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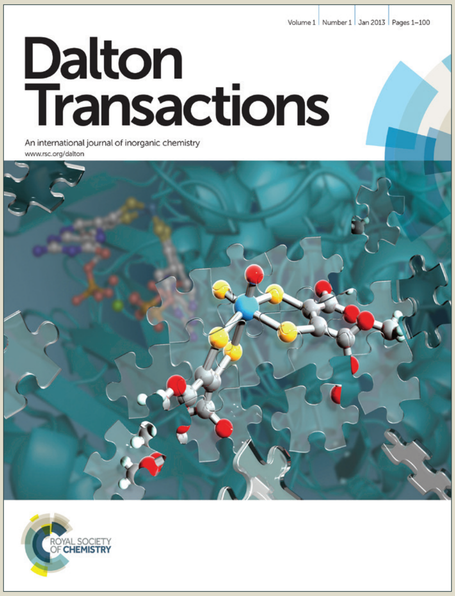

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Reactivity of TCNE and TCNQ derivatives of quinonoid zwitterions with Cu(I)†

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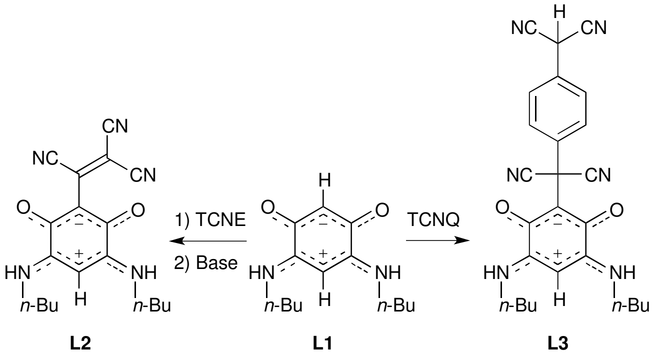
The reactions of TCNE- and TCNQ-functionalized (TCNE: tetracyanoethylene and TCNQ: 7,7',8,8'-tetracyanoquinodimethane) zwitterionic benzoquinonemonoimines with a Cu(I)-BIAN complex (BIAN = bis(*o,o'*-bis*iso*propylphenyl)acenaphthenequinonediimine) have been investigated and found to follow a diversity of interesting patterns. The complexes [Cu(BIAN)(NCMe)(**L2**)]BF_4 (**2**) and [Cu(BIAN)$(\mathbf{L2})_2$]BF_4 (**4**) were obtained by reacting [Cu(BIAN)$(NCMe)_2$]BF_4 (**1**) with one and two equivalents of **L2**, respectively. Following similar procedures, the complexes [Cu(BIAN)(NCMe)(**L3**)]BF_4 (**6**) and [Cu(BIAN)$(\mathbf{L3})_2$]BF_4 (**7**) were obtained by reaction of **1** with **L3**. The reaction of **2** with 0.5 equiv. of 4,4'-bipyridine afforded $[\{Cu(BIAN)(\mathbf{L2})\}_2(\mu\text{-}4,4'\text{-bipyridine})](BF_4)_2$ (**3**). The complexes were characterized by multinuclear NMR, IR and UV-Vis spectroscopic techniques, mass spectrometry, cyclic voltammetry and elemental analysis. The molecular structures of complexes **3**·4CH_2Cl_2 and **4**·CH_2Cl_2 were determined by single crystal X-ray diffraction. An unexpected coordination polymer $[Cu(\mathbf{L2}^-)_2]_\infty$ (**5**) was also structurally characterized, which contains Cu(II) centres chelated by two N,O-bound ligands resulting from the monodeprotonation of **L2**.

Introduction

Potentially antiaromatic zwitterionic benzoquinone monoimines of the **L1** type (Scheme 1)[1] have attracted the interest of numerous theoreticians,[2] because they show a remarkable electronic delocalisation of their π system which leads to two chemically connected, but electronically separated 6π-electron subunits. First reported by our group in 2005, an unprecedented transamination reaction allows easy access to a large variety of functional zwitterionic benzoquinone monoimines such as **L1** (Scheme 1).[3] Derivatives of **L1** have been applied in coordination chemistry[4] and their metal complexes have been evaluated in homogenous catalysis[5] and for potential application in optical recording.[6] These ligands also readily form supramolecular arrangements[3] and can be used as bridges between electroactive metal centres, such as Ru(II)[7] and Cu(I).[8] In Pd(II) azobenzene complexes, a double redox activity involving both coordinated ligands has been evidenced.[9] These zwitterions were also shown to enable exceptionally strong electronic coupling between two quadruply bonded dimolybdenum units, leading to record values for comproportionation constants.[10] More recently, their physical properties have been investigated after deposition on metal surfaces.[11]

TCNE (tetracyanoethylene) and TCNQ (7,7',8,8'-tetracyanoquinodimethane) show a very rich coordination chemistry.[12] They have been widely used as non-chelating polydentate ligands and they both offer a variety of donor sites and bonding modes to metal centres. Furthermore, due to their low reduction potential, they can also act as non-innocent ligands in oligonuclear complexes,[13] and lead to materials endowed with interesting physical properties relevant to *e.g.* superconductivity, field emission, or magnetism.[14] We reported in 2011 the synthesis of (*6E*)-4-(butylamino)-6-(butyliminio)-3-oxo-2-(1,2,2-tricyanoethenyl)cyclohexa-1,4-dien-1-olate), $[C_6H\text{-}2\text{-}\{C(CN){=}C(CN)_2\}]\text{-}4,6\text{-}(\underline{\cdots}NH\mathit{n}\text{-}Bu)_2\text{-}1,3\text{-}(\underline{\cdots}O)_2)$ (**L2**). It was formed from (*6E*)-4-(butylamino)-6-(butyliminio)-3-oxo-2-(1,1,2,2-

tetracyanoethyl)cyclohexa-1,4-dien-1-olate, [C_6H-2-{$C(CN)_2C(CN)_2H$}]-4,6-($\underline{\cdots}$NH*n*-Bu$)_2$-1,3($\underline{\cdots}$O$)_2$, itself resulting from formal, regioselective insertion of TCNE into the O$\underline{\cdots}$C$\underline{\cdots}$*CH*$\underline{\cdots}$C$\underline{\cdots}$O bond of the quinonoid zwitterion **L1**, as a result of a base-induced HCN elimination reaction. [15] The TCNQ analogue, (*6E*)-4-(butylamino)-6-(butyliminio)-2-(dicyano(4-(dicyanomethyl)phenyl)methyl)-3-oxocyclohexa-1,4-dien-1-olate, [C_6H-2-{C-$(CN)_2$*p*-$C_6H_4C(CN)_2H$}]-4,6-($\underline{\cdots}$NH*n*-Bu$)_2$-1,3-($\underline{\cdots}$O$)_2$) (**L3**) was also characterized.[16]



Scheme 1. Synthesis of ligands **L2** and **L3** from **L1**.[15,16]

In 2001, Kaim *et al.* examined the reaction of [$Cu(NCMe)_4$]BF_4 with π-conjugated tetracyano molecules, such as TCNE and TCNQ, in the presence of Me_3TANC (1,4,7-trimethyl-1,4,7-triazacyclononane) to create *in situ* the electron-rich Cu(Me_3TANC$)^+$ fragment and these authors obtained tetranuclear complexes.[17]

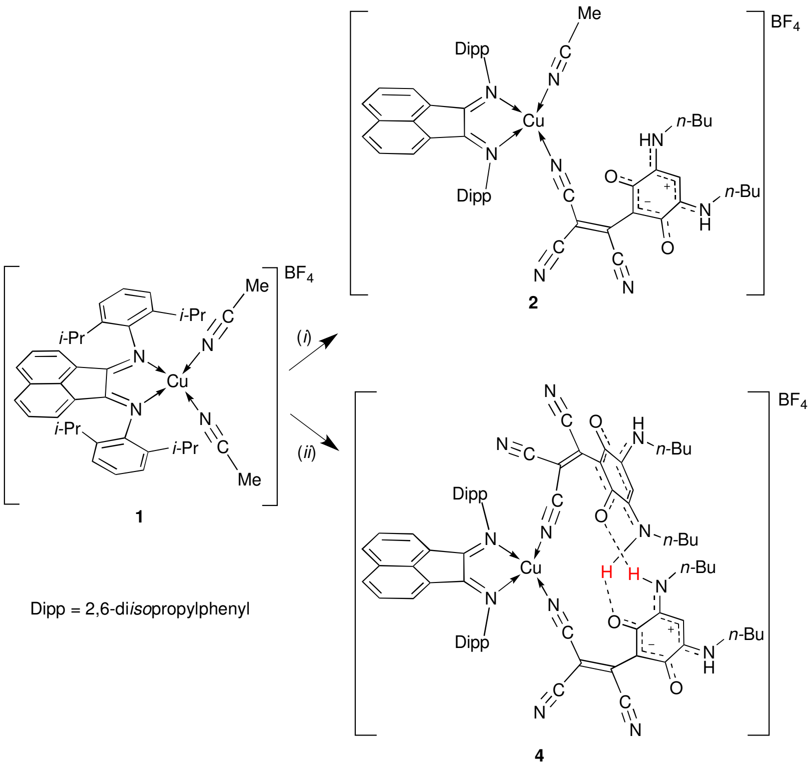
Ligands **L2** and **L3** combine structural moieties derived from both TCNE/TCNQ and the quinonoid zwitterion, and we wanted to explore the coordination properties, stability and redox behaviour of the resulting Cu(I) complexes. All the complexes were fully characterized and the molecular structures of two complexes are described, as well as that of an unexpected product constituted of a polymeric arrangement of ligand **L2** and Cu(II) ions.

