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Introduction

Peculiar properties of homoleptic Cu complexes with dipyrromethene derivatives[†]

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In view of preparing Cu polynuclear complexes with dipyrromethene ligands, the mononuclear complexes $[Cu(II)(dipy)_2]$ (dipyH = 5-phenyldipyrromethene) and $[Cu(III)(dpdipy)_2]$ (dpdipyH = 1,5,9-triphenyldipyrromethene) have been prepared and characterized by X-ray crystallography, mass spectrometry and EPR spectroscopy. Their peculiar redox and spectroscopic (absorption/emission) behaviours are discussed. In contrast to Cu^{II} complexes of 1,1'-bidypyrrin, the reduction electrolysis of $[Cu(III)(dpdipy)_2]$ leads to decomposition products on a time scale of a few hours. Moreover in relation to this observation, $[Cu(II)(dpdipy)_2]^-$ could not be synthesized in spite of the Cu^{II} core protection by the phenyl substituents in *ortho* position of the nitrogen atoms. Theoretical calculations provide some explanations for this instability. Interestingly $[Cu(III)(dipy)_2]$ and $[Cu(III)(dpdipy)_2]$ display weak luminescence at room temperature, attributed to a ligand centered emission.

Cu complexes with polyazaaromatic ligands have attracted several research teams mainly because these compounds exhibit a peculiar property, which consists of changing the structure or coordination number from Cu^{I} to Cu^{II} and *vice versa*. Thus the properties of these complexes depend very much not only on the ligands, but also on the oxidation state of the metal ion. Indeed it was demonstrated several years ago that Cu^{I} complexes can be prepared as tetrahedral diamagnetic compounds with two bidentate ligands such as 1,10-phenanthroline (phen) for example.¹⁻⁴ However they are not very

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Spectrométrie de masse (CISMA), Université de Mons, UMons, 20 Place du Parc, B-7000 Mons, Belgium stable in solution due to their oxidation of Cu^I into Cu^{II}, except if bulky substituents such as phenyl groups are present in *ortho* position of the nitrogen atoms of the phen ligand that protect the Cu^I centre. Such complexes are usually distorted as compared to an ideal tetrahedral geometry,⁵ in which the two chelating ligands are perpendicular to each other. Paramagnetic Cu^{II} complexes in contrast can adopt different geometries⁶⁻¹⁰ such as distorted octahedra, square pyramids or trigonal bipyramids. The changes of geometries according to the oxidation state adopted by the Cu ion led to interesting and very nice applications highlighted by J. P. Sauvage's team. Thus Cu complexes were used as templates in the synthesis of catenanes and rotaxanes¹¹⁻¹³ and their change of structure by electrochemical oxidation/reduction was exploited for triggering movements.¹⁴⁻¹⁸

Such modifications of configuration by a change of the oxidation state of the Cu ion can be induced not only electrochemically but also by light absorption.¹⁹ Indeed, this type of Cu^I complex has a first absorption band in the visible region of the spectrum corresponding to an MLCT (Metal to Ligand Charge Transfer) transition. Therefore excitation in this band promotes an electron from Cu^I to one of the ligands, generating in this way a Cu^{II} transient excited state.^{20,21} The resulting movement initiated by this sudden change of oxidation state and occurring with nonprotecting phen ligands makes the Cu core accessible to a fifth monodentate nucleophilic ligand such as Cl⁻ or a water molecule, responsible for the short excited state lifetimes of these nonprotected Cu^I complexes.^{22,23} This type of excited state quenching is prevented when the phen

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Fig. 1 Structure of the free ligands dipyH (5-phenyldipyrromethene) and dpdipyH (1,5,9-triphenyldipyrromethene).

ligands are substituted in *ortho* position of the chelated nitrogen atoms by phenyl groups. Therefore these Cu^I complexes are luminescent and have long excited state lifetimes.^{24–26}

In the past in our lab, we have examined the properties of some Cu^I complexes²⁷ and their behaviour as SnO₂ photosensitizers.²⁸ In the present work, our ultimate goal was to construct large polynuclear species with CuI/CuII ions and bridging organic ligands for testing their possible novel properties. Ligands that would be symmetric and very easily derivatized had thus to be used. In this frame, mononuclear Cu^{II} complexes have already been obtained with dipyrrin ligands also called dipyrromethene, $^{29-33}$ as well as polynuclear Cu^{II} complexes with meso-pyridyl dipyrrins.34 Moreover the dipyrromethene chelates of BF2⁺, thus the well known BODIPY derivatives, have been shown to exhibit quite remarkable tunable optical properties by varying the substituents on the ligands.³⁵⁻³⁷ For those different reasons, we decided to consider dipyrromethene derivatives for our future polynuclear Cu^{II} and Cu^I complexes. However, before undertaking such a study, the knowledge of the properties of the mononuclear Cu compounds was a prerequisite. Although several dipyrromethene CuII complexes have been prepared and examined in the literature,^{32,38} the specific properties of the herein targeted dipyH and dpdipyH ligands (Fig. 1) necessary before starting the study of polynuclear species have not been described. Moreover, the literature on the Cu-dipyrromethene complexes neither discusses the electrochemical and the emission characteristics of the Cu^{II} complexes nor reports the synthesis of the corresponding Cu^I complexes. To the best of our knowledge, only tridentate Cu^I complexes with one tetraphenylazadipyrromethene and one triphenylphosphine have been synthesized in the literature.39 Therefore, in this work we report the electrochemical behaviour and electronic absorption as well as emission spectroscopy of the mononuclear homoleptic Cu complexes comprising two dipyrromethene ligands (Fig. 1). Attempts to explain by theoretical considerations the origin of some intriguing results are also presented.

Results

Syntheses

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dpdipyH (1,5,9-triphenyldipyrromethene) ligands was the same as the one described in the literature for similar Cu complexes based on substituted dipyrromethene ligands.^{12,34,38,40,41} Two equivalents of dipyH or dpdipyH were thus reacted with one equivalent of $Cu(OAc)_2 \cdot H_2O$ in the presence of a base. While the complexation of two "non-sterically hindered" dipyrromethene ligands (dipyH) could be performed at room temperature for obtaining $[Cu(\pi)(dipy)_2]$, the formation of $[Cu(\pi)(dpdipy)_2]$ needed higher temperatures due to the steric hindrance caused by the phenyl groups of the dpdipyH ligands. Both complexes were easily purified by silica column chromatography.

For the Cu^I complexes, as mentioned in the introduction, the ligand dipyH which has no substituent in ortho position of the chelating nitrogen atoms cannot sufficiently protect the metallic Cu^I core *versus* oxidation. We anticipated that phenyl protecting groups were required for the preparation of Cu^I complexes. Thus the dpdipyH ligand has been used in order to obtain the anion $[Cu(I)(dpdipy)_2]^-$. The preparation has been performed at a vacuum line and under Ar according to procedures described for many other Cu^I complexes of the literature and our previous Cu^I compounds²⁷ based on phen type ligands.^{1-4,42} Thus Cu(1)(MeCN)₄BF₄ was first prepared from $Cu(II)(BF_4)_2$ reduction by Cu(0) in anhydrous MeCN. The soobtained Cu(I) intermediate was treated with two equivalents of dpdipyH ligands always at the vacuum line and under Ar, under anhydrous conditions and in the presence of triethylamine. After evaporation of the solvent under an Ar atmosphere, the crude solid was analyzed by ESI mass spectrometry. In other trials, the complex was recrystallized in hexane under Ar at the vacuum line.[‡] NMR spectroscopy brought no valuable structural information on the prepared Cu^I complex (see further).

