A dinuclear extension to constrained heteroleptic Cu(I) systems†

Belén Gil, Gareth A. Cooke, Deanne Nolan, Gearóid M. Ó Máille, Sunil Varughese, Longsheng Wang and Sylvia M. Draper*

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This article reports the synthesis and optical properties of three dinuclear, cationic copper complexes [Cu(µ-dppm)(µ-L)](NO₃)₂ (dppm diphenyldiphosphinomethane, Lₐ 3,6-bis(2-pyridyl)-4,5-diphenyl-pyridazine, Lₐ 3,6-bis(2-pyridyl)-4,5-di(4-pyridyl)pyridazine and Lₐ 3,6-bis(2-pyridyl)-8,9-diazafluoranthene). These were formed on the reaction of [Cu(µ-dppm)(NO₃)], with a series of N-donor (bppn) ligands L. The single crystal X-ray structures of [Cu(µ-dppm)(µ-L)](NO₃)₂. CH₂Cl₂ were determined and revealed that in both, the two copper atoms are held by three bridging ligands, two dppm ligands and one bppn ligand acting as a tetradentate bridge. The absorption spectra of the complexes present a MLCT [Cu → π*(N=N)] band in the λ 370–425 nm region. These new complexes exhibit red-orange MLCT-based emission in the solid-state with lifetimes in the microsecond range. In oxygen-free dichloromethane solution, the complex [Cu(µ-dppm)(µ-Lₐ)]²⁺ has a long lifetime of 22.8 μs. The long emission lifetimes are attributed to a rigid conformation that precludes the possible distortion of the copper in the excited state.

Introduction

Although few in number, recent publications have begun to expose the potential of Cu(I) complexes as an alternative to Ru(II) in low-cost solar-conversion devices.¹⁻³ The rich photochemistry of Ru(II),⁴ Pt(II),⁵ and Ir(III)⁶ complexes is undermined by the reliance on expensive, rare metals, which in some cases exhibit an undesirable level of toxicity. The ease of preparation of Cu(I) complexes, their ability to absorb light in the visible region, intense luminescence and low cost has captured the interest of researchers in the field. Cu(I), however, undergoes a conformational change on oxidation to Cu(II), thus decreasing device efficiencies. Strategies to overcome the resultant low quantum yields and short luminescence lifetimes of [Cu(N=N)]²⁺ complexes require further development.¹⁻³

The electronic nature, bulk and rigidity of the diimine ligand all play an important role in determining the photophysical properties of Cu(I) complexes.³ Traditionally bipyridyl or phenanthroline-based systems have been used but there is scope to rethink and redesign ligand systems. A synthetic protocol which can be extended to multiple systems is very attractive and new aromatic ligands generated by Diels–Alder cycloaddition have come to the fore in Ru(II) chemistry.⁷⁻¹⁰

One development in copper chemistry has been the inclusion of stabilizing phosphine ligands, offering a significant improvement on the photophysical properties. McMillin and co-workers have demonstrated that bulky bidentate phosphines (such as POP = bis[2-(biphenylphosphino)phenyl]ether) inhibit the formation of quenching exciplexes, providing unusually long emission lifetimes and rather good quantum yields, typically in the green spectral window.¹¹⁻¹²

Another possibility is to increase the number of metal centers or to seek cooperative interactions between metal centers in a diimine-based system.¹³ Only a few examples of binuclear systems exist and these use ligands such as bipyrimidine¹⁴,¹⁵ or 2,5-bis(2-pyridyl)pyrazine.¹⁶ One downside is that the overall rigidity is reduced, e.g. in a transoid disposition. Rigid systems are needed to prevent distortion and/or exciplet-quenching of the excited state and thus enhance the optical properties. 2,5-Bis(2-pyridyl)tetrazines, can favour cisoid conformation and as precursors via inverse electron demand Diels–Alder to pyridazines offer a synthetic procedure for the inclusion of new chromophores.¹⁷,¹⁸

Results and discussion

Synthesis

Trans-stilbene and 1,4-bis(4-pyridyl)ethylene were each reacted with 3,4-bis(2-pyridyl)-1,2,4,5-tetrazine (hptz) in toluene by heating to reflux overnight in a sealed tube. On the loss of the characteristic pink colour of hptz, the products were
purified by column chromatography to give good yields of the respective bright yellow hydropyridazines (3,6-bis(2-pyridyl)-4,5-diphenyl-hydropyridazine, 75%; 3,6-bis(2-pyridyl)-4,5-bis(4-pyridyl)-hydropyridazine, 92%). Oxidation by blowing nitrous gases through a dichloromethane solution of the compounds at 0 °C gave the bispyridylpyridazine (bppn) ligands (L1, 74%, L2 50%, see Scheme 1). The lower yield observed for L2 may be due to the more electron-withdrawing 4-pyridyl substituents on the hydropyridazine ring rendering oxidation more difficult. The synthesis of L2 has been reported as has the synthesis of ligand L1, albeit under different conditions.

Treatment of a colourless solution of [Cu(m-dppm)(NO3)Cl] in dichloromethane at room temperature with an equivalent amount of bppn (L = L1, L2, L3) affords orange solutions. After stirring for 1 h, the resulting mixtures were filtered through Celite and concentrated (~2 mL). The addition of Et2O (~20 mL) precipitates [Cu(m-dppm)(m-L)](NO3)2 as an orange solid (81%–97%). Using a 1 : 2 molar ratio of metal precursor to L, the same products and unreacted adduct, the structures of complexes [Cu2(m-dppm)(m-L)][NO3]2(CH2Cl2) (L = L1, L2) were determined by single crystal X-ray diffraction.‡ Suitable, orange, block-shaped crystals were obtained by slow diffusion of hexane into a dry, dichloromethane solution of the respective complexes. [Cu(m-dppm)(m-L)][NO3]2 (L = L1, L2) crystallize in the space groups P21/n and P21/c, respectively. For both complexes, one cation and two nitrate anions are found in the asymmetric unit together with one molecule of dichloromethane. The structures of the cations are shown in Fig. 1 for [Cu(m-dppm)(m-L)]2+ and Fig. S1 for [Cu(m-dppm)(m-L)]2+.† Selected bonds and angles are presented in Table 1. The anions and solvent molecules do not take part in any significant intermolecular interactions in the crystal packing.

In each case, the two copper atoms are held in close proximity by three bridging ligands: two dppm bonded through phosphorus and one bppn L molecule. The Cu–Cu separation ([Cu(m-dppm)(m-L)][NO3]2, L1, 3.406 Å, L2, 3.390 Å) is significantly longer than the sum of the van der Waals radii indicating the absence of a Cu–Cu interaction.‡ Looking through the Cu···Cu axis, the conformations of the two PCuCuP bridges in each complex are approximately “eclipsed” (PCuCuP torsion angle (~70°). The conformations of the PCuCuP bridges in the two complexes are similar, with the bridging dppm ligands not oriented parallel to each other. The PCuCuP torsion angles are 37° and 34° for complexes L1 and L2, respectively.

**Table 1**

<table>
<thead>
<tr>
<th>L1</th>
<th>L2</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu–Cu separation (Å)</td>
<td>3.406</td>
</tr>
<tr>
<td>Interatomic N–Cu–N (°)</td>
<td>115.0(2)</td>
</tr>
<tr>
<td>Crystallographic data</td>
<td>[Cu2(dppm)2(L1)][NO3]2.CH2Cl2 have been deposited at the Cambridge Crystallographic Data Centre, CCDC numbers 768169 and 768170. Crystal data for [Cu2(dppm)2(L2)][NO3]2.CH2Cl2, C26H26Cl2Cu2N8O6P4, M = 1491.20, monoclinic, a = 14.673(3), b = 19.077(4), c = 26.536(6) Å, β = 96.795(4)°, U = 7374(3) Å3, T = 301(2) K, space group P21/c, 4, 4032 reflections measured, 12385 unique (Rint = 0.1040), which were used in all calculations. The final R1 (all data) was 0.1471 and wR2(F2) (all data) was 0.2649. Crystal data for [Cu2(dppm)2(L2'][NO3]2.CH2Cl2, C26H26Cl2Cu2N8O6P4, M = 1493.19, monoclinic, a = 14.570(4), b = 19.092(5), c = 26.482(8) Å, β = 96.897(7)°, U = 7313(4) Å3, T = 298(2) K, space group P21/c, Z = 4, 62142 reflections measured, 10613 unique (Rint = 0.1526) which were used in all calculations. The final R1 (all data) was 0.0781 and wR2(F2) (all data) was 0.1283.</td>
</tr>
</tbody>
</table>
angles range from 1.47° to 4.81°). Together they form an eight-membered Cu(&#946;/dppm)&bull;Cu ring in a boat-chair conformation (see Fig. 1b). A similar feature has been observed in other compounds such as [Cu(&#946;/dppm),(&#946;/PPDMe)][23] (PPDMe 3,6-bis(3,5-dimethylpyrazol-1-yl)pyridazine).[23]