Results and Discussion

In our attempts to study the reactivity of ligands **L2** and **L3** towards Cu(I) and Cu(II) precursors, we were confronted with insolubility issues. The direct reaction of usual copper salts with these ligands resulted in compounds insoluble in common organic solvents, challenging their study and full characterization. These compounds were probably polymeric in nature, resulting from the coordination to copper of the TCNE or the TCNQ nitrile functions and/or of the oxygen and nitrogen donors of the quinonoid moiety, as described below for the coordination polymer **5**. In order to avoid the formation of such complex structures, we decided to use a Cu(I) precursor complex containing a bidentate chelating ligand to block two coordination sites and thus allow a better control of their coordination reactivity. We choose the chelating ligand bis(*o,o'*-bis*iso*propylphenyl)acenaphthenequinone diimine (BIAN) because of its rigidity and well explored Cu(I) and Cu(II) coordination chemistry.[18,19] Recently it has been shown that this ligand reacts with [$Cu(NCMe)_4$]BF_4 in a 1:1 ratio to form exclusively the mononuclear complex [Cu(BIAN)$(NCMe)_2$]BF_4 (**1**),[18] which we used as precursor.

Synthesis and crystal structure of the complexes

Complexes with ligand L2. Examples of Cu complexes bearing a bis-imine and two nitrile ligands remain scarce and limited to small nitrile molecules that were either used as solvent or already present in the precursor.[18,19,20] The use of a ligand such as **L2** or **L3** could allow the formation of polynuclear complexes or supramolecular assemblies. Complex **2** was obtained by the straightforward reaction between the precursor **1** and one equiv. **L2** in CH_2Cl_2. Successive washings with Et_2O and pentane removed the uncoordinated MeCN and compound **2** was isolated as a red powder (Scheme 2).



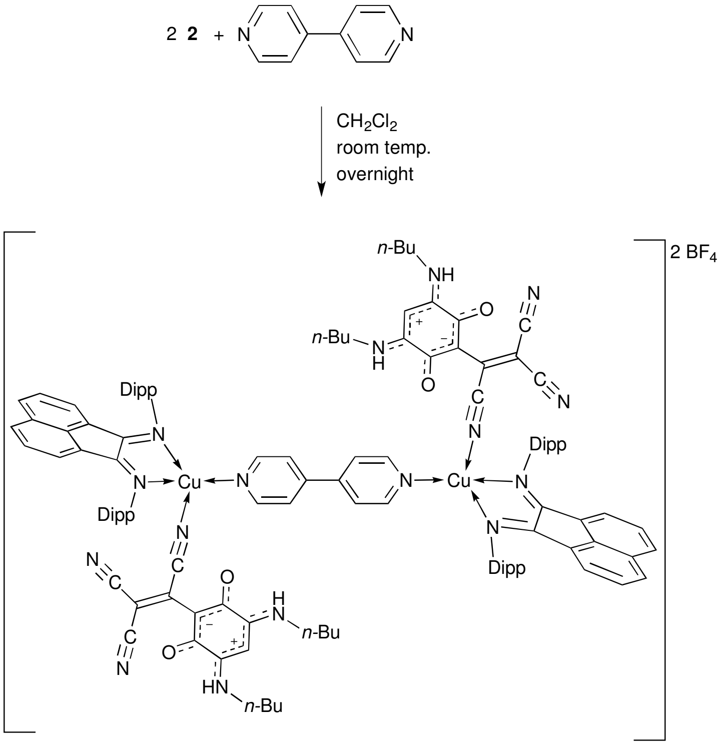
Scheme 2. Synthesis of complexes **2** and **4**. (*i*) 1 equiv. of **1** and 1 equiv. of **L2**, CH_2Cl_2, room temp., 12 h. (*ii*) 1 equiv. of **1** and 2 equiv. of **L2**, CH_2Cl_2, room temp., 12 h.

The main signal in the mass spectrum at *m/z* = 914 confirms the presence of a cationic complex in [Cu(BIAN)(NCMe)(**L2**)]BF_4 (**2**) (see Experimental Section). Furthermore, a shift of the (NC-*C*-CN) signal was observed in the $^{13}C\{^1H\}$ NMR spectrum, from 105.53 for **L2** to 107.99 ppm for **2**. Consistently, the IR spectrum of **2** contains ν_{CN} absorptions at 2218, 2168 and 2115 cm^{-1}, which are different from those of ligand **L2** and therefore indicate coordination of the nitrile functions (Table 1).

Table 1. Infrared spectral data of ligands and complexes in the ν_{CN} region

Compound	ν_{CN} (cm^{-1})	medium
TCNE	2245, 2210*	KBr
TCNE	2257, 2219*	Nujol
$TCNE^{\bullet -}$	2253, 2198, 2178, 2171*	KBr
$[\{Cu(Me_3TACN)\}_4(\mu_4\text{-}TCNE)](BF_4)_4$	2212,2165*	KBr
$[\{Cu(Me_3TACN)\}_4(\mu_4\text{-}TCNE)](BF_4)_4$	2212, 2164*	Nujol
L2	2221	neat
1[18]	2375, 2333	Nujol
2	2218, 2168, 2115	neat
3	2225, 2218	neat
4	2217	
TCNQ	2228*	KBr
$TCNQ^{\bullet -}$	2197, 2166*	KBr
$[\{Cu(Me_3TACN)\}_4(\mu_4\text{-}TCNE)](BF_4)_4$	2213, 2158*	KBr
L3	2256	neat
6	2200, 2138	neat
7	2198, 2139	neat

* From ref. 17 and references cited therein



3

Scheme 3. Synthesis of complex **3**.

Taking advantage of the potential lability of the coordinated acetonitrile ligand in **2**, the latter was reacted with 0.5 equiv. of 4,4'-bipyridine and compound **3** was obtained as a red solid in 74% yield (Scheme 3). Its formulation as a dinuclear complex [{Cu(BIAN)(**L2**)}$_2$(μ-4,4'-bipyridine)](BF$_4$)$_2$ was established by a single crystal X-ray diffraction analysis of **3**·4CH$_2$Cl$_2$. The centrosymmetric dication contains Cu(I) centres in a slightly distorted tetrahedral coordination environment composed of a chelating BIAN ligand, a monodentate ligand **L2** coordinated through the CN group in α-position to its zwitterionic part, and a nitrogen donor of a bridging 4,4'-bipyridine ligand. The centre of symmetry of the molecule is situated on the middle of the C-C bond connecting the two halves of the 4,4'-bipyridine ligand. Selected bond distances (Å) and angles (°) are summarized in Table 2.

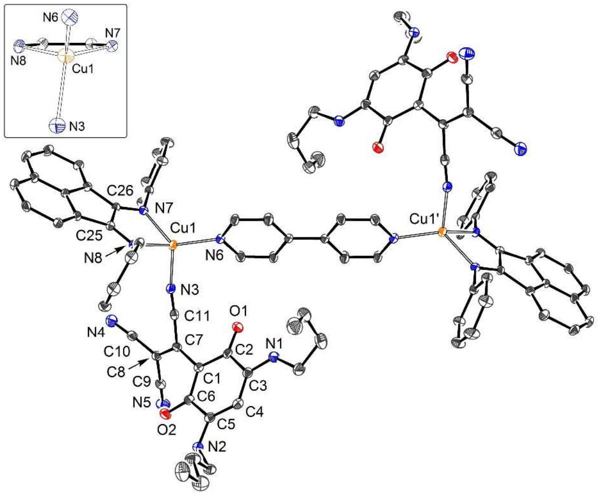


Figure 1. Molecular structure of **3** in **3**·4CH$_2$Cl$_2$. Ellipsoids include 30% of the electron density. Hydrogen atoms, solvent molecules, two BF$_4$ ions and all *i*Pr groups were omitted for clarity. The slightly distorted tetrahedral coordination geometry of the Cu1 centre is

highlighted in the inset.