Mass spectroscopy

The first characterizations were performed by mass spectrometry. The main mass spectrometry results are shown in Table 1. Cu has two major isotopes, namely ⁶³Cu (69%) and ⁶⁵Cu (31%). For the discussion, we will use only ⁶³Cu as the reference atom for the mass-to-charge ratio description, and this as well for the Cu^I as for the Cu^{II} complexes.

Upon ESI analysis in the positive ion mode, *i.e.* ESI(+) of $[Cu(\pi)(dipy)_2]$ (501 Da) in acetonitrile (entry 1), only decomposition products are detected at m/z 282 and correspond to $[Cu(\pi)(dipy)]^+$ ions. When analyzed by MALDI(+), the presence of the expected $[Cu(\pi)(dipy)_2]$ complex (entry 2) is confirmed since a unique signal at m/z 501, which corresponds to $[Cu(\pi)(dipy)_2]^+$ ions, is observed (Fig. S1[†]). It is important to emphasize that, at variance with ESI where protonation is likely to be the dominant ionization process, the ions detected upon MALDI correspond to one electron removal from the neutral complex; this could explain why ions corresponding to the

The procedure adopted for the syntheses of the Cu^{II} complexes with the dipyH (5-phenyldipyrromethene) and the new

[‡]Different parameters have been changed for this synthesis such as (i) time of reaction, (ii) absence of base, (iii) order of addition of the reagents and (iv) the use of a commercial anhydrous solvent.

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Cu(n)(dpdipy)(dpdipyH)]⁺

Cf ESI(+) of Cu(II)(dpdipy)₂]

Cu(II)(dpdipy)₂]

[Cu(I)(dpdipyH)₂]

 $[Cu(i)(dpdipy)_2]$

used as the reference atom for the mass-to-charge fatto description						
Entry	Targeted complexes	Ionization methods	Detected ions (m/z)	Ion identification		
1	[Cu(II)(dipy) ₂]	ESI(+)	282	[Cu(II)(dipy)] ⁺ decomposition		
2	[Cu(II)(dipy) ₂]	MALDI(+)	501 (S1)	[Cu(II)(dipy) ₂] ⁺		
3	[Cu(II)(dpdipy)_]	MALDI(+)	805	$[Cu(u)(dpdipy)_{2}]^{+}$		

806 (S2b)

805 (S2a)

805 (S2c)

806 (S2d)

807 (most intense, Fig. 2a)

ESI(+)

ESI(-)

ESI(-)

ESI(+)

ESI(+)

 Table 1
 Mass spectrometry results. The complexes are dissolved in acetonitrile. Among the two major isotopes, namely ⁶³Cu (69%) and ⁶⁵Cu (31%), only ⁶³Cu was used as the reference atom for the mass-to-charge ratio description

$[{\rm Cu}(\pi)({\rm dipy})_2]$ are observed in MALDI and not in ESI. For $[{\rm Cu}(\pi)-$
$(dpdipy)_2$] (entry 3), a unique signal at m/z 805, corresponding
also to an electron removal, is observed in MALDI(+).

 $[Cu(\pi)(dpdipy)_2]$

Cu(II)(dpdipy)₂

Cu(I)(dpdipy)₂]⁻ crude

 $[Cu(i)(dpdipy)_2]^-$ crude $[Cu(i)(dpdipy)_2]^-$ small crystals

The ESI(+) mass spectrum of $[Cu(\pi)(dpdipy)_2]$ in contrast to that of $[Cu(\pi)(dipy)_2]$ allows the confirmation of the presence of the targeted complex. Indeed, by ESI(+) the dominant peak is observed at m/z 806 (entry 4) (Fig. S2b†) which corresponds to protonation of neutral $[Cu(dpdipy)_2]$, affording $[Cu(\pi)-(dpdipy)(dpdipyH)]^+$. In this case, no decomplexation process is observed in contrast to $[Cu(\pi)(dipy)_2]$ (entry 1). This observation could point to the higher stability of $[Cu(\pi)(dpdipy)_2]$ in comparison with $[Cu(\pi)(dipy)_2]$ arising from the presence of the bulky ligands dpdipy. We also examined the behaviour of the Cu^{II} complex upon ESI(-). As demonstrated by the comparison of the ESI(+) and ESI(-) data (Fig. S2a and S2b†), the most dominant peak in ESI(-) corresponds to m/z 805 (entry 5), thus to one electron reduction of $[Cu(\pi)(dpdipy)_2]$ into $[Cu(\pi)(dpdipy)_2]^-$.

Based on the anionic nature of the prepared Cu^I complex, *i.e.* $[Cu(I)(dpdipy)_2]^-$ (805 Da), an ESI(-) analysis seems a priori suitable to probe the presence of the Cu^{I} complex. The ESI(-) mass spectrum (Fig. S2c⁺) of an acetonitrile solution of the crude $[Cu(I)(dpdipy)_2]^-$ (entry 6) reveals the presence of a signal at m/z 805 which could correspond to the expected complex $[Cu(I)(dpdipy)_2]^-$. Nevertheless, as already revealed here above, when subjected to ESI(-), the Cu^{II} complex (entry 5) also leads to the production of m/z 805 anions (Fig. S2a⁺). In other words, the observation of the m/z 805 ions in the ESI(-) spectrum of the Cu^I complex does not safely demonstrate the presence of the expected Cu^I complex. Finally, an ESI(+) mass spectrum of the prepared $[Cu(I)(dpdipy)_2]^-$ (entry 7) was also recorded. In that case, two protons are required to obtain cationic species yielding m/z 807 ions. However, when analyzing the pattern of signals in the ESI(+) of the Cu^I complex (entry 7) (Fig. S2d⁺) the most intense peak is observed at m/z 806 and not at m/z 807 as expected. Crystallized [Cu(I)(dpdipy)₂]⁻ was also analyzed by mass spectrometry. Two distinct populations of crystals were obtained and could be described as small and large crystals. The ESI(+) mass spectrum of the larger crystals does not show any difference to the ESI(+) mass spectrum of the Cu^{II} complex (Fig. 2b). However, in the ESI(+) mass spectrum obtained from the smaller crystals (entry 8) (Fig. 2a), the pattern of the signals is significantly different from the previous cases and is dominated by the m/z 807 signal that could



Fig. 2 Attempts to synthesize the $[Cu(i)(dpDipy)_2]^-$ complex. Mass spectrometry analyses of the crystalline products obtained from a toluene solution of the crude reaction product upon slow addition of heptane: ESI(+) mass spectra for (a) the thin crystals (Table 1, entry 8) and (b) the large crystals, see text for more details.

be attributed to the $[Cu(1)(dpDipyH)_2]^+$ cations (thus to the diprotonation of $[Cu(1)(dpdipy)_2]^-$).

In conclusion, the mass spectrometry analyses confirm that the expected Cu^{II} complexes have been isolated. As far as the Cu^{I} complex is concerned, no direct evidence of its preparation has been obtained from mass spectrometry. Only, its presence could be proposed in the smaller crystals prepared upon crystallization of the $[Cu(i)(dpdipy)_2]^-$ complex.

