NMR in $CDCl_3$: 8.06 (d, 2H J = 8.0 Hz, Pyr.); 7.90 (d, 2H, J = 7.9 Hz, pyr.); 7.20–7.30 (m, 8H, arom.); 7.16 (t, 8H, J = 7.3 Hz, arom.); 6.92 (d, 2H, J = 7.7 Hz, pyr.); 6.90–6.99 (m, 10H, arom.); 6.85–6.91 (m, 2H, arom.). 2.18 ppm (s, 6H, CH_3). ^{13}C NMR in $CDCl_3$: 158.13; 152.42; 132.98; 132.91; 130.07; 128.8; 126.09; 120.46; 26.54 ppm. ESI-MS: 784.9 M^+; 600.9 $Cu(P\hat{}P)^+$. Elem. anal. %: C: 65.26 (calc. 66.03); H: 4.12 (calc. 4.62); N: 2.93 (calc. 3.21).

Complex **2c**. ^{1}H NMR in $CDCl_3$: 8.02 (d, 2H, J = 7.9 Hz, pyr.); 7.87 (d, 2H, J = 7.8 Hz, pyr.); 7.61 (d, 2H, J = 7.9 Hz, pyr.); 7.30 (t, 6H, J = 7.7 Hz, arom.); 7.16 (t, 10H, arom.); 7.00–7.09 (m, 8H, arom.); 6.82 (m, 2H, arom.); 1.98 (s, 6H, CH_3); 1.66 ppm (s, 6H, CH_3). ^{13}C NMR in $CDCl_3$: 157.73; 155.11; 152.11; 139.11; 133.17; 130.18; 128.88; 125.72; 120.05; 36.17; 28.39; 26.66 ppm. ESI-MS: 824.9 M^+; 640.9 $Cu(P\hat{}P)^+$. Elem. anal. %: C: 66.42 (calc. 67.08); H: 4.41 (calc. 4.86); N: 3.00 (calc. 3.07).

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