Table 2. Selected bond lengths (Å) and angles (deg) in **3**·$4CH_2Cl_2$ and **4**·CH_2Cl_2

Compound	**3**·$4CH_2Cl_2$		**4**·CH_2Cl_2
Cu-N (BIAN)		Cu-N (BIAN)	
Cu1-N7	2.069(3)	Cu1-N12	2.147(3)
Cu1-N8	2.151(3)	Cu1-N11	2.063(3)
Cu-N (**L2**)		Cu-N (**L2**)	
Cu1-N3	1.983(4)	Cu1-N3	1.919(4)
Cu1-N6	2.001(3)	Cu1-N8	1.932(4)
C=N (BIAN)		C=N (**L4**)	
C26-N7	1.292(5)	C39-N12	1.285(5)
C25-N8	1.289(5)	C40-N11	1.274(5)
C≡N (bonded)		C≡N (bonded)	
C11-N3	1.149(5)	C11-N3	1.132(5)
		C30-N8	1.161(6)
C≡N (free)		C≡N (free)	
C10-N4	1.151(6)	C-N (aver.)	1.143(6)
C9-N5	1.143(6)		
Angles			
N8-Cu1-N7	80.85 (1)	N12-Cu1-N11	81.09(1)
N6-Cu1-N3	102.9(1)	N8-Cu1-N3	114.5(2)
(C9,C10,C11)-(C1,C4,C6)	47.04	(C8,C10,C11)-(C1-C6)	32.56
		(C27,C29,C30)-(C20-C25)	38.72
(N7,Cu1,N8)-(N3,Cu1,N6)	82.88	(N11,Cu1,N12)-(N3,Cu1,N8)	84.02

A comparison between the IR spectra of the non-crystalline solid **3** and of a crystal of **3** showed no significant difference. This indicates firstly that the coordination depicted in Figure 1 also prevails in the non-crystalline state and is thus not induced by the crystallisation process and secondly that non-crystalline **3** consists of only one coordination isomer.

When the Cu(I) precursor **1** was reacted with 2 equiv. of **L2** in CH_2Cl_2 overnight, both MeCN ligands of **1** were replaced by two molecules of **L2**, yielding compound **4** as a red-brown powder in 53% yield (Scheme 2).

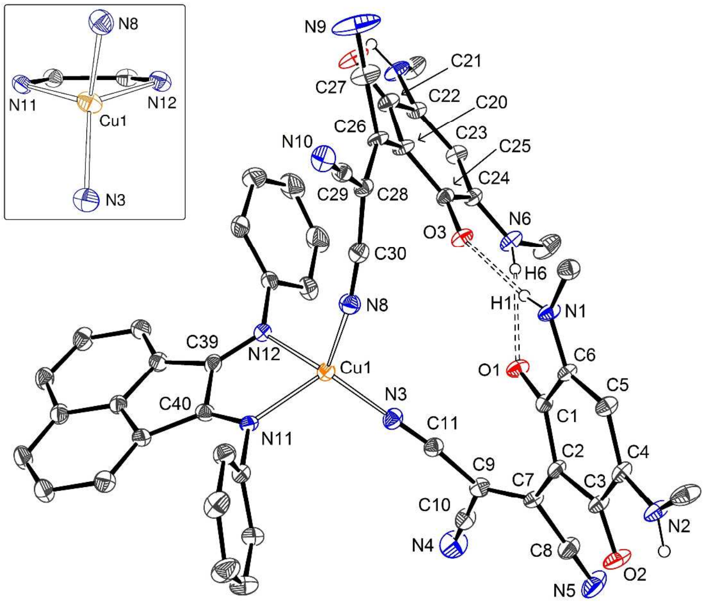


Figure 2. Molecular structure of **4** in **4**$\cdot CH_2Cl_2$. Ellipsoids include 30% of the electron density. Hydrogen atoms, except at N2 and N6, solvent molecules, BF_4^- anion and all *i*Pr groups were omitted for clarity. Only the N-*C* carbons of the *n*-butyl chains are shown, for clarity. Selected bond distances (Å) and angles (°) are summarized in Table 2. The slightly distorted tetrahedral coordination geometry of the Cu1 centre is highlighted in the inset.

The composition of **4** as [Cu(BIAN)(**L2**)$_2$]BF_4 and its molecular structure in **4**$\cdot CH_2Cl_2$ were established by X-ray diffraction. This complex contains a Cu(I) centre in a slightly distorted tetrahedral environment consisting of four nitrogen-based ligands, a chelating BIAN ligand and two molecules of **L2**. In contrast to the situation in **3** (see above), the two ligands **L2** interact with the copper centre in **4** through the C≡N group at C9 and C28, in β-position to the zwitterionic *core* and *syn* to it. We believe that this arrangement is preferred because it allows the formation of H-bonds between two zwitterionic ligands **L2**, H1···O3 and H6···O1, as a result of the short distances between N1···O3 and N6···O1 of 2.923(5) and 3.283(6) Å, respectively. The resulting pseudo-chelation confers additional stability to the complex. Intermolecular H-bonds between the C=O and NH groups of the zwitterionic ligands **L2** are also present in the crystal packing. It is interesting to note that the self-assembly of chelating bidentate ligands through H-bonding between monodentate ligands has found interesting applications in homogeneous catalysis.[21] In order to investigate whether these H-bonding interactions are required for the formation of **4**, we reacted this complex with one equivalent of $NaN(SiMe_3)_2$.

The ^{1}H-NMR spectrum of the crude reaction mixture indicated deprotonation of only one of the NH-groups of one of the zwitterionic ligands. Neither the free ligand **L2** nor complex **4** could be detected in the reaction mixture. Attempts to crystallize the product of this reaction led to the formation of a three dimensional Cu(II) coordination polymer **5**, resulting from the adventitious presence of traces of oxygen in the Schlenk tube. The molecular structure of this neutral complex is shown in Figure 3, along with selected bond distances and angles.