X-ray crystallography

The structures of $[Cu(II)(dipy)_2]$ and $[Cu(II)(dpdipy)_2]$ were determined by X-ray diffraction (Fig. 3). The crystals were obtained by slow evaporation of the complex solution in MeOH–CHCl₃ for $[Cu(II)(dipy)_2]$ and in CHCl₃–heptane for $[Cu(II)(dpdipy)_2]$. Like other Cu^{II} complexes based on dipyrrin ligands,^{38,43,44} $[Cu(II)(dipy)_2]$ displays a four-coordinate distorted square-plane geometry (Fig. 3a and Tables 2 and 3). The asymmetric unit comprises two distinct molecules of $[Cu(II)-(dipy)_2]$: one exhibits a dihedral angle between the two opposite N–Cu–N planes of 45.8° (Fig. 3a, bottom) and the other 46.2° (Fig. 3a, top). The large deviation from 0 arises from the steric hindrance of the protons in alpha position of the nitrogen atoms.§ For $[Cu(II)(dpdipy)_2]$ (Fig. 3b, Tables 2 and 3) the presence of the two additional phenyl groups leads to an even more important angle (63.0°) as obtained by the present X-ray

[§] This angle is comparable to that estimated from spectroscopic data for a similar complex with a *p*-nitrophenyl group in the *meso* position instead of a phenyl substituent.³⁸ Based on an experimental relation²⁹ between the absorption coefficient of the most bathochromic band of the complex and this dihedral angle, Dolphin *et al.*³⁸ obtained an angle of 48°.



 $\label{eq:Fig.3} (a) \mbox{ View of crystal structure of } [Cu(\ensuremath{\shortparallel})(Dipy)_2] \mbox{ (two molecules in the asymmetric unit shown). (b) \mbox{ View of crystal structure of } [Cu(\ensuremath{\shortparallel})(dpDipy)_2].$

data.¶ For both $[Cu(\pi)(dipy)_2]$ and $[Cu(\pi)(dpdipy)_2]$, the two pyrrole rings are not coplanar: the angle extends from 1.1 to 8.8° in $[Cu(\pi)(dipy)_2]$ and from 14.8 to 36.1° in $[Cu(\pi)(dpdipy)_2]$ (Tables S1–4†). Moreover, the phenyl groups in *meso* position are not in the same plane as that of the dipyrrin moieties, due to steric hindrances.

In the case of $[Cu(i)(dpdipy)_2]^-$ as mentioned above, the crude solid obtained after evaporation of the solvent under Ar was crystallized from a toluene solution by slowly adding heptane under Ar. Under these conditions, two types of crystals have been obtained and separated. First, thin, small crystals were collected and filtered off under an argon atmosphere. Afterwards, larger crystals started to be observed from the filtrate, which was kept under argon. Only the larger crystals could be analyzed by X-ray diffraction and they correspond (Fig. S3[†]) without ambiguity to the Cu^{II} complex [Cu(II)-

Та	hle	2	XR	data
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	Cu(n)(Dipy) ₂	[Cu(II)(dpDipy) ₂] ⁻ (elusive)
Formula	C ₃₀ H ₂₂ CuN ₄	C54H38CuN4
$M(\text{g mol}^{-1})$	502.06	806.42
Crystal dimensions (mm ³)	0.5 imes 0.2 imes 0.1	0.4 imes 0.3 imes 0.2
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/c$	$P2_1/n$
a (Å)	17.0388(7)	13.7700(4)
$b(\dot{A})$	15.6229(7)	13.5622(4)
c (Å)	19.7025(7)	21.6416(6)
α (°)	90.00	90.00
β (°)	115.496(2)	94.943(2)
γ (°)	90.00	90.00
$V(Å^3)$	4734.0(3)	4026.6(2)
Z	4	4
$D_{\rm calc} (\rm g \ cm^3)$	1.409	1.330
$\theta_{\max}(\circ)$	71.30	71.48
λ (Å)	1.54178 (CuKα)	1.54178 (CuKα)
F(000)	2072	1676
$T(\mathbf{K})$	100(2)	100(2)
Measured reflections	47 610	39 7 9 3
Unique reflections	9195	7712
Observed reflections	6864	6382
$(I_{\rm o} > 2\sigma(I_{\rm o}))$		
Parameters refined	632	532
R_1	0.0468	0.0412
$\omega R_2^{a,b}$	0.1094^{a}	0.0988^{b}
R_1 (all data)	0.0686	0.0524
ωR_2 (all data)	0.1229	0.1059
GOOF	1.068	1.058
$\mu (\mathrm{mm}^{-1})$	1.500	1.097

^{*a*} Weighting scheme as defined for Cu(II)(Dipy)₂: $\omega = 1/[\sigma^2(F_o^2) + (0.0608 P)^2 + 1.6118 P]$, $P = (F_o^2 + 2F_c^2)/3$. ^{*b*} Weighting scheme as defined for Cu(II)(dpDipy)₂: $\omega = 1/[\sigma^2(F_o^2) + (0.0530 P)^2 + 1.8201 P]$, $P = (F_o^2 + 2F_c^2)/3$.

Table 3 Selected bond lengths [Å] and angles [°] for $[Cu({\scriptstyle II})(Dipy)_2]$ and $[Cu({\scriptstyle II})(dpDipy)_2]$

[Cu(II)(Dipy) ₂]		[Cu(II)(dpDipy) ₂]	
Cu1-N2	1.950(5)	Cu1-N2	1.9582(16)
Cu1-N12	1.919(6)	Cu1-N12	1.9690(16)
Cu1-N19	1.973(5)	Cu1-N31	1.9524(16)
Cu1-N29	1.920(5)	Cu1-N41	1.9711(16)
N2-Cu1-N12	92.0(2)	N2-Cu1-N12	95.38(7)
N12-Cu1-N29	96.8(2)	N12-Cu1-N41	105.81(7)
N29-Cu1-N19	92.0(2)	N41-Cu1-N31	94.76(7)
N19-Cu1-N2	97.2(2)	N31-Cu1-N2	98.16(7)
Cu36-N37	1.964(6)		
Cu36-N47	1.926(6)		
Cu36-N54	1.979(5)		
Cu36-N64	1.912(6)		
N37-Cu36-N47	91.85(16)		
N47-Cu36-N64	96.5(2)		
N64-Cu36-N54	92.35(16)		
N54-Cu36-N37	97.6(2)		

Dihedral angle between $N_2Cu_1N_{12}$ and $N_{19}Cu_1N_{29},\ [Cu(\pi)(Dipy)_2]$ 45.791° (Fig. 3a, bottom). Dihedral angle between $N_{37}Cu_{36}N_{47}$ and $N_{54}Cu_{36}N_{64},\ [Cu(\pi)(Dipy)_2]$ 46.167° (Fig. 3a, top). Dihedral angle between lines $N_2Cu_1N_{12}$ and $N_{31}Cu_1N_{41},\ [Cu(\pi)(dpDipy)_2]$ 63.043° (Fig. 3b).

[¶]Such an effect of phenyl substituents in those positions of dipyrromethene had also been evidenced, but in that case without phenyl in *meso*-position and from the same experimental relation,²⁹ the authors³⁸ obtained a dihedral angle of 73°.