In each complex, the copper atoms have a distorted tetrahedral arrangement determined by two phosphorus atoms (of two dppm ligands) and two nitrogen atoms (one from the pyridazine, one from a pyridine of L). The N-Cu-N angles are acute [range 76.0(1)°–77.7(3)°] due to the small chelating bite angle typical of bppn ligands.[24] The P-Cu-P units are non-linear [range 124.21(5)°–130.57(5)°], resulting in a folding of the Cu,P4 core along the Cu…Cu axis in an analogous disposition to that of the starting material [Cu(dppm)(NO3)]2+. This is consistent with the electronic configuration of the Cu(II) ion (Fig. 1c). In agreement with the solid-state molecular structure, the presence of these binuclear structures in solution is confirmed by 1H NMR spectroscopy (CDCl3, room temperature).

Electrochemical studies of the ligands showed no oxidation processes in the potential ranges (0 V–2 V vs. SCE). The ligand reduction of the three complexes and the reductions of the free ligands were reversible and lowered upon complexation (see Table 2). This is consistent with σ-bonding of the ligand to the metal.
The irreversible character of the oxidation process in all cases indicates that the Cu(II) species rapidly decompose on forming, as revealed by the disappearance of the oxidation peak under repetitive scans (Fig. S5†). The intensity and the broad character of the oxidations imply that multiple electron-transfer is occurring, which must originate from the presence of two metal centres. H NMR investigations of the electrochemically oxidised solutions did not shed any light on the identity of the decomposition products.

All the ligands and their respective copper complexes were weakly luminescent in the solid state, in solution at room temperature and in frozen solution at 77 K. Photoluminescence spectra and lifetime data are summarised in Table 3 (complexes) and Table S1† (ligands). For the copper systems, all the spectra are broad without vibronic progression, suggesting that the emissive excited states have charge transfer character. In solid state, the ligands bppn L present high energy emissions (~ 350–490 nm) with excited state lifetimes in the nanosecond range. In the case of Lc, a lower energy band is also observed (~ 600 nm). Considering the longer lifetime of this band, this emission could have some triplet charge transfer in nature (Table S1†).

In the solid state at room temperature, the compounds exhibit a red-orange luminescence (see Fig. 3), with the bands detected in the range between 587 and 676 nm ascribable to radiative decay from the MLCT states. In the case of [Cu,(μ-dppm),Lc]2+ (λem 635 nm) and [Cu,(μ-dppm),Lc]2+ (λem 642 nm), the emissions are similar, but for [Cu,(μ-dppm),Lc]2+ (λem 676 nm), the emission is red shifted due to the presence of the diazafluoranthene chromophore, which increases the degree of π-conjugation.

### Table 2

<table>
<thead>
<tr>
<th>Lc</th>
<th>λ/µm</th>
<th>Ered/ V</th>
<th>Evol/ V</th>
</tr>
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<tbody>
<tr>
<td>L1</td>
<td>266 (16.9), 325 (1.2)</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>L2</td>
<td>268 (26.9), 329 (0.9)</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>Lc</td>
<td>271 (28.2), 308 (17.8), 326 (13.2), 370 (13.4)</td>
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<td>—</td>
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<tr>
<td>Cu(II)</td>
<td>260 (71.6), 328 (21.6), 380 (10.2)</td>
<td>1.17*</td>
<td>—</td>
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<tr>
<td>Cu(II)</td>
<td>274 (76.7), 331 (21.2), 373 (11.7)</td>
<td>1.07*</td>
<td>—</td>
</tr>
<tr>
<td>Cu(II)</td>
<td>275 (72.5), 326 (36.0), 374 (32.8), 426 (16.1)</td>
<td>1.15*</td>
<td>—</td>
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* quasi-reversible, * irreversible process, peak potentials quoted.