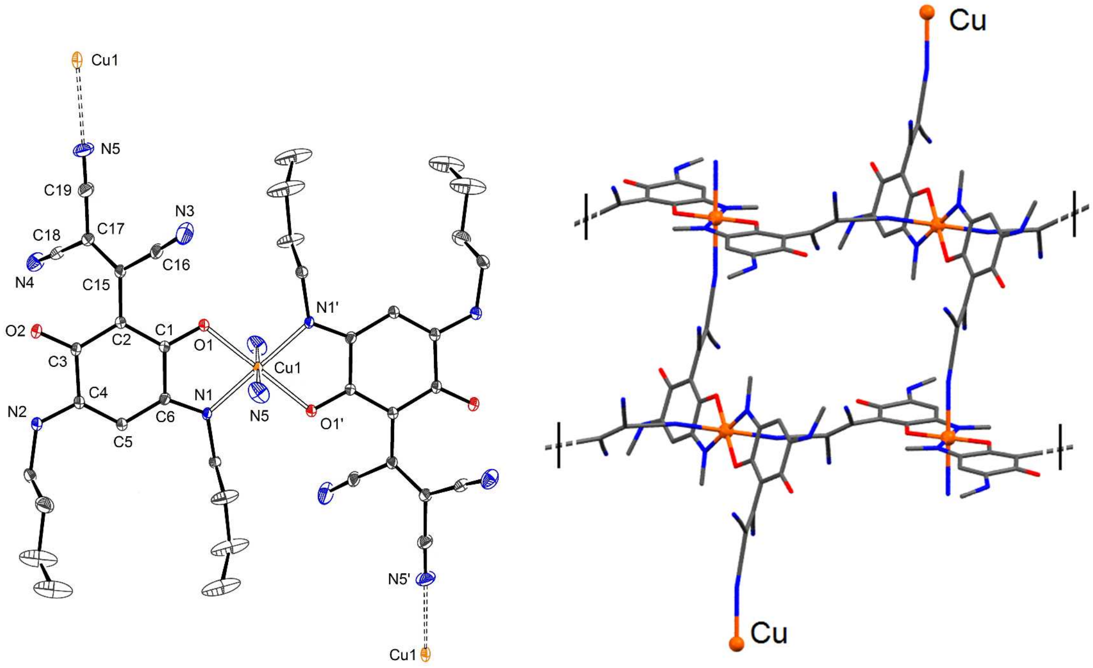
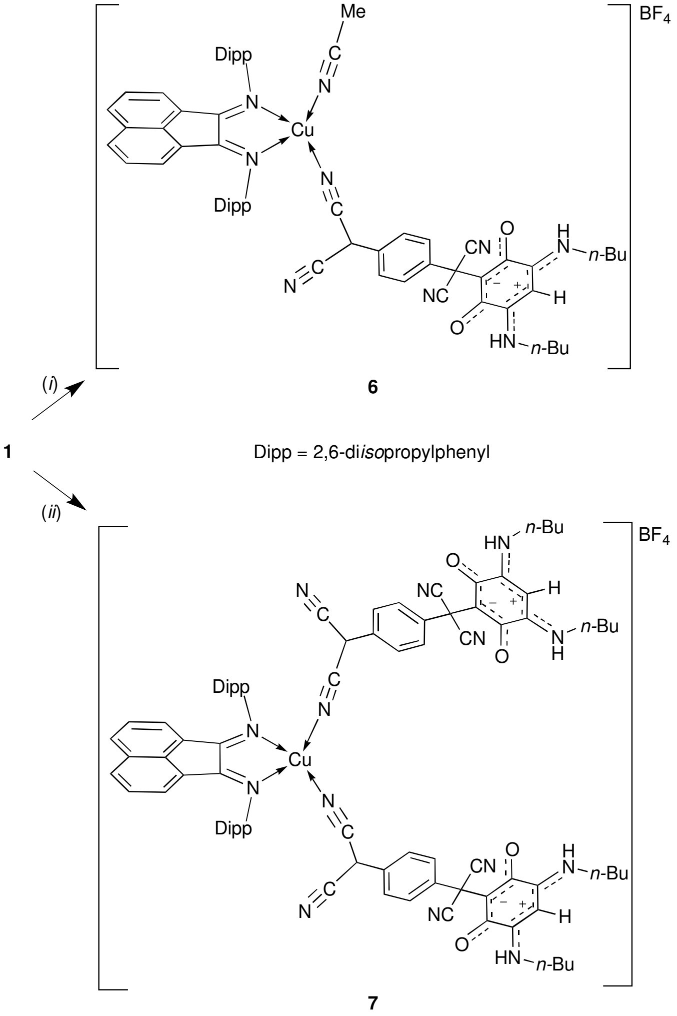


Figure 3. (Left) Molecular structure of the Cu(II) in the coordination polymer $[\mathrm{Cu}(\mathbf{L2}^{-})_2]_\infty$ (**5**). Ellipsoids include 30% of the electron density. Hydrogen atoms omitted for clarity. Selected distances (Å): Cu1-N1 1.958(3), Cu1-O1 1.974(2), Cu1-N5 2.612(5), C1-O1 1.257(4), C6-N1 1.298(4), C3-O2 1.220(4), C4-N2 1.329(5), C1-C2 1.412(5), C2-C3 1.448(5), C1-C6 1.511(5), C3-C4 1.515(5), C4-C5 1.371(5), C5-C6 1.409(5); and angles (°) N1-Cu1-O1 82.4(1), N1-Cu1-O1' 97.6(1), (O1-Cu1-N1)-Cu1-N5 90.38. (Right) View of the 2D coordination polymer assembly in **5**. Only the N-*C* carbons of the *n*-butyl chains are shown, for clarity.

In the crystal structure of **5**, the copper ion occupies a centre of symmetry for the molecule and the BIAN chelate has been displaced. The metal is now bis-chelated by two mutually *trans* zwitterionic, monodeprotonated *p*-benzoquinonemonoimine-type ligands $\mathbf{L2}^-$, each of them establishing with the copper(II) centre formally one *σ*-bond and one dative bond involving the nitrogen (deprotonated NH group) and the oxygen donors, respectively. A nitrile group from two other molecules complete the octahedral coordination sphere of the metal (Figure 3, right). Further investigations toward a direct synthesis of **5** and more detailed characterisation are in progress.

We have previously synthesized and structurally characterized various square-planar Pd(II) complexes chelated by a deprotonated ligand of type $\mathbf{L1}^-$.[2b,4] Square-planar complexes of Ni, Zn, Cu and Pd, bis-chelated by two anionic ligands $\mathbf{L1}^-$ could be formed but were never structurally characterized. Only two examples of Ni(II) and Zn(II) complexes bearing two mono-anionic ligands of type $\mathbf{L1}^-$ with a $-(CH_2)_2NMe_2$ moiety as R-group could be crystallized, and their metal centre exhibited a slightly distorted octahedral coordination geometry, the coordination sphere being completed by an additional NMe_2 neutral donor.[3b,5] Complex **5** represents the first example of structurally characterized complex with two coplanar ligands of type $\mathbf{L1}^-$.

Complexes with ligand L3. Complex **6** was isolated as a brownish solid in 81% yield after an overnight reaction of **1** with one equiv. of **L3** in CH_2Cl_2 (Scheme 4).



Scheme 4. Synthesis of complexes **6** and **7**. (*i*) 1 equiv. of **1** and 1 equiv. of **L3**, CH_2Cl_2, room temp., 12 h. (*ii*) one equiv. of **1** and 2 equiv. of **L3**, CH_2Cl_2, room temp., 12 h.

Attempts to synthesize a 4,4'-bipyridine-bridged compound from **6**, as was done with **3**, remained unsuccessful. This is surprising since the steric demand of the $HC(CN)_2$-C_6H_4-$C(CN)_2$ moiety of **L3** should be comparable to that of the tricyanoethenyl moiety of **L2** and therefore occupation of the fourth coordination site of the Cu ion in **6** should be possible. This is confirmed by the reaction of **1** with 2 equiv. of **L3** in CH_2Cl_2 in an overnight reaction at room temperature which afforded **7** as a brownish solid in 45% yield (Scheme 4).

IR spectroscopy. The nitrile stretching vibrations of the zwitterionic ligands in our complexes appear well separated from the other absorptions and can thus provide useful information about the coordination mode of the ligand. Furthermore, they could allow a conservative estimate of the extent of metal-to-ligand electron transfer as an increased occupation of the nitrile π^*MOs lowers the ν_{CN} values.[22] Table 1 provides a comparison between the ν_{CN} values of our complexes with those of related compounds. A comparison between the ν_{CN} values for ligands **L2** and **L3** with those of the corresponding complexes **2**-**7** indicates a shift from which we conclude that in all our complexes the zwitterionic ligand is coordinated to the copper centre through at least one of its nitrile functions. While the shifts for the complexes with **L2** turned out to be very small, the complexes derived from **L3** showed a much larger shift of the nitrile absorption bands.

We compared these shifts to those observed for TCNE/TCNQ in their tetranuclear Cu(I) complexes which were found to show a "modest amount of metal-to-ligand electron transfer".[17] Based on these data, the complexes of **L2** do not exhibit much metal-to-ligand charge transfer. This can be explained by an already persisting partial charge transfer in **L2** from the negative part of the zwitterionic moiety to the tricyanoethenyl part.

The complexes derived from **L3**, however, show a shift of the ν_{CN} values when compared to **L3** which is superior to those in Kaim's tetranuclear Cu(I) complexes, which indicates more metal-to-ligand electron transfer. However, the NMR spectra of complexes **6** and **7**, showing only a slight broadening (quadrupole) indicate that in these complexes, the oxidation state of the diamagnetic Cu(I) centre has been retained. Therefore, we believe that if the charge transfer in these complexes may be larger than in Kaim's complexes, they remain rather weak.

Electronic spectra. UV-Vis measurements were made and their results, presented in Table 3, compared with the available data in literature. Ligands **L2** and **L3** display two strong absorptions, at 349 and 357, and at 336 and 349 nm, respectively. This type of absorption is characteristic of the parent zwitterion **L1**.[2b] While **L2** presents a red-shift when compared to **L1**, **L3** exhibits an opposite trend probably due to an antagonistic effect of their substituents, TCNE and TCNQ respectively.

Table 3. UV-Vis Spectroscopic data.