EPR spectroscopy

The structures of the dipy and dpdipy Cu^{II} complexes have also been examined in organic solution by EPR spectroscopy. The X-band EPR spectra of the Cu^{II} complexes at 100 K exhibit an (S = 1/2) signal with axial symmetry (Fig. 4, Table 4). The observed four-line pattern arises from the hyperfine interaction between the electronic spin and the copper nucleus ($I_{Cu} = 3/2$). Because of the broadening of the spectrum of $[Cu(\pi)(dipy)_2]$ in benzonitrile (likely due to intermolecular spin exchange), we additionally measured it in a benzonitrilemethanol (1:3) mixture, which allows for a better spin isolation. From simulation of the experimental spectra, the sets of spin Hamiltonian parameters $g_{\perp} = 2.049, g_{\parallel} = 2.214$ with $A_{\perp} = 2.0$ mT, $A_{\parallel} = 17.0$ mT and $g_{\perp} = 2.083$, $g_{\parallel} = 2.269$ with $A_{\perp} = 1.5 \text{ mT}, A_{\parallel} = 11.20 \text{ mT}$ could be obtained for $[Cu(\pi)(dipy)_2]$ and $[Cu(\pi)(dpdipy)_2]$ respectively. Interestingly, a superhyperfine structure could be observed in the spectrum of [Cu(II)- $(dipy)_2$], which corresponds to the interaction of the unpaired electron with the nuclear spins of four equivalent ¹⁴N nuclei $(A \perp = 1.28 \text{ mT}; A_{\parallel} = 1.21 \text{ mT}).$

The g_{\parallel} value is known to be indicative of the extent of tetrahedral distortion in tetracoordinated copper(II) ions.^{47,48} For instance, Cu^{II} porphyrins that could be considered as simple bis(dipyrromethenate) Cu^{II} complexes involving a square planar metal ion typically exhibit g_{\parallel} values within the range, or lower than 2.20. In contrast, the g_{\parallel} value reported for CuCl₄²⁻ that could be considered as tetrahedral is close to 2.40.47,48 This behaviour originates from a mixing of the d_{z^2} orbital into the $d_{x^2-y^2}$ orbital that hosts the unpaired electron when tetrahedral distortions are present. A comparison between [Cu(II)- $(dipy)_2$ and $[Cu(\pi)(dpdipy)_2]$ reveals a larger g_{\parallel} value for the latter complex (2.269 vs. 2.214). This is consistent with an increased tetrahedral distortion in [Cu(II)(dpdipy)2]. A qualitative relationship between the g_{\parallel} value and the dihedral angle between the two N-Cu-N chelate rings of complexes involving a N₄ coordination sphere has been established by Addison *et al.*⁴⁸ By considering the experimental g_{\parallel} values of 2.214 and 2.269, the angles of $\sim 40^{\circ}$ and $\sim 60^{\circ}$ are predicted for [Cu(II)- $(dipy)_2$ and $[Cu(\pi)(dpdipy)_2]$, respectively. These angles are in fairly good agreement with the ones calculated on the basis of X-ray diffraction data, which indicates that the structures and especially the dihedral angles are preserved in solution.



Fig. 4 (a) X-band EPR spectrum of the $[Cu(n)(dipy)_2]$ complex at 100 K in MeOH–benzonitrile (3 : 1). Solid line: experimental spectrum; dotted line: simulation using the parameters given in the text. Microwave Freq.: 9.34 GHz, power: 5 mW, Mod. Amp.: 0.4 mT, Freq.: 100 kHz. (b) X-band EPR spectrum of the $[Cu(n)-(dpdipy)_2]$ complex at 100 K in benzonitrile. Solid line: experimental spectrum; dotted line: simulation using the parameters given in the text. Microwave Freq. 9.33 GHz, power = 20 mW, Mod. Amp. 0.2 mT, Mod. Freq. 100 kHz.

The solutions prepared with the thin, small crystals of the putative Cu(1) complexes are paramagnetic, indicating that the copper is mainly at the (+ π) and not (+1) oxidation state. Double integration of the spectrum and comparison with that of genuine Cu(π) samples indicate (Fig. S4a,b†) the presence at 95 ± 5% of [Cu(π)(dpdipy)₂]. Thus even with the small crystals, the Cu^I complex cannot be detected.

Table 4 g values, hyperfine and superhyperfine constants determined for $[Cu(i)(dipy)_2]$, $[Cu(i)(dpdipy)_2]$ and for reference compounds

	g_{\parallel}	g⊥	$A_{\parallel (Cu)} (mT)$	$A\perp_{(Cu)} (mT)$	$g_{\parallel}/A_{\parallel (\mathrm{Cu})} (\mathrm{cm}^{-1})$	$A_{\parallel (N)} (mT)$	$A\perp_{(N)} (mT)$
$[Cu(II)(Dipy)_2]$	2.214	2.049	17.0	2	139	1.21	1.28
$\left[Cu(n)(dpDipy)_2\right]$	2.269	2.083	11.20	1.5	191		
[Cu(II)(porphyrin)] ⁴⁵	2.189	2.035	21.0	3.3	107		
$[Cu(u)Cl_{2}]^{2-46a}$	2.4						

^{*a*} Different values of *g* are observed along the *x* and *y* axes and no *A* value is mentioned in the literature for this complex.

Electrochemistry

The redox potentials of $[Cu(\pi)(dipy)_2]$ and $[Cu(\pi)(dpdipy)_2]$ determined by cyclic voltammetry (CV) in dry deoxygenated benzonitrile with 0.1 M Bu₄NPF₆ are shown in Table 5 (Fig. S5 and S6[†]). When scanning towards the anodic region of potentials the two complexes display a different behaviour. While [Cu(II)(dipy)₂] shows irreversible waves whose intensities decrease with the number of scans, $[Cu(\pi)(dpdipy)_2]$ exhibits two reversible monoelectronic oxidation waves. We attribute them to the sequential oxidation of the two dpdipy ligands, as for the Cu^{II} complexes based on derivatives of the 1,1'-bidipyrrin ligand (composed of two dipyrrin skeletons linked in their 1 and 1' positions).⁴⁹ In the case of $[Cu(II)(dipy)_2]$ it might be possible that a polymerization reaction between the oxidized dipyrrin skeletons occurs during the successive cycles, as reported in the literature for free pyrrol groups.^{50,51} In contrast, this polymerization does not occur with $[Cu(II)(dpdipy)_2]$, probably due to the phenyl substituents in alpha positions of the chelated nitrogens that protect the produced radical cations from polymerization.

In reduction, $[Cu(II)(dipy)_2]$ (Fig. S6[†]) and $[Cu(II)(dpdipy)_2]$ (Fig. 5a) exhibit a first reversible monoelectronic wave at -0.83 and -0.59 V vs. SCE respectively. If we take the 1,1'-bidipyrrin

Table 5 Electrochemical data determined with a platinum electrode in a benzonitrile solution with 0.1 M Bu_4NPF_6 for $[Cu(II)(dipy)_2]$, $[Cu(II)(dpdipy)_2]$ and reference compounds

Complexes	Oxidation, V/SCE		Reduction, V/SCE		CE	
$\begin{array}{c} [Cu(\pi)(dipy)_2] \\ [Cu(\pi)(dpdipy)_2] \\ [Cu(\pi)(1,1'-bidipyrrin)]^{49} \\ [Cu(\pi)(dmp)_2]^{2+52\ b} \end{array}$	+1.02 ^{<i>a</i>} +0.80 +0.23	+1.15 ^{<i>a</i>} +1.08 +0.70	+1.50 ^a	-0.83 -0.59 -1.05 +0.58	-1.60	-1.75

^{*a*} A decrease of these waves is observed during the different scans. ^{*b*} dmp = 2,9-dimethyl-1,10-phenanthroline (counter-ions: NO_3^- ; solvent: DMF).