### Table 3

<table>
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<tr>
<th>Complex</th>
<th>T/K</th>
<th>λem/ nm</th>
<th>φ</th>
<th>τ/µs</th>
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<tr>
<td>[Cu,(μ-dppm),Lc]2+</td>
<td>solid</td>
<td>298</td>
<td>587 (sh), 635, 660 (sh) (λem 500)</td>
<td>1.0 (100%) (λem\ 640 – λem\ 630)</td>
</tr>
<tr>
<td></td>
<td>77</td>
<td>670 (λem 495)</td>
<td>5.2 (74%), 0.7 (26%) (λem\ 460 – λem\ 670)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>CH2Cl2</td>
<td>298</td>
<td>670 br (λem 400)</td>
<td>1.1 (89%), 1.3 (11%) (λem\ 460 – λem\ 630)</td>
</tr>
<tr>
<td></td>
<td>77</td>
<td>643, 664 (λem 500)</td>
<td>5.2 (74%), 0.7 (26%) (λem\ 460 – λem\ 670)</td>
<td></td>
</tr>
<tr>
<td>[Cu,(μ-dppm),Lc]2+</td>
<td>solid</td>
<td>298</td>
<td>642, 666 (sh) (λem 490)</td>
<td>0.3 (100%) (λem\ 460 – λem\ 640)</td>
</tr>
<tr>
<td></td>
<td>77</td>
<td>681 (λem 500)</td>
<td>4.6 (73%), 0.6 (27%) (λem\ 460 – λem\ 680)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>CH2Cl2</td>
<td>298</td>
<td>675 br (λem 450)</td>
<td>2.3 (87%), 0.1 (13%) (λem\ 460 – λem\ 675)</td>
</tr>
<tr>
<td></td>
<td>77</td>
<td>678 (λem 450)</td>
<td>2.3 (87%), 0.1 (13%) (λem\ 460 – λem\ 675)</td>
<td></td>
</tr>
<tr>
<td>[Cu,(μ-dppm),Lc]2+</td>
<td>solid</td>
<td>298</td>
<td>676 (λem 550)</td>
<td>0.6 (100%) (λem\ 460 – λem\ 675)</td>
</tr>
<tr>
<td></td>
<td>77</td>
<td>645 (sh), 695 (λem 495)</td>
<td>2.3 (87%), 0.1 (13%) (λem\ 460 – λem\ 675)</td>
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<tr>
<td>CH2Cl2</td>
<td>298</td>
<td>675 br (λem 450)</td>
<td>2.3 (87%), 0.1 (13%) (λem\ 460 – λem\ 675)</td>
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<tr>
<td></td>
<td>77</td>
<td>685 (λem 450)</td>
<td>2.3 (87%), 0.1 (13%) (λem\ 460 – λem\ 675)</td>
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</table>

Fig. 2 The UV-vis spectra in dichloromethane of Lc (broken line) and [Cu,(μ-dppm),Lc]2+ (solid line) where the MLCT is clearly observed.

centre and the positive charge of the metal complex, which render the ligands more electron-accepting on complexation. The first reduction potential for [Cu,(μ-dppm),Lc]2+ reflects the greater electron-accepting nature of the aromatic platform in Lc, but subsequent reductions appear to be affected by the pyridyl or phenyl substituents. A broad irreversible oxidation band was observed for each complex that was assigned to the Cu(I)/Cu(II) redox couple on comparison with similar data reported in the literature (see Fig. S5† and Table 2). Such oxidations occur at high potentials because of the need to radically alter the complex geometry for Cu(II) and are indicative of ligand rigidity. The irreversible character of the oxidation process in all cases indicates that the Cu(II) species rapidly decompose on forming, as revealed by the disappearance of the oxidation peak under repetitive scans (Fig. S5†). The intensity and the broad character of the oxidations imply that multiple electron-transfer is occurring, which must originate from the presence of two metal centres. H NMR investigations of the electrochemically oxidised solutions did not shed any light on the identity of the decomposition products.