Compound	λmax/nm (ε/10^4 M^{-1} cm^{-1})
L1[2b]	343, 350
L2	252 (0.085), *sh* 349 (0.184), 357 (0.191), 428 (0.121)
L3	254 (0.102), 336 (0.262), 349 (0.277), 502 (0.005)
1[18]	262, 320, 332*sh*, 414, 567
2	233 (1.194), *sh* 260 (0.500), *sh* 325 (0.387), 342 (0.473), 355 (0.438), 399 (0.253), 426 (0.273)
3	234 (0.927), *sh* 262 (0.473), *sh* 325 (0.381), 343 (0.503), *sh* 395 (0.244), 427 (0.297)
4	233 (1.438), *sh* 255 (0.739), 344 (0.840), 356 (0.827), *sh* 397 (0.433), 427 (0.527)
6	233 (1.097), *sh* 256 (0.584), 336 (0.609), *sh* 348 (0.535), 525 (0.040)
7	232 (2.360), *sh* 256 (1.369), 336 (1.893), 501 (0.072)

All complexes synthetized in this work show the presence of an intense absorption band at around 233 nm (from 232 to 234 nm). This UV-Vis absorption is generally assigned to π-π* ligand-centred transitions from both the acenaphthene and the aryl moiety.[23] Complexes **2** and **4** show in comparison with **L2** a red-shift of the two intense bands assigned to the zwitterion. This effect is not noticeable when comparing complexes **6** and **7** with ligand **L3**.

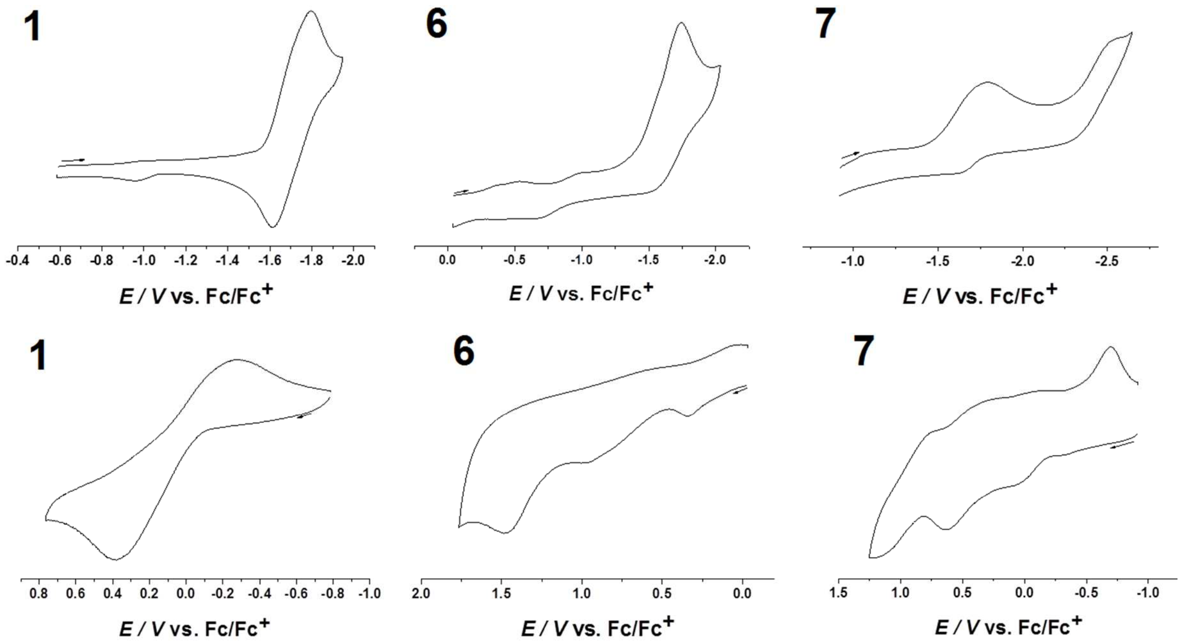


Figure 4. Cyclic voltammetry of **1**, **6** and **7** in CH_2Cl_2 / 0.1 M [*n*-Bu_4N]PF_6. Reductive side (top) and oxidative side (bottom).

Cyclic voltammetry. Cyclic voltammetric measurements were carried out in CH_2Cl_2 / 0.1 M [*n*-Bu_4N]PF_6 to elucidate the redox properties of the copper complexes. Unfortunately, all redox processes turned out to be electrochemically irreversible, and the reversibility did not improve either on changing scan rates or on lowering the temperature. Hence, the assignments presented can only be seen as tentative. The precursor complex **1** shows a reduction peak at -1.8 V *vs*. Fc/Fc^+ which at a first glance appears reversible (Figure 4-**1**, top). However, a careful look at the voltammogram shows that apart from the re-oxidation peak at -1.6 V, an additional re-oxidation peak appears at -0.96 V which is a follow-up of the reduction peak at -1.8 V. A reduction peak at similar potentials has been observed for various aryl-BIAN ligands in the free form.[23] Hence, we believe that this reduction peak is associated with the reduction of this redox-active ligand and not with the reduction of Cu(I) to Cu(0). On the anodic side, complex **1** displays an oxidation peak at 0.38 V, with the corresponding re-reduction peak appearing at -0.27 V (Figure 4-**1**, bottom). This process is assigned to the oxidation of the Cu(I) centre to Cu(II). The large difference in potential between the anodic and cathodic peaks is related to the large re-organization energy that is required due to the very different coordination demands of copper in those two oxidation states.

For complexes **6** and **7**, where the acetonitrile ligands from **1** have been replaced by one or two of the TCNQ based **L3** zwitterionic ligands, the reduction potentials for the irreversible first reduction are -1.73 and -1.77 V, respectively (Figure 4-**6** and **7**, top). These values are similar to that observed in **1** and BIAN. Hence, we assign this reduction peak to the reduction of the BIAN ligand. For **7**, an additional reduction peak is observed at -2.51 V, which is tentatively assigned to a reduction based on the zwitterionic **L3** ligand. Complex **6** displays multiple irreversible oxidation waves at 0.33, 0.95 and 1.47 V. For **7**, irreversible oxidation peaks are observed at -0.33, 0.04, 0.63 and 1.08 V (Figure 4-**6** and **7**, bottom). This is to be expected as both the Cu(I) centre as well as the ligand **L3** can be oxidized.[8b] Observation of more number of oxidation steps for **7** which contains two **L3** ligands as compared to **6** that contains only one **L3** ligand also supports this assignment.

For **2**, that contains the TCNE containing zwitterionic ligand **L2**, irreversible reduction steps are observed at -1.66 and -2.01 V. An additional wave of lesser intensity is also seen at -0.65 V (Fig. S1-**2**). Cu(I) complexes containing monodentate N-donors might lose ligands on changes in the redox state. Hence, the appearance of this small wave might be related to a ligand dissociated complex. Complex **4** that contains two **L2** ligands shows irreversible reduction waves at -1.62, -2.01 and -2.47 V (Fig. S1-**4**). The shift of the redox potentials to the positive direction as compared to **6** and **7** is likely related to the ease of reduction for the TCNE-substituted **L2** as compared to the TCNQ-substituted **L3**. The reduction sites here are likely the same as those discussed for **6** and **7** above. Complex **2** displays two irreversible oxidation waves at 0.26 and 0.82 V, whereas for **4** irreversible oxidation waves are observed at 0.16, 0.68 and 0.91 V (Fig. S1-**4**).

The 4,4´-bpy bridged complex **3** shows two irreversible reduction waves at -1.63 and -2.05 V (Fig. S1-**3**). In view of the similarity of these reduction potentials to those observed for **2**, we believe that these are each two electron redox processes, where the BIAN ligands as well as the **L2** ligands on the two remote copper centres are reduced at the same potentials, respectively. Irreversible oxidation steps for **3** are observed at 0.14 and 1.05 V (Fig. S1-**3**) and these are likely to be the simultaneous two-electron oxidation of the two remote Cu(I) centres and the two remote zwitterionic **L2** ligands.

Conclusions

The use of a copper(I) precursor complex bearing an α-diimine ligand (BIAN) allowed access to relatively soluble coordination complexes bearing nitrile-functionalized zwitterionic ligands. This successful synthetic way provided an opportunity to study the chemoselectivity of the interactions between the TCNE- and TCNQ-derived quinonemonoimine ligands and the metal centre. The strongest absorptions determined by UV-Vis spectroscopy, present in both ligands, were determined to belong to the parent zwitterion. While complexes bearing ligand **L2** exhibit a red shift of their absorptions, this effect is not noticeable in the case of complexes bearing ligand **L3**. Infrared studies confirmed the coordination of a nitrile function of the ligands **L2** and **L3** to a copper ion in the newly synthetized complexes, evidenced by a shift of their nitrile values when comparing ligands and complexes IR spectra. The electronic effect of the copper centre on the nitrile function is more significant for complexes bearing **L3** than for **L2**. The comparison between our complexes and those studied by Kaim *et al*. establishes a greater but overall weak charge transfer character. Cyclic voltammetry measurements delivered irreversible redox responses for all the investigated copper complexes. However, a comparison of the redox potentials have helped us to established the first reduction step in all complexes as BIAN centred and the oxidation steps as being centred on copper and the zwitterionic ligands.