Fig. 5 CV curve of (a) $[Cu^{II}(dpdipy)_2]$ before reduction electrolysis, (b) the free ligand Hdpdipy (c) $[Cu^{II}(dpdipy)_2]$ after reduction electrolysis, with concentrations of 1 mM in a benzonitrile solution (+0.1 M TBAPF₆) at a platinum disc, recorded under argon. Scan rate = 0.1 V s⁻¹. *T* = 298 K. The potential values are converted against the SCE electrode.

Cu^{II} complexes mentioned above as a reference for a comparison, these reduction waves could correspond to the addition of one electron on one of the two ligands. This seems reasonable since the reduction wave of $[Cu(\pi)(dpdipy)_2]$ is less negative (by 240 mV) than that of $[Cu(\pi)(dipy)_2]$. Such a shift can be attributed to some conjugation induced by the presence of the additional phenyl groups. Although this assignment seems reasonable, we performed exhaustive reduction electrolysis of the dpdipy complex (a priori the most stable in reduction in comparison to the dipy complex) in order to confirm unambiguously this attribution. The electrolysis of $[Cu^{II}(dpdipy)_2]$, 1 mM in benzonitrile, in a glove box at a potential corresponding to the first reduction wave has thus been carried out. Electrolysis was monitored by chrono-amperometry and Coulometry. It was stopped when the residual current was 5% of the initial value (after 3 h 30 min at room temperature). Coulometry revealed that 0.95 electron was exchanged, consistent with a monoelectronic redox process. The CV curve of the electrochemically generated mono-anion (Fig. 5c) exhibits a reversible one-electron oxidation wave at -0.59 V/SCE, i.e. a potential value that matches the $E_{\rm red}$ value of $[Cu^{\rm II}(dpdipy)_2]$. However, its intensity is about half that of the starting $[Cu^{II}(dpdipy)_2]$. In addition, two other reduction waves can be evidenced (Fig. S7[†]), one of them being close to that measured for the free ligand (compare Fig. 5b with 5c). The change in the shape of the CV curves before and after electrolysis (Fig. 5, S7[†]) suggests that during the reduction process, the complex has evolved, likely by release of one ligand molecule. The solution after electrolysis also exhibits a change in the absorption spectrum (Fig. S6b[†]) but no absorption band above 600 nm (that may be indicative of the presence of a ligand radical anion) can be observed as for the reduction of the Cu^{II} complexes with 1,1'-bidipyrrins.49 The electrolytic solution containing the reduced species was also analyzed by EPR spectroscopy at 100 K (Fig. S4c[†]). A quenching of 95% of the EPR signal was observed after reduction. The amount of quenching correlates perfectly with the faradic yield of electrolysis, showing that the reduced species is EPR-silent, which suggests that it corresponds to a Cu^I complex. Exposure of the EPR tube to air for a couple of hours restored a Cu^{II} EPR spectrum with a yield of ca. 80%, indicating that the reduced species is not stable under air.

In conclusion, exhaustive reductive electrolysis of $[Cu(\pi)-(dpdipy)_2]$ shows that the corresponding monoanion is not stable chemically. This instability is not due to oxidation by adventitious dioxygen since: (i) slow decomposition (during the 3 h 30 min electrolysis) is observed under an Ar atmosphere in the glove box with probable formation of the free ligand and (ii) we did not observe the appearance of an (S = 1/2) copper(π) signal during decomposition. Moreover it can be concluded that the reduction electrolysis of $[Cu(\pi)-(dpdipy)_2]$ does not behave like the one of the 1,1'-bidipyrrin Cu^{II} complex described in the literature.⁴⁹ Indeed in that case, the authors could demonstrate unambiguously that the addition of the first electron takes place on the ligand without decomposition during a reduction electrolysis (occurrence of a

	Absorbance, $\lambda_{\text{max}}/\text{nm}$ ($\varepsilon \times 10^3 \text{ M}^{-1} \text{ cm}^{-1}$)	
	UV	vis
dipyH	312	436 (31,5)
dipyH ₂ ⁺	368	470 (49,0)
dpdipyH	302	518 (40,6)
$dpdipyH_2^+$	403	576 (121,7)
Dipyrromethane ³⁸	266	
$[Cu(n)(dipy)_2]$	323, 370	464 (42,3), 501 ^{sh}
[Cu(II)(dpdipy) ₂]	293, 340 ^{sh} , 395 ^{sh}	480, 553 (83,0)
$\left[Cu(II)(NO_2 dipy)_2\right]^{38 a}$	274, 314, 368	474 (52,4), 504 ^{sh}
[Cu(n)(tetraphenyl-	300	567, 640 (65,7)
$azadipyrrine)_{2}$		

^{*a*} NO₂Dipy = 5-(4-nitrophenyl)-dipyrromethene. ^{*b*} Tetraphenylazadipyrrine = 1,3,7,9-tetraphenyl-5-aza-dipyromethene.

bathochromic electronic absorption). In contrast, for $[Cu(\pi)-(dpdipy)_2]$ the reduction electrolysis is accompanied by a slow release of the ligand and the results suggest that a reduction on the Cu(π) is more likely than on the ligand.

Concerning the small crystals of targeted $[Cu(I)(dpdipy)_2]^-$, the CV curves of the corresponding solution in benzonitrile have been recorded on different samples. The CV curves are similar to those of $[Cu(II)(dpdipy)_2]$ but with a somewhat lower current intensity for a concentration of elusive $[Cu(I)-(dpdipy)_2]^-$ similar to that of $[Cu(II)(dpdipy)_2]$, suggesting that the sample of the elusive compound contains Cu^{II} .

Absorption and emission of the Cu^{II} complexes

The absorption data are shown in Table 6 (Fig. S8 and 9[†]) together with the data for some reference complexes and the free ligands dipyH and dpdipyH (nonprotonated and protonated). The visible absorption spectra of the complexes are bathochromically shifted in comparison with those of the nonprotonated free ligands, as also observed in the literature for similar complexes.^{34,43,53} The electronic transitions in the visible region of the spectrum for $[Cu(\pi)(dipy)_2]$ and $[Cu(\pi)(dpdipy)_2]$ could correspond to ligand centered (LC) transitions or LC mixed with Ligand to Metal Charge Transfer (LMCT) transitions, on the basis of the electrochemical data.

The literature on Cu^{II} complexes with dipyH ligand derivatives does not contain any information on the emission characteristics.^{43,44} However, the two Cu^{II} complexes examined in this work exhibit weak luminescence at room temperature.|| Table 7 gives the emission λ_{max} values in different solvents and Fig. 6a and b exhibit the normalized absorption and luminescence spectra (at 77 K and 110 K). It has been verified by recording the excitation spectrum (Fig. S14†) that the emission cannot originate from the presence of an impurity such as the free ligand (in addition to the fact that the emission λ_{max} of **Table 7** Emission maxima of $[Cu(n)(dipy)_2]$ and $[Cu(n)(dpdipy)_2]$ in different solvents of increasing polarity

	Emission λ_{\max} (nm)				
	Toluene	Butyronitrile	Chloroform	Ethanol	
Cu(II)(dipy) ₂] Cu(II)(dpdipy) ₂]	500 593, 628	503 590, 630	504 593, 645	501 a	

^{*a*} The complex is not soluble in EtOH.