All the ligands and their respective copper complexes were weakly luminescent in the solid state, in solution at room temperature and in frozen solution at 77 K. Photoluminescence spectra and lifetime data are summarised in Table 3 (complexes) and Table S1† (ligands). For the copper systems, all the spectra are broad without vibronic progression, suggesting that the emissive excited states have charge transfer character. In solid state, the ligands bppn L present high energy emissions (~ 350–490 nm) with excited state lifetimes in the nanosecond range. In the case of Lc, a lower energy band is also observed (~ 600 nm). Considering the longer lifetime of this band, this emission could have some triplet state character (e.g. from a \(1\pi\pi^*\) excited state localised on the π-conjugated fluoranthene chromophore), or could be intra-ligand charge transfer in nature (Table S1†).

In the solid state at room temperature, the compounds exhibit a red-orange luminescence (see Fig. 3), with the bands detected in the range between 587 and 676 nm ascribable to radiative decay from the MLCT states. In the case of [Cu,(μ-dppm),Lc]2+ (λem 635 nm) and [Cu,(μ-dppm),Lc]2+ (λem 642 nm), the emissions are similar, but for [Cu,(μ-dppm),Lc]2+ (λem 676 nm), the emission is red shifted due to the presence of the diazafluoranthene chromophore, which increases the degree of π-conjugation.
undergo a small red-shift and are less intense (\(\text{Cu}_2(\mu\text{-dppm})(\mu\text{-L}_A)\))\(^{2+}\) solid \(0.3\) \(\mu\)s, \(\text{CH}_2\text{Cl}_2\) 2.3 \(\mu\)s. The presence of the weak \(\pi\cdots\pi\) interactions observed in crystalline samples could increase the non-radiative relaxation paths and thus explain the shorter lifetimes in the solid state. The excited state lifetime of \([\text{Cu}_2(\mu\text{-dppm})(\mu\text{-L}_A)]^{2+}\) as a solid is shorter than that observed for the others (0.6 \(\mu\)s), here \(\pi\cdots\pi\) interactions involving the fluoranthene moieties would be expected to be stronger than those observed for \([\text{Cu}_2(\mu\text{-dppm})(\mu\text{-L})]^{2+}\) \((\text{L = L}_A, \text{L}_B)\) and could contribute to the deactivation of the excited state. However, in oxygen-free solution, this complex \([\text{Cu}_2(\mu\text{-dppm})(\mu\text{-L}_A)]^{2+}\) has a longer lifetime of 22.8 \(\mu\)s. As far as we know, this value is the longest found for a system of the type [\(\text{Cu}(\text{N}^3\text{N})(\text{P}^3\text{P})\)]\(^{2+}\), being longer than that previously described by Armaroli for \([\text{Cu}(\text{POP})(\text{dmdp-phen})]^{2+}\) (2,9-dimethyl-4,7-diphenylphenanthroline) under the same conditions (17.3 \(\mu\)s in dichloromethane at room temperature).\(^{12}\) It should be noted however that the neutral amidophosphine complexes of copper \([\text{PN}]\text{Cu(L)}\), reported by Miller and co-workers in some cases present longer lifetimes (16–150 \(\mu\)s).\(^{39}\) Although neutral complexes are highly desirable, some examples of OLED devices with charged species as active materials have been reported.\(^{40}\) In all cases the consideration of emission lifetimes is important; guest phosphors ideally exhibit a phosphorescence lifetime in the region of 5–50 \(\mu\)s at room temperature.\(^{41}\) The desirable solid-state photophysics of the simple systems reported here can be attributed to the rigid conformation of the eight-membered ring, which precludes the possible distortion of the copper in the excited state and the formation of quenching exciplexes.

Fig. 3 Excitation (broken line) and emission (solid line) spectra of \([\text{Cu}_2(\mu\text{-dppm})(\mu\text{-L}_A)](\text{NO}_3)_2\) in solid state at room temperature (black) and at 77 K (grey).