All compounds synthesized, with the exception of **5**, were diamagnetic and each compound was fully characterized by NMR spectroscopy, despite the difficulty to obtain ^{13}C-NMR spectra, to some degree for all compounds but predominantly for the Cu(I) complexes, indicated that the electronic environment of the nitrile carbons lead to a slow relaxation response, increasing the difficulty to obtain unambiguous information. Nevertheless, these results, in addition to the information gathered by ^{1}H-NMR and in combination with the other spectroscopic and spectrometric techniques, lead to coherent and unequivocal conclusions even in the case of compounds for which no X-ray diffraction studies are available. Compounds **3** and **4** exhibit the same slightly distorted tetrahedral geometry coordinated by four nitrogen-based ligands, two **L2** and one BIAN ligands for **4** and one **L2**, one BIAN and one 4,4'-bipyridine molecules for **3**. Upon addition of $NaN(SiMe_3)_2$ to **4**, an oxidation product was obtained, **5**, but only in the form of few single crystals. A more rational synthesis and complete characterization of that compound is planned. The molecular structure of **5** consists in a bi-dimensional coordination polymer in which two monodeprotonated ligands **L2**$^-$ chelate a Cu(II) centre, formally through a N1-Cu1 σ-bond and a O1-Cu1 dative bond. The formation of a 2D network in the solid-state results from the coordination of two *trans* cyano groups from two other complex molecules, which occupy the apical positions of the Cu(O,N)$_2$ based octahedron.

Table 4. Crystallographic details of **3**·$4CH_2Cl_2$, **4**·CH_2Cl_2 and **5**.

Compound	**3**·$4CH_2Cl_2$	**4**·CH_2Cl_2	**5**
CCDC	1039320	1039321	1039322
Chemical formula	$C_{120}H_{130}B_2Cu_2F_8N_{16}O_4·4CH_2Cl_2$	$C_{74}H_{82}BCuF_4N_{12}O_4·CH_2Cl_2$	$C_{38}H_{40}CuN_{10}O_4$
Formula Mass	2500.80	1438.79	764.34
Crystal system	Triclinic	Triclinic	Monoclinic
a/Å	12.9140(8)	14.8235(5)	11.0282(5)
b/Å	14.2234(7)	17.2794(7)	13.5670(7)
c/Å	18.4642(8)	17.8129(6)	14.6751(5)
α/°	104.264(3)	92.405(2)	90.00
β/°	92.349(3)	109.546(2)	108.707(2)
γ/°	105.810(2)	108.388(2)	90.00
Volume/Å^3	3141.3(3)	4024.3(3)	2079.69(16)
Temperature/K	173(2)	173(2)	173(2)
Space group	$P\ \text{-}1$	$P\ \text{-}1$	$P2_1/c$
Z	1	2	2
Reflections measured	18166	27157	12679
Independent reflections	12262	18316	4761
R_{int}	0.0396	0.0417	0.0640
R_1 values ($I > 2\sigma(I)$)	0.0745	0.0987	0.0753
$wR(F^2)$ values ($I > 2\sigma(I)$)	0.1605	0.2511	0.2102
R_1 values (all data)	0.1378	0.1660	0.1090
$wR(F^2)$ values (all data)	0.2020	0.2800	0.2349

Experimental section

Materials and instrumentation. The ligands **L2**, **L3**[15a] and the precursor complex **1**[18] were prepared according to reported procedures. 4,6-Diaminoresorcinol dihydrochloride was purchased from Acros. All other reagents are commercially available and were used as received. Solvents were freshly distilled under argon prior to use. All reactions for air- and water sensitive compounds were performed using standard Schlenk techniques under dry argon atmosphere. NMR spectra were recorded at room temperature on a Bruker AVANCE 400 ^{1}H NMR (400.13 MHz) and ^{13}C NMR (100.61 MHz) or on a Bruker AVANCE 300 ^{1}H NMR (300.17 MHz) and ^{13}C NMR (75.49 MHz) and referenced using the residual (^{1}H and ^{13}C) solvent resonance. For some of the complexes we could not observe all ^{13}C-NMR signals, probably due to relaxation issues from carbons related to the size of the molecule. Mass spectrometric measurements were recorded on a microTOF (Bruker Daltonics, Bremen, Germany) using nitrogen as drying agent and nebulising gas. Elementary analyses were performed by the “Service de Microanalyses, Université de Strasbourg”, (Strasbourg, France). Cyclic voltammetry was carried out at 298 K with scan rates of 100mV/s. n-Bu_4NPF_6 was used as conducting salt at a concentration of 0.1 M.

Crystal structure determinations. Crystals of **3**·$4CH_2Cl_2$ suitable for X-ray diffraction were obtained, as red blocks, by slow diffusion of pentane into a saturated solution of **3** in CH_2Cl_2 at ambient temperature. Similarly, red crystals were obtained by slow diffusion of pentane into a saturated solution of **4** in CH_2Cl_2 at ambient temperature. Three CH_2Cl_2 solvent molecules cocrystallized with **4**, two of them were found severely disordered and since attempts to identify their atomic positions failed, a PLATON-SQUEEZE[24] procedure was applied. The residual electron density was assigned to two molecules of the dichloromethane solvent [131/2 = 66e per asymmetric unit; two molecules of CH_2Cl_2 would give 84e]. This data treatment resulted in an improved quality of the model **4**·CH_2Cl_2; the refinement was carried out using SHELX-2013.[25] Crystals of the polymer **5** were obtained as red plates by slow diffusion of pentane into a solution of the reaction product of compound **4** and $NaN(SiMe_3)_2$ (see above). The crystals were placed in oil and a single crystal was selected, mounted on a glass fibre and placed in a low-temperature N_2 stream. X-Ray diffraction data collection was carried out at 173(2) K on a

Nonius Kappa-CCD diffractometer[26] equipped with an Oxford Cryosystem liquid N_2 device, using graphite-monochromated Mo-Kα radiation (λ = 0.71073 Å). The crystal-detector distance was 36 mm. Crystallographic and experimental details for the structure are summarized in Table 4. The structures of **3**·4CH_2Cl_2 and **5** were solved by direct methods using the programme SHELXS-97.[27] The refinement and all further calculations were carried out using SHELXL-97.[28] The H atoms were included in calculated positions and treated as riding atoms using SHELXL default parameters.