Fig. 6 (a) Comparison between the normalized absorption spectrum (at 298 K) in CHCl₃ and emission spectrum (at 77 K) of $[Cu(\iota)/(dipy)_2]$ in the mixture EtOH–MeOH (4/1). (b) Comparison between the normalized absorption spectrum (at 298 K) in CHCl₃ and emission spectrum (at 110 K) of $[Cu(\iota)/(dpdipy)_2]$ in butyronitrile.

the complex does not correspond to that of the free ligand) (Fig. S10 and 11). Several arguments indicate that the complex luminescence is controlled by the dipyrromethene ligands, and thus by singlet LC states as emitting excited species. Indeed (i) there is almost no shift of emission λ_{max} with the polarity of the solvent or from a solution at RT to a glass at 77 K (Fig. S12 and 13[†]); (ii) the emission and absorption spectra are quasi symmetrical to each other; (iii) in agreement with a ¹LC fluorescence, the excited state lifetimes are typical

 $^{\|}$ The quantum yield of emission for $[Cu(\pi)(dpdipy)_2]$ in ButCN at room temperature is estimated to be 1 \times 10⁻³, using the complex $[Ru(bpy)_3]^{2+}$ as the reference.

of singlet excited states: at room temperature they are shorter than or on the order of 1 ns and, at low temperature, shorter or on the order of 10 ns (Table S5[†]); (iv) LMCT excited states usually do not emit and the ligands of the Cu^{II} complexes of this work are not particularly rigid, which might favor lumine-scence from LMCT states.

Computational results

Geometry optimization at the DFT/B3LYP level predicts for $[Cu(n)(dpdipy)_2]$ a geometry with a dihedral angle of 68° between the two dpdipy planes (experimental angle of 63°) and Cu–N bond distances and angles that are consistent with the X-ray crystallography results (Tables S6 and S7†). In addition, the first lowest-lying excited states of $[Cu(n)(dpdipy)_2]$ have been evaluated within the vertical TD-DFT approximation. The HOMO corresponds to a ligand centered molecular orbital, thus in agreement with the electrochemical data. In line with the attribution of the first absorption band and emission of $[Cu(n)(dpdipy)_2]$, the lowest unoccupied molecular orbitals are centered on the ligand, with the exception however of the LUMO centered on the Cu, which has an extremely small oscillator strength and the LUMO + 4 which exhibits a very slight contribution of the Cu (Fig. S15†).

As outlined above, despite our efforts to prepare the Cu^I complex $[Cu(i)(dpdipy)_2]^-$, we mainly isolated the Cu^{II} compound. Therefore we were wondering whether a Cu^I complex with two dpdipy ligands would be too unstable for simply existing from a theoretical point of view. We tested this hypothesis of instability by calculating the total electronic energy of $[Cu(i)(dpdipy)_2]^-$ as compared to that of $[Cu(I)(dpdipy)_2]$, after geometry optimization. The calculations predict in gas-phase (Table 8) a global stabilization of the $[Cu(I)(dpdipy)_2]^-$ complex compared to the corresponding Cu^{II} complex (relative energy estimated *in vacuo* at -2.07 eV). When included, the solvent effects (dichloromethane and acetonitrile, as in the experiments) favor even more the Cu^I complex relative to that of Cu^{II}. These results would thus indicate that the Cu^I complex should exist at least in the absence of reactive species.

It was thought that a comparison of the atomic charge density on the ligands in the Cu^{I} and Cu^{II} complexes could possibly bring some explanation. The results for the nitrogen atoms for the two complexes and dpdipy⁻ (the free dpdipyH

Table 8Total electronic energy of $[Cu(i)(dpDipy)_2]^-$ and $[Cu(ii)(dpDipy)_2]$ in gasphase, in CH₂Cl₂ and in CH₃CN, calculated at the DFT/B3LYP level with the basis6-1G* (for the atoms C, N and H) and the Stuttgart pseudo potential (for the Cuatom) in DFT. The energies with the solvents have been evaluated with themodel of the continuous solvent COSMO (Conductor-like Screening Model). a.u.= atomic units; eV = electron-volts; 1 a.u. = 27.2 eV

	[Cu(ı)-	[Cu(п)-	Energy	Energy
	(dpdipy) ₂] ⁻ /	(dpdipy) ₂]/	difference/	difference/
	a.u.	a.u.	a.u.	eV
Gas phase	-2497.1296	-2497.0535	-0.0761	-2.07
CH ₂ Cl ₂	-2497.2112	-2497.0812	-0.1300	-3.54
CH ₃ CN	-2497.2204	-2497.0843	-0.1361	-3.71

Table 9 Calculation of charge density for each N atom of $[Cu(i)(dpdipy)_2]^-$, $[Cu(i)(dpdipy)_2]$ and the deprotonated free ligand "dpdipy", and for $[Cu(i)-(dmp)_2]^+$, $[Cu(i)(dmp)_2]^{2+}$ and the free ligand dmp (dmp = 2,9-dimethyl-1,10-phenanthroline). The values represent an average of the values obtained for the N of each compound from the analysis method of Mulliken's populations

	[Cu(ı)- (dpdipy) ₂] ⁻	[Cu(II)- (dpdipy) ₂]	"dpdipy""
Charge density on each	-0.603	-0.643	-0.557
iv atom (average)	$[Cu(i)(dmp)_2]^+$ -0.616	[Cu(II)(dmp) ₂] ²⁺ -0.685	dmp -0.528

minus one proton) are given in Table 9. They indicate that the density of negative charge on the nitrogen atoms is more important for the Cu^{II} complex (-0.643) than for the Cu^I complex (-0.603) and for dpdipy⁻ (-0.557). The density of negative charge on the ligand is thus not correlated with the fact that the whole molecule is negatively charged or neutral. As this density is higher for the two complexes than for dpdipy⁻, it should originate from the metal ion. Therefore, a higher charge density might be attributed to better backbonding from the metal in the Cu^{II} than in the Cu^I complex. In order to check this hypothesis of increased stability by back bonding, we also calculated the negative charge density for $[Cu(I)(dmp)_2]^+$, $[Cu(II)(dmp)_2]^{2+}$, and dmp (dmp = 2,9-dimethylphenanthroline, Table 9). In these cases too, a higher density of charge on the nitrogen is obtained for the Cu^{II} (-0.685) than for the Cu^I (-0.616) complex. Moreover, a comparison between the values for the dpdipy complexes and dmp complexes indicates that the $[Cu(I)(dpdipy)_2]^-$ has the lowest negative charge density on its nitrogen atoms; this complex would thus exhibit the weakest back-bonding. This might be one of the reasons why it was not possible to isolate this complex. In conclusion, even if the anion [Cu(I)(dpdipy)2], in its equilibrium geometry (thus according to the total electronic energy), is more stable than the neutral species, the Cu-N bond breaking (thus related to the energy of dissociation) is much easier in the anion than in the neutral species.