Fig. 4 Normalized emission spectrum of \([\text{Cu}_2(\mu\text{-dppm})(\mu\text{-L}_A)](\text{NO}_3)_2\) in degassed dichloromethane solution at room temperature (a) and its emission decay with fitting (b).
Conclusions

The use of extended polyaromatic pyridazines and azafluoranthenes as new N-donor ligand motifs in the formation of dimeric Cu(t) bisphosphine complexes has resulted in three novel sterically hindered dication systems. The N-donor ligands act as bridging supports to a rigid eight-membered ring comprising Cu(µ-dppm),Cu and provide a stable framework to secure the distorted tetrahedral geometry of the Cu centres. Red-orange MLCT emission is characteristic of these complexes and the structural features give rise to emission lifetimes in the microsecond range similar to those associated with neutral amidophosphine complexes.

Experimental

General Methods

Elemental analyses were carried out in a Perkin–Elmer 240-B analyser. NMR spectra were recorded on a DPX-400 spectrometer by using the standard references. Electrospray ionization mass spectra were recorded on a micromass LCT electrospray mass spectrometer. Nuclear magnetic resonance spectra were recorded with a Brucker Avance DPX-400 MHz at the following frequencies: 400.1 MHz for 1H, 100.6 MHz for 13C{1H} and 162.2 for 31P{1H}. Chemical shifts are reported in ppm relative to external standards (SiMe₄ for 1H and 13C{1H} and 85% H₃PO₄ for 31P{1H}) and all the coupling constants are given in Hz to two decimal places.

UV-vis spectra were obtained on a Shimadzu UV-2401PC UV-vis spectrometer. Emission and excitation spectra were obtained on a Fluorolog FL-3-11 spectrofluorimeter. A Jobin Yvon FluoroHub single photon counting controller fitted with an appropriate wavelength Jobin Yvon NanoLED was used to measure lifetimes, which were determined from the observed decays using DataStaView v.2.4. The solution emission quantum yields were measured by the Demas and Crosby method using [Ru(bipy)₃]Cl₂ in degassed water as standard (φ₂,mon = 0.042). All electrochemical experiments were performed with a CH Instrument Potentiostat, model 660B. Cyclic voltammograms were measured on 1 mM solutions of the complexes in dry, degassed acetonitrile or dimethyformamide with tetrabutylammonium hexafluorophosphate (TBAPF₆, 0.1 M) as the supporting electrolyte with a glassy carbon working electrode, a Pt wire counter electrode and a saturated calomel electrode as the reference electrode. All the potentials were referenced to internal ferrocene added at the end of each experiment.

3,6-bis(2-pyridyl)-1,2,4,5-tetrazine (bptz),²⁹ 3,6-bis(2-pyridyl)-8,9-diazafluoranthen (Lc)²⁹ and [Cu(µ-dppm)(NO₃)]₃ were prepared by literature methods. Trans-stilbene and 1,4-di(4-pyridyl)ethylene were purchased from Aldrich.

Synthesis of 3,6-bis(2-pyridyl)-4,5-diphenyl pyridazine (LA).

Synthesis of 3,6-bis(2-pyridyl)-4,5-diphenyl hydropyridazine. 3,4-bis(2-pyridyl)-1,2,4,5-tetrazine (0.600 g, 2.540 mmol) and trans-stilbene (0.469 g, 2.600 mmol) were refluxed in 20 mL of toluene for 24 h. At this stage, the colour of the solution had changed from dark pink to bright yellow. The solvent was removed under vacuum, and the reaction mixture was purified by running it through a column of silica (10% diethyl ether in dichloromethane) obtaining as a pure yellow solid (0.906 g, 92%). Anal. calc'd for C₁₃H₂₀N₄ (388.47): C 80.39, H 5.19, N 14.42. Found: C 79.99, H 5.67, N 14.50. δH (400 MHz; CDCl₃; Me₄Si) 9.43 (s, 1H, H¹⁵), 8.61 (d, 1H, H², J = 3.8 Hz), 8.61 (d, 1H, H¹, J = 4.4 Hz), 8.10 (d, 1H, H², J = 7.9 Hz), 7.63 (³P{d}, 1H, H, J = 7.8, 1.8 Hz), 7.57 (d, 2H, H, δCν = 7.0 Hz), 7.40 (³P{d}, 1H, H, J = 7.8, 1.5 Hz), 7.30–7.17 (m, 11H, HPh), 5.82 ppm (s, 1H, H₁₂).