Synthesis of complex [Cu(BIAN)(NCMe)(**L2**)]BF_4 (**2**). Under exclusion of moisture and air, the copper complex **1** (0.568 g, 0.775 mmol) and the zwitterion **L2** (0.272 g, 0.775 mmol) were dissolved in 50 ml of dry dichloromethane. The resulting solution was stirred overnight at ambient temperature. Then the solution was concentrated to about 10 ml and dry pentane was added. The precipitate was filtered off, washed with Et_2O and pentane and dried under reduced pressure to give compound **2** (0.604 g, 0.602 mmol, 78%) as a red powder. ^{1}H-NMR (300 MHz, CD_2Cl_2) δ = 0.88-0.94 (m, due to overlap of CH_3 of Bu and *i*-Pr moieties, 18H), 1.20 (d, ^3J(H,H) = 5.1 Hz, 12H, $\mathrm{CHC}\mathit{H}_3$), 1.32-1.43 (m, 4H, $\mathrm{C}\mathit{H}_2\mathrm{CH}_3$), 1.60-1.69 (m, 4H, $\mathrm{C}\mathit{H}_2\mathrm{CH}_2\mathrm{CH}_3$), 3.02-3.06 (m, 4H, $\mathrm{C}\mathit{H}\mathrm{CH}_3$), 3.50 (q owing to overlap dt, ^3J(H,H) = 6.1 Hz, 4H, NCH_2), 5.84 (s, 1H, N$\overset{\cdots}{-}$C$\overset{\cdots}{-}$CH), 6.68 (d, ^3J(H,H) = 7.2 Hz, 2H, aromatic C-H), 7.37-7.54 (m, 8H, aromatic C-H), 8.01 (br. s, 2H, NH), 8.12 (d, ^3J(H,H) = 8.3 Hz, 2H, aromatic C-H) ppm; ^{13}C{^{1}H}-NMR (75 MHz, CD_2Cl_2) δ = 13.75 ($\mathrm{CH}_2\mathit{C}\mathrm{H}_3$), 20.37 ($\mathit{C}\mathrm{H}_2\mathrm{CH}_3$), 24.23 ($\mathrm{CH}\mathit{C}\mathrm{H}_3$), 24.51 ($\mathrm{CH}\mathit{C}\mathrm{H}_3$), 29.06 ($\mathit{C}\mathrm{HCH}_3$), 30.53 ($\mathrm{NCH}_2\mathit{C}\mathrm{H}_2$), 80.76 (N$\overset{\cdots}{-}C\overset{\cdots}{-}$*C*H), 107.99 (NC-*C*-CN), 125.14 (aromatic C-H), 125.82 (aromatic C-H), 127.18 I, 127.58 (aromatic C-H), 129.22 (aromatic C-H), 131.57 I, 131.90 (aromatic C-H), 138.34 (2xC), 143.30 I, 143.54 I, 153.76 (C$\overset{\cdots}{-}$N), 165.67 (C-N=*C*), 171.42 (C$\overset{\cdots}{-}$O) ppm; MS (ESI): *m/z* = 914 [M-(MeCN + BF_4)]$^+$; FTIR: ν_{max} (pure, diamond orbit)/cm^{-1} 3254 brm, 3065w, 2960m, 2929m, 2870m, 2218w, 2168w, 2115w, 1653w, 1577vs, 1519m, 1460s, 1436s, 1398vs, 1362s, 1349s, 1286m, 1255m, 1224m. 1187m, 1050brvs, 955m, 945m, 937m, 834m, 800m, 780s, 758s, 735m, 715m; Anal. Calc. For $C_{57}H_{64}BcuF_4N_8O_2$ (1043.52): C, 65.61; H, 6.18; N, 10.74. Found: C, 65.99; H, 6.28; N, 10.70.

Synthesis of complex [{Cu(BIAN)(**L2**)}$_2$(μ-4,4'-bipyridine)](BF_4)$_2$ (**3**). Solid 4,4'-bipyridine (0.0078 g, 0.050 mmol) was added to a solution of **2** (0.100 g, 0.100 mmol) in freshly distilled CH_2Cl_2. The resulting mixture was stirred at room temperature and under inert conditions for 15 h. The solution was concentrated to about 10 ml and pentane was added. The precipitate was collected by filtration and washed with diethyl ether and pentane. After all volatile components were removed under reduced pressure, **3** was obtained as a red brown powder (0.081 g, 0.037 mmol, 74%). ^{1}H-NMR (300 MHz, CD_2Cl_2) δ = 0.94-0.97 (m, due to overlap of CH_3 of Bu and *i*-Pr signals, 36H), 1.18 (d, ^3J(H,H) = 5.1 Hz, 24H, $\mathrm{CHC}\mathit{H}_3$), 1.39-1.46 (m, 8H, $\mathrm{C}\mathit{H}_2\mathrm{CH}_3$), 1.69-1.73 (m, 8H, $\mathrm{C}\mathit{H}_2\mathrm{CH}_2\mathrm{CH}_3$), 3.02-3.09 (m, 8H, $\mathrm{C}\mathit{H}\mathrm{CH}_3$), 3.48 (q owing to overlap dt, ^3J(H,H) = 6.1 Hz, 8H, NCH_2), 5.66 (s, 2H, N$\overset{\cdots}{-}$C$\overset{\cdots}{-}$CH), 6.74 (d, ^3J(H,H) = 7.9 Hz, 4H, aromatic C-H), 7.39-7.55 (m, 16H, aromatic C-H), 7.85 (br. S, 4H, NH), 8.12 (d, ^3J(H,H) = 9.7 Hz, 4H, aromatic C-H), 8.19 (m, 4H, aromatic C-H) ppm, 8.57 (b, 4H, aromatic C-H) ppm; ^{13}C{^{1}H}-NMR signals could not be observed because of the low solubility of compound **3** in CD_2Cl_2. MS (ESI): *m/z* = 1023 [([Cu(BIAN)(**L2**)]BF_4)$_2$Na]$^+$; 1039 [([Cu(BIAN)(**L2**)]BF_4)$_2$K]$^+$; FTIR: ν_{max} (pure, diamond orbit)/cm^{-1} 3245w, 2960m, 2929m, 2870m, 2225w, 2218w, 1645w, 1578s, 1511s, 1463m, 1438m, 1394vs, 1363m, 1350m, 1324m, 1310m, 1286m, 1255m, 1223m, 1188m, 1151m, 1128m, 1054vs, 1031s, 956m, 945m, 937m, 834m, 827m, 810m, 799m, 780m, 767m, 755m, 731m, 714m; Anal. calc. for $C_{120}H_{130}B_2Cu_2F_8N_{16}O_4$ (2158.91): C, 66.69; H, 6.06; N, 10.37. Found: C, 67.09; H, 6.26; N, 10.41;

Synthesis of complex [Cu(BIAN)(**L2**)$_2$]BF_4 (**4**). Under the exclusion of air and moisture a solution of complex **1** (0.521 g, 0.711 mmol) and ligand **L2** (0.500 g, 1.42 mmol) in 50 ml of dry dichloromethane was stirred overnight. Then all volatile components were removed under reduced pressure. The residue was recrystallized from CH_2Cl_2/pentane. In order to remove traces of Cu^{2+} the compound was taken up in CH_2Cl_2 and filtered through Celite. Evaporation of the solvent afforded compound **4** as a red-brown powder (0.510 g, 0.380 mmol, 53%). ^{1}H-NMR (300 MHz, $CDCl_3$) δ = 0.90-0.97 (m, owing to overlap of CH_3, 24H, CH_3), 1.28 (br. s, 12H, CH_3), 1.36-1.48 (m, 8H, $\mathrm{C}\mathit{H}_2\mathrm{CH}_3$), 1.65-1.75 (m, 8H, $\mathrm{NCH}_2\mathrm{C}\mathit{H}_2$), 3.05 (br. s, 4H, CH), 3.55 (q, owing to overlap dt, ^3J(H,H) = 6.7 Hz, 8H, NCH_2), 5.60 (s, 2H, N$\overset{\cdots}{-}$C$\overset{\cdots}{-}$CH), 6.64 (d, ^3J(H,H) = 7.1 Hz, 2H, aromatic C-H), 7.37-7.51 (m, 8H, aromatic C-H), 8.06 (d, ^3J(H,H) = 8.3 Hz, 2H, aromatic C-H), 8.15 (br. s, 4H, NH) ppm; ^{13}C{^{1}H}-NMR (100 MHz, $CDCl_3$) δ = 13.71 ($\mathrm{CH}_2\mathit{C}\mathrm{H}_3$), 20.09 ($\mathit{C}\mathrm{H}_2\mathrm{CH}_3$), 24.21 (br. s, $\mathrm{CH}\mathit{C}\mathrm{H}_3$), 28.80

(*C*HCH$_3$), 30.52 (NCH$_2$*C*H$_2$), 43.94 (NCH$_2$), 85.98 (N⎓C⎓*C*H), 107.03 (NC*C*CN), 124.71 (aromatic C-H), 125.27 (aromatic C-H), 126.94 (C), 127.15 (aromatic C-H), 128.72 (aromatic C-H), 131.15 (C), 131.36 (aromatic C-H), 133.82 (C), 138.09 (C), 142.66 (C), 143.28 (C), 153.63 (C⎓N), 164.78 (C-N=*C*), 170.88 (C⎓O) ppm; MS (ESI): *m/z* = 1209 [M-BF$_4$-C$_4$H$_9$]$^+$; FTIR: ν_{max} (pure, diamond orbit)/cm^{-1} 3249brm, 2959m, 2929m, 2869m, 2217m, 1654w, 1571vs, 1513s, 1459s, 1395vs, 1347s, 1285s, 1254m, 1223m, 1187m, 1148m, 1049s, 1034s, 955m, 945m, 938m, 833m, 799m, 779m, 757s, 733m, 714m; Anal. calc. for C$_{74}$H$_{82}$BCuF$_4$N$_{12}$O$_4$ (1343.06): C, 66.18; H, 6.15; N, 12.51. Found: C, 65.93; H, 6.24; N, 12.08.