Discussion and conclusions

We did not expect problems with the study of Cu-dipyrromethene homoleptic complexes since some of them have been prepared in the literature.^{29–33} However, it has to be reminded that in spite of these publications, to the best of our knowledge, no corresponding Cu^I complexes have been synthesized and no data on the electrochemical behaviour and luminescence were published (except for derivatives of 1,1'-bidipyrrin ligands, which look like porphyrins).⁴⁹

A first interesting finding with the ligands dipyH and dpdipyH is the luminescence of the corresponding homoleptic Cu^{II} complexes, although rather weak. This emission could be attributed to LC excited states and seems typical of homoleptic Cu^{II} complexes with dipyrromethene ligands since usually the Cu^{II} complexes do not emit at all.

Concerning the synthesis of $[Cu(I)(dpdipy)_2]^-$, as indicated by the ESI(+) mass analysis (Table 1, entry 8) of the small crystals in MeCN, some Cu^I complexes could maybe be present. Indeed in the spectrum, the observed ions would correspond to the diprotonated species $[Cu(I)(dpdipyH)_2]^+$ in which each ligand would form only one Cu-nitrogen bond. The rest of the analyzed sample contains the homoleptic Cu^{II} complex, as shown also by X-ray crystallography of the big crystals originating from the elusive $[Cu(I)(dpdipy)_2]^-$. If during the synthesis, $[Cu(I)(dpdipy)_2]^-$ is formed *in situ* from the precursor [Cu(I)- $(MeCN)_4$ ⁺, it is probably transformed into the Cu^{II} corresponding compound during the isolation procedure, by contact with air. This is strange since owing to the phenyl substituents in the supposedly tetrahedral geometry of $[Cu(I)(dpdipy)_2]^-$, the Cu^I core should be protected from oxygen. However as indicated by the conclusions from the theoretical results, the back bonding in the Cu^I complex should be rather weak as compared to that in the corresponding Cu^{II} complex or Cu^I complexes with phen ligands. This would yield a very loose Cu-nitrogen bond, so that it could be speculated that the Cu^I species in solution would be better described by an equilibrium between the two species $[Cu(I)(dpdipy)_2]^-$ and [Cu(I)-(dpdipy)(dpDipy')]⁻ in which dpdipy' would correspond to a ligand with only one Cu-nitrogen bond (reaction 1). Under such conditions, the Cu^I centre would not be well protected by the phenyl substituted ligands versus oxidation by oxygen, so that during the first contact with air during the isolation procedure, mainly [Cu(II)(dpdipy)2] would be obtained (reaction 2).

$$[Cu(I)(dpdipy)_2]^{-} \rightleftharpoons [Cu(I)(dpdipy)(dpdipy')]^{-}$$
(1)

$$[Cu(I)(dpdipy)(dpdipy')]^{-} + air \rightarrow [Cu(II)(dpdipy)_{2}]$$
(2)

This hypothesis could be conciliated with the electrochemical behaviour of $[Cu(\pi)(dpdipy)_2]$ in reduction. Indeed addition of the first electron to $[Cu(\pi)(dpdipy)_2]$ leads to a first reversible wave, meaning that in the CV time scale in PhCN under argon the reduced complex does not decompose. However, decomposition takes place on a longer time scale since the CV curve after electrolysis reveals the presence of free ligand. Moreover, there is no indication of the presence of complexed ligand radical anion after electrolysis. Based on those data, it could be speculated that the reduction of $[Cu(\pi)(dpdipy)_2]$ would give rise to a species like $[Cu(I)(dpdipy)(dpdipy')]^-$ (see reaction 3), thus similar to the species formed during the synthesis with a Cu^{I} core (reaction 1). Reaction 3 would be reversible at the electrode and would correspond to the first redox wave (-0.59 V/SCE) in the negative applied potentials range (Fig. 5).

$$[Cu(II)(dpDipy)_2] + e^{-} \rightleftharpoons [Cu(I)(dpDipy)(dpDipy')]^{-}$$
(3)

$$\begin{split} & [Cu(I)(dpDipy)(dpDipy')]^- + H_2O \\ & \rightarrow decomposition \ products \end{split} \tag{4}$$

In order to explain the weaker intensity of this first reversible wave after the reduction electrolysis, decomposition should occur (reaction 4) due, for example, to proton attacks from water traces in PhCN and responsible for dechelation of the ligand as detected in the CV (compare Fig. 5b with 5c). The speculated reaction scheme (1)–(4) would thus be compatible with the electrochemical results and with the fact that we could not isolate $[Cu(i)(dpdipy)_2]^-$. The electrochemical results would also indicate that the LUMO involved in the reduction process would be different from that controlling the absorption and emission.**

In conclusion, we have shown in this work that mononuclear homoleptic Cu complexes comprising two dipyrromethene ligands exhibit unexpected behaviours such as luminescence and properties different from those that could be anticipated from bis-phenanthroline or 1,1'-bidipyrrin copper complexes.

Experimental section

The reagents $(Cu(OAc)_2 \cdot H_2O, NH_4OH)$ and solvents (MeOH, CHCl₃, PhCN) were obtained from Sigma-Aldrich and used without further purification. Water was purified with a Milli-Q system.

Instrumentation

Mass spectrometry analyses. (i) MALDI mass spectra were recorded using a Waters QToF Premier mass spectrometer equipped with a nitrogen laser, operating at 337 nm with a maximum output of 500 J m⁻² delivered to the sample in 4 ns pulses at 20 Hz repeating rate. Time-of-flight mass analyses were performed in the reflectron mode at a resolution of about 10 000 at m/z 500. The matrix, trans-2-[3-(4-tert-butyl-phenyl)-2methyl-2-propenylidene] malononitrile (DCTB), was prepared in chloroform (20 mg ml⁻¹). The matrix solution (1 μ L) was applied to a stainless steel target and air dried. Samples were dissolved in chloroform (1 mg ml⁻¹). 1 μ L aliquots of these solutions were applied to the target area already bearing the matrix crystals, and then air dried. For the recording of the single-stage MALDI-MS spectra, the quadrupole (rf-only mode) was set to pass ions from m/z 50 to 1000, and all ions were transmitted into the pusher region of the time-of-flight analyzer where they were mass analyzed with 1 s integration time. Data were acquired in continuum mode until acceptable averaged data were obtained. (ii) The ESI analyses were performed on a Waters QToF2 mass spectrometer. The sample solutions $(1 \text{ mg ml}^{-1} \text{ in acetonitrile})$ were delivered to the ESI source by a Harvard Apparatus syringe pump at a flow rate of 5 µL min^{-1} . Typical ESI conditions were: capillary voltage, ± 3.1 kV (positive or negative ion mode); cone voltage, ±30 V; source temperature, 80 °C; desolvation temperature, 120 °C. Dry

^{**}In contrast, it could also be argued that the first electron (reaction 3) would be added to the dpdipy ligand, in agreement with the assignment of the lowest absorption band and emission to LC transitions. During the electrolysis, the added electron would finally be localized on the Cu core. However, in such a case, the observation of the same redox wave after and before electrolysis cannot be explained.

nitrogen was used as the ESI gas. The quadrupole was set to pass ions from m/z 50 to 1000 and all ions were transmitted into the pusher region of the time-of-flight analyser for massanalysis with 1 s integration time. Data were acquired in continuum mode until acceptable average data were obtained (typically 20 scans).