δ (101 MHz; CDCl₃; Me₄Si) 154.18 (1C, C₁₁), 151.56 (1C C₁₄), 149.15 (1C C₆), 145.01 (1C C₁₂), 141.85 (1C CQ), 135.86 (1C C₁₄), 135.11 (1C CQ), 128.54 (1C C₃), 128.27 (1C C₅), 128.25 (1C), 127.16 (1C), 126.70 (1C), 124.47 (1C), 123.02 (1C), 122.67 (1C), 121.48 (1C), 108.15 (1C C₁₃), 41.54 ppm (1C C₁₂). HRMS (CH₃CN); [MH]+ m/z 389.1766, found: 389.1782.
Synthesis of 3,6-bis(2-pyridyl)-4,5-bis(4-pyridyl)-pyridazine (LA). This compound was prepared as an off-white product LB (0.308 g, 50%) similarly to compound IA, starting from NaNO2 (20 mL, 6 M), HCl (12 mL) and 3,6-bis(2-pyridyl)-4,5-bis(4-pyridyl)-1,4-dihydripyrazidine (0.618 g, 1.587 mmol). It was purified by column chromatography on silica (50% ether, 50% methanol). Anal. calc'd for C24H19N6: [M + H]+ 387.1515, Found: 387.1505; 626.1102, found: 626.1081. The resulting mixture was stirred for 1 h, filtered through Celite and concentrated to 2 mL. The addition of Et2O (20 mL) affords the resulting mixture was stirred for 1 h, filtered through Celite and concentrated to 2 mL. The addition of Et2O (20 mL) affords the complex [Cu2(μ-dppm)(μ-La)(NO3)]NO3 (LA), (LA) (19 mg, 0.049 mmol) and [Cu(μ-dppm)(NO3)]2 (50 mg, 0.049 mmol). The product was filtered, washed with cold MeOH and dried. Anal. calc'd for C24H19N6Cu2P2O2 (388.43) C 74.21, H 4.15, N 7.10. Found C 74.30, H 4.15, N 7.09.

Synthesis of [Cu2(μ-dppm)(μ-Lb)(NO3)]NO3. This complex [Cu2(μ-dppm)(μ-Lb)(NO3)]NO3 (55 mg, 81%) was prepared as a deep orange solid similarly to [Cu2(μ-dppm)(μ-La)(NO3)]NO3: starting from 3,6-bis(2-pyridyl)-8,9-diazafluoranthene (Le) (35 mg, 0.049 mmol) and [Cu(μ-dppm)(NO3)]2 (50 mg, 0.049 mmol). The product was filtered, washed with cold MeOH and dried. Anal. calc'd for C24H19N6Cu2P2O2 (388.43) C 74.21, H 4.15, N 7.10. Found C 74.30, H 4.15, N 7.09.

Synthesis of [Cu(μ-dppm)(μ-La)(NO3)]2. This complex [Cu(μ-dppm)(μ-La)(NO3)]2, (LA) (19 mg, 0.049 mmol) was prepared as a colourless solid similar to [Cu(μ-dppm)(μ-La)(NO3)]2: starting from 3,6-bis(2-pyridyl)-8,9-diazafluoranthene (Le) (35 mg, 0.049 mmol) and [Cu(μ-dppm)(NO3)]2 (50 mg, 0.049 mmol). The product was filtered, washed with cold MeOH and dried. Anal. calc'd for C24H19N6Cu2P2O2 (388.43) C 74.21, H 4.15, N 7.10. Found C 74.30, H 4.15, N 7.09.

Synthesis of [Cu(μ-dppm)(μ-Lb)(NO3)]2. This complex [Cu(μ-dppm)(μ-Lb)(NO3)]2 (LA) (19 mg, 0.049 mmol) was prepared as a colourless solid similar to [Cu(μ-dppm)(μ-La)(NO3)]2: starting from 3,6-bis(2-pyridyl)-8,9-diazafluoranthene (Le) (35 mg, 0.049 mmol) and [Cu(μ-dppm)(NO3)]2 (50 mg, 0.049 mmol). The product was filtered, washed with cold MeOH and dried. Anal. calc'd for C24H19N6Cu2P2O2 (388.43) C 74.21, H 4.15, N 7.10. Found C 74.30, H 4.15, N 7.09.

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References