Synthesis of complex [Cu(BIAN)(NCMe)(**L3**)]BF$_4$ (**6**). Under exclusion of air and moisture, the zwitterion **L3** (0.446 g, 0.982 mmol) was added to a solution of copper complex **1** (0.600 g, 0.818 mmol) in 40 ml of dry dichloromethane. The resulting mixture was stirred for 15 h at room temperature and then filtered through Celite. The volatile components were removed under reduced pressure and the residue was washed with dry pentane and ether and dried under vacuum. Compound **6** (0.881 g, 0.797 mmol, 81%) was obtained as a brown powder. ^{1}H-NMR (300 MHz, CD$_2$Cl$_2$) δ = 0.90-0-97 (m, overlap of CH$_3$, 18H), 1.18 (d, ^3J(H,H) = 4.5 Hz, 12H, CH$_3$), 1.33-1.47 (m, 4H, C*H$_2$*CH$_3$), 1.60-1.73 (m, 4H, NCH$_2$C*H$_2$*), 2.94-3.03 (m, 4H, C*H*CH$_3$), 3.38 (q, owing to overlap dt, ^3J(H,H) = 6.7 Hz, 4H, NCH$_2$), 5.31-5.33 (m, overlap of NCCHCN and N=C=CH, 2H), 6.54 (d, ^3J(H,H) = 8.1 Hz, 1H, aromatic C-H), 6.76(d, ^3J(H,H) = 5.4 Hz, 2H, aromatic C-H), 7.17 (d, ^3J(H,H) = 6.9 Hz, 1H, aromatic C-H), 7.31-7.53 (m, 9H, aromatic C-H), 7.81 (d, ^3J(H,H) = 8.3 Hz, 1H, aromatic C-H), 8.10-8.12 (m, 4H, overlap of aromatic CH and NH) ppm; ^{13}C{^{1}H}-NMR (100 MHz, CDCl$_3$) δ = 13.58 (CH$_2$*C*H$_3$), 13.65 (CH$_2$*C*H$_3$), 19.96 (*C*H$_2$CH$_3$), 20.03 (*C*H$_2$CH$_3$), 23.24 (CH*C*H$_3$), 23.70 (CH*C*H$_3$), 28.89 (br. s, overlap of *C*HCH$_3$ and NC*C*HCN), 30.15 (NCH$_2$*C*H$_2$), 43.40 (NCH$_2$), 81.88 (N⎓C⎓CH), 105.06 (O⎓C⎓*C*), 111.57 (CN), 114.46 (CN), 124.44 (2 x aromatic C-H), 124.92 (aromatic C-H), 126.16 (C), 127.03 (C), 127.82 (aromatic C-H), 128.15 (aromatic C-H), 128.83(aromatic C-H), 128.87 (aromatic C-H), 131.19 (C), 137.52 (C), 143.02 (*C*-N=C), 154.86 (C⎓N), 168.24 (C=N), 168.31 (C⎓O) ppm, not all ^{13}C-NMR signals could be observed because of the low solubility of compound **6** in CDCl$_3$; MS (ESI): *m/z* = 1017 [MH-BF$_4$]$^+$; FTIR: ν_{max} (pure, diamond orbit)/cm^{-1} 3265brm, 3064w, 2960m, 2928m, 2869m, 2360w, 2200m, 2138m, 1651m, 1598m, 1555vs, 1501s, 1490s, 1460s, 1435s, 1419s, 1384s, 1363s, 1325m, 1285s, 1254m, 1223m, 1188m, 1144m, 1048brs, 955m, 944m, 935m, 833s, 799s, 780s, 756s, 734s; Anal. calc. for C$_{64}$H$_{69}$BCuF$_4$N$_9$O$_2$ (1146.64): C, 67.04; H, 6.07; N, 10.99. Found: C, 67.44; H, 6.23; N, 10.50.

Synthesis of complex [Cu(BIAN)(**L3**)$_2$]BF$_4$ (**7**). Under inert conditions solid zwitterion **L3** (0.700 g, 1.54 mmol) was added to a solution of **1** (0.470 g, 0.641 mmol) in freshly distilled CH$_2$Cl$_2$. The resulting solution was stirred for 15 h at ambient temperature. Then the solution was concentrated to about 10 mL and pentane was added. The resulting precipitate was collected by filtration and washed with dry pentane. After removing the volatile components under reduced pressure, compound **7** was obtained as a brown powder (1.08 g, 0.694 mmol, 45%). ^{1}H-NMR (300 MHz, CD$_2$Cl$_2$) δ = 0.93-0.98 (m, owing to overlap of CH$_3$, 24H), 1.20-1.22 (m, 12H, CH$_3$), 1.36-1.49 (m, 8H, C*H$_2$*CH$_3$), 1.64-1.74 (m, 8H, NCH$_2$C*H$_2$*), 2.96-3.00 (m, 4H, CH), 3.39 (q, owing to overlap dt, ^3J(H,H) = 6.8 Hz, 8H, NCH$_2$), 5.33 (s, 1H, N⎓C⎓CH), 5.40 (s, 1H, N⎓C⎓CH), 6.72 (d, ^3J(H,H) = 7.2 Hz, 2H, aromatic C-H), 7.32-7.53 (m, 12H, aromatic C-H), 7.63-7.68 (m, 1H, aromatic C-H), 7.81 (d, ^3J(H,H) = 8.4 Hz, 4H, aryl), 8.07 (m, ^3J(H,H) = 8.3 Hz, 2H, aromatic C-H), 8.14-8.18 (m, 4H, NH) ppm. ^{13}C{^{1}H}-NMR (100 MHz, CDCl$_3$) δ = 13.62 (CH$_2$*C*H$_3$), 20.10 (*C*H$_2$CH$_3$), 23.82 (CH*C*H$_3$), 27.67 (*C*HCH$_3$), 28.80 (NC*C*HCN), 30.19 (NCH$_2$*C*H$_2$), 43.46 (NCH$_2$), 81.82 (N⎓C⎓CH), 101.26 (O⎓C⎓*C*), 111.78 (CN), 114.66 (CN), 124.54 (aromatic C-H), 125.02 (aromatic C-H), 127.22(aromatic C-H), 127.86 (aromatic C-H), 128.21 (aromatic C-H), 128.50 (aromatic C-H), 128.78 (aromatic C-H), 129.00 (aromatic C-H), 131.19 (C), 131.38 (C), 137.51 (C), 137.85 (C), 143.15 (C), 154.94 (C⎓N), 168.35 (C=N), 169.07 (C⎓O) ppm, not all ^{13}C-NMR signals could be observed because of the low solubility of compound **7** in CDCl$_3$; MS (ESI): *m/z* = 1472 [MH-BF$_4$]$^+$; FTIR: ν_{max}(pure, diamond orbit)/cm^{-1} 3262brm, 3068 vw, 2960m, 2929m, 2870m, 2286w, 2198w, 2139w, 1650w, 1598m, 1550vs, 1489s, 1459s, 1418m, 1384m, 1363m, 1325m, 1285m, 1254m, 1222m, 1187m, 1143m, 1049brs, 1021m, 955m, 945m, 934m, 832m, 808m, 800m, 780m, 757m, 731m; Anal. calc. for C$_{88}$H$_{92}$BCuF$_4$N$_{14}$O$_4$ (1560.11): C, 67.75; H, 5.94; N, 12.57. Found: C, 67.44; H, 6.02; N, 12.50.

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Notes and references

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† Electronic Supplementary Information (ESI) available: Cyclic voltammetry curves of **2**, **3** and **4** and X-ray crystallographic data in CIF for **3**·4CH_2Cl_2, **4**·CH_2Cl_2 and **5**. CCDC reference numbers: 1039320-1039322. See DOI: 10.1039/b000000x/

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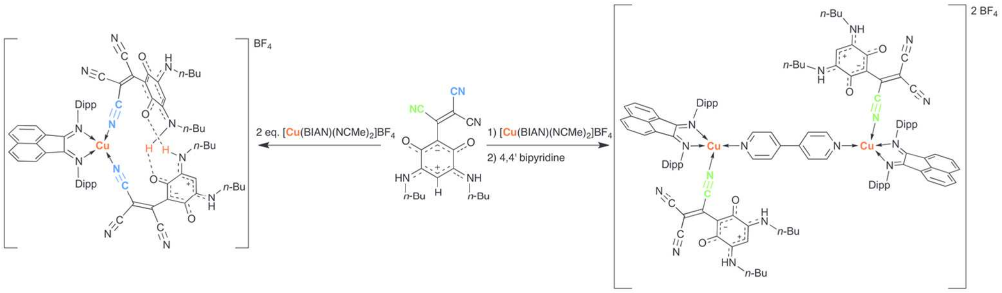

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