Structure determination. The structures of $[Cu(\pi)(dipy)_2]$ and $[Cu(II)(dpdipy)_2]$ were determined by X-ray diffraction (Fig. 3). The crystals of $[Cu(\pi)(dipy)_2]$ were obtained by slow evaporation of the complex solution in MeOH-CHCl₃. For $[Cu(II)(dpdipy)_2]$ two types of crystals were obtained from a CHCl₃-heptane solution. X-ray diffraction data were collected at a temperature of 100 K using CuKa radiation and phi and omega scans on a SMART 6000 diffractometer equipped with a CCD detector and crossed Göbel mirrors. Cell refinement and data reduction were carried out using the program SAINT.54 For the absorption correction the program SADABS was used.55 The structures were solved by direct methods and refined by full-matrix least squares on $|F^2|$ using the SHELXTL program package.⁵⁶ The crystal of Cu(II)(dipy)₂ was found to be twinned (twin law -100 0-10 101). Non-hydrogen atoms were anisotropically refined and the hydrogen atoms were placed in calculated positions with temperature factors fixed at 1.2 times $U_{\rm eq}$ of the parent atoms. The crystallographic data are given in Tables 2 and 3.

Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-909364–909366.

The EPR spectra were recorded using an X-Band BRUKER EMX plus spectrometer equipped with a nitrogen flow cryostat and a BRUKER Teslameter. The spectra have been recorded at 100 K on 400 μ L samples. The spectra were simulated using the BRUKER Simfonia software.

Cyclic voltammetry was carried out with a platinum disk working electrode in dried benzonitrile with tetrabutylammonium hexafluorophosphate (0.1 mol L⁻¹) as a supporting electrolyte. The potential of the working electrode was controlled by an Autolab PGSTAT 100 potentiostat interfaced with a PC, with a scan rate of 100 mV s⁻¹ between -2 and +2 V *versus* SCE. The counter electrode was a platinum foil and the reference electrode a Saturated Calomel Electrode (SCE). All the measurements were performed in a single compartment cell. The concentration of the complexes was 1×10^{-3} mol L⁻¹.

The UV-vis absorption spectra (accuracy ± 2 nm) were recorded using a Perkin-Elmer Lambda 35 UV-vis spectrophotometer. The determination of the molar absorption coefficients was performed by weight and absorption measurements.

The emission spectra were recorded using a Shimadzu RF-5001 spectrofluorimeter and the emission lifetimes either using an Edinburgh instruments FL-900 CDT, or an excitation source composed of a frequency-tripled (355 nm) Nd:YAG Q-switched laser (Continuum Inc.) coupled with an optical parametric oscillator (Continuum Inc.) and equipped with a CCD camera (Princeton Instruments).

Syntheses

5-Phenyldipyrromethene was prepared according to literature procedures.¹² 1,5,9-Triphenyldipyrromethene was prepared through an acid catalyzed condensation of benzaldehyde and 2-phenylpyrrole, followed by oxidation with DDQ. To a solution of 2-phenylpyrrole (2.86 g, 10 mmol) in dichloromethane (50 ml) under a nitrogen atmosphere was added benzaldehyde (1.06 g, 10 mmol). A catalytic amount of trifluoroacetic acid (1 drop) was added to the mixture and the reaction turned dark immediately. After stirring at room temperature for 30 minutes, DDQ (2.27 g, 10 mmol) was added and stirring was continued for 2 h at room temperature. The red solution was evaporated to dryness, and the crude product was purified chromatographically (Silica, DCM) to yield dark red shiny crystals (1.17 g, 63% yield). ¹H-NMR (Fig. S16[†]): 13.98 (s, br, H, NH), 7.94 (m, 4H, J = Hz), 7.58–7.37 (m, 11H), 6.85 (d, 2H, J = 3.66 Hz), 6.71 (d, 1H, J = 3.66 Hz) ppm; ¹³C-NMR: 169.8, 154.4, 142.3, 141.1, 140.0, 137.5, 133.5, 131.2, 130.7, 130.3, 129.4, 128.1, 126.6, 126.5, 126.1, 116.0 ppm; LRMS(EI) 372 (M⁺), 295 $(M^+ - Ph)$; HRMS (EI): Calculated for $C_{27}H_{20}N_2$ 372.1626, found 372.1621; UV-VIS: 517(s), 290(s).

 $[Cu(n)(dipy)_2]$ The synthesis of $[Cu(n)(dipy)_2]$ was based on the procedure described in the literature for the $[Cu(n)-(NO_2Dipy)_2]$ complex. The reaction product was vacuum-dried at room temperature and purified by column chromatography (CHCl₃-MeOH, 99/1). Yield: 92.6 mg (88%). Crystals were grown by slow evaporation of the solvents MeOH-CHCl₃ (50/50). MALDI-TOF (CH₂Cl₂): m/z 501.1.

 $[Cu(II)(dpdipy)_2]$ 100 mg (0.27 mmol) of 1,5,9-triphenyldipyrromethene were dissolved in 80 ml of CH₃CN with 33 µL of NH₄OH (8.2 M). 26.5 mg (0.13 mmol) of Cu(OAc)_2·H₂O dissolved in 10 ml of methanol were added to the solution. The reaction was heated at 85 °C followed by thin layer chromatography (cyclohexane–ethyl acetate, 70/30) and UV-vis absorption spectroscopy. After one hour, the reaction product was vacuum-dried at room temperature and the excess of free ligand was removed by column chromatography (cyclohexane– ethyl acetate, 70/30). Yield: 75.3 mg (72%). Crystals were grown by slow evaporation of the solvents CHCl₃–heptane (50/50). MALDI-TOF (CH₂Cl₂): *m/z* 805.2. ESMS (CH₂Cl₂): *m/z* 805.2 in negative mode and *m/z* 806.0 in positive mode.

Theoretical calculations

For the comparison of the total electronic energy of the dpdipy complexes with Cu^I and Cu^{II}, the geometries of the two complexes were first optimized *in vacuo* at the B3LYP level of theory⁵⁷ with the NWChem computational chemistry package.⁵⁸ The 6-31G* basis set⁵⁹ was used for the C, N and H atoms while the "Stuttgart RSC 1997 ECP"⁶⁰ relativistic effective core potential and associated basis set were employed to describe the Cu atom. The bulk solvent effects (dichloromethane and acetonitrile, as in the experiments) have also been included through the Conductor-like Screening Model (COSMO).⁶¹ These calculations were performed at the B3LYP/ 6-31G*/Stuttgart level of theory using the *in vacuo* optimized

geometries of the complexes. The atomic charge density on the ligands in Cu^I and Cu^{II} complexes was calculated by the method of analysis of Mulliken's populations,⁶² at the B3LYP/ 6-31G*/MDF10 level of theory using the Gaussian03 program package.⁶³ In order to determine the assignment of lowest electronic transitions in absorption, the first lowest-lying excited states of $[Cu(\pi)(dpdipy)_2]$ have been evaluated within the vertical Time-Dependent Density Functional Theory (TD-DFT) approximation using the 6-31G*/MDF10 level of theory. These calculations have been performed with the B3LYP functional that is known to be effective for a variety of properties of metal complexes, including absorption spectra.

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