

Preliminary communication / Communication

Synthesis and properties of copper quinonoid complexes for optical recording application

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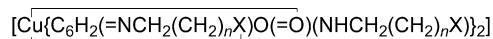
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Abstract

We describe the synthesis of novel quinonemonimines Cu(II) coordination complexes, of the type:

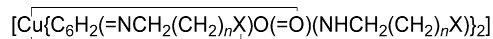


which, in addition to their intrinsic interest, have potential application in optical recording. The following key parameters have been highlighted: (i) the presence of coordinating arms on the quinonoid core of the ligand leads to octahedral complexes with increased solubility, (ii) the presence of Cu(II) as a metal centre leads to a favourable exothermic decomposition, (iii) the presence of quinonoid moieties results in the optical absorption to be in the desired wavelength range. **To cite this article: P. Braunstein et al., C. R. Chimie 9 (2006).**

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Résumé

Nous décrivons la synthèse de complexes quinonemonimines du cuivre(II) originaux, du type :



qui, en plus de leur intérêt propre en chimie de coordination, présentent un potentiel d'application pour l'enregistrement optique. Les paramètres suivants ont été mis en évidence : (i) la présence de bras coordinants sur la partie quinonique du ligand conduit à des complexes de meilleure solubilité, (ii) la présence de Cu(II) comme centre métallique favorise une décomposition exothermique, (iii) l'absorption optique dans la gamme de longueur d'onde désirée est due à la présence d'entités quinoïdes. **Pour citer cet article : P. Braunstein et al., C. R. Chimie 9 (2006).**

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Keywords: Quinone; Ligand; Complex; Copper; Optical recording; Zwitterion

Mots clés : Quinone ; Ligand ; Complexe ; Cuivre ; Enregistrement optique ; Zwitterion

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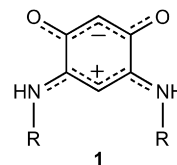
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1. Introduction

Over the last years, optical information recording media possessing higher recording density have become very attractive for industry [1]. To meet this goal, an optical disc referred to as a write-once digital versatile disc (DVD-R) has been proposed and successfully introduced on the market. The recording principle is the same for recordable compact discs CD-R and DVD-R, the difference remaining the spot size and the wavelength of the laser light used. CD-R are writable at a wavelength comprised between 770 and 830 nm. More recently, the use of compact high-performance red diode lasers with wavelengths ranging from 600 to 700 nm allowed for DVD-R a six- to eight-fold improvement in data packing density in comparison with conventional CDs. However, considering factors such as the recent spread of networks (e.g. Internet) and the emergence of high definition television (HDTV) broadcasting, cheap and convenient recording media, capable of recording image information at even larger capacity, are now required. While DVD-R discs currently serve as high-capacity recording media, demand for larger capacity and higher density has increased. Blu-ray[®] discs (Blu-ray[®] disc is a standard developed by Hitachi Ltd., LG Electronics Inc., Matsushita Electric Industrial Co. Ltd., Pioneer Corporation, Royal Philips Electronics, Samsung Electronics Co. Ltd., Sharp Corporation, Sony Corporation, Thomson Multimedia) or HD-DVD discs (a standard developed by Toshiba and NEC) are going to be the next milestone in optical recording technology [2]. By adopting a blue diode laser with a wavelength of 405 nm, the data storage may be increased up to 45 Gigabytes for a 12 cm diameter disc and a 0.6 mm thickness [2]. This high-capacity disc family is going to be the next solution in optical recording technology, turning personal computers into real entertainment devices. Organic dyes have attracted considerable attention in the field of diode laser optical storage for industrial applications. Commercial CD-R and DVD-R contain, as recording layers, numerous dyes based on phthalocyanines [3], hemicyanines [4], cyanines [5] and metallised azo structures [6]. Already present on CD-R and DVD-R as very efficient recording layers, metal complex dyes are adaptable to the upcoming blue laser technology. Basic requirements for such dye media are: (i) strong absorption in the range 350–450 nm (the highest the epsilon, the more efficient is the laser light absorption and the sharper is the pit on the disc), (ii) thermal stability (sharp decomposition

above 200 °C), (iii) no melting and flowing of the unrecorded/recorded dye up to the thermal decomposition temperature, (iv) solubility in organic solvents and filterability of their solution allowing the use of a spin coating process to prepare thin films.

Quinonoid molecules possess remarkable chemical and physical properties [7]. The synthesis of unprecedented $6\pi + 6\pi$ electron, potentially antiaromatic quinonoid zwitterions (molecules of type **1**) has recently been reported [8–10].



In addition to their fundamental interest [11–16], such molecules appear very promising in different research areas including organic [9,12,17] and supramolecular chemistry [10,17], biochemistry [17], hair colouring [18–20] and coordination chemistry [9,10,21,22]. Here we extend the family of transition metal complexes based on **1** and show that copper compounds can be used as inorganic dyes for potential optical recording application.

2. Experimental section

All solvents were dried and distilled using common techniques unless otherwise stated. ¹H NMR (300 MHz) and ¹³C NMR (75 MHz) spectra were recorded on a Bruker AC-300 instrument. MALDI-TOF mass spectra were recorded on a Biflex III Bruker mass spectrometer. Elemental analyses were performed by the ‘Service de microanalyse du CNRS, université Louis-Pasteur’ (Strasbourg, France). The detailed synthesis and characterising data of compounds **2–6**, **8–10**, **12** and **13** have been described elsewhere [8–10,21,22].

2.1. General procedure for the synthesis of ligands **7** and **11**

Typically, diaminoresorcinol dihydrochloride (0.500 g, 2.35 mmol) was dissolved in water (ca. 10 ml) and then excess of amine (ca. 7 equiv.) was added to the solution. After the reaction mixture was stirred for 2 h, it was extracted with CH₂Cl₂. The organic layer was collected and dried with MgSO₄. After filtration and concentration to 10 ml, Et₂O was

added to precipitate the product. The product was isolated by filtration.

7: Yield: 70%. Ms (MALDI-TOF⁺): m/z : 309.2 [M + 1]⁺; ¹H NMR (300 MHz, CDCl₃): δ = 1.83 (pent, ³J = 6.3 Hz, 4H, CH₂CH₂NH), 2.22 (s, 12H, CH₃), 2.40 (t, ³J = 6.3 Hz, 4H, CH₂N), 3.43 (t, ³J = 6.3 Hz, 4H, CH₂NH), 5.18 (s, 1H, N[⋯]C[⋯]CH), 5.39 (s, 1H, O[⋯]C[⋯]CH), 9.18 (br s, 2H, NH); ¹³C{¹H} NMR (75 MHz, CDCl₃) δ = 25.43 (s, CH₂CH₂NH), 42.45 (s, CH₃), 45.31 (s, CH₂N), 57.29 (s, CH₂NH), 80.59 (s, N[⋯]C[⋯]C), 99.11 (s, O[⋯]C[⋯]C), 156.77 (s, N[⋯]C), 172.88 (s, O[⋯]C); Anal. Calcd. for C₁₆H₂₈N₄O₂·1.25H₂O: C, 58.07; H, 9.29; N, 16.93. Found: C, 58.06; H, 8.97; N, 16.32.

11: Yield: 76%. Ms (MALDI-TOF⁺): m/z : 393.3 [M + 1]⁺; ¹H NMR (300 MHz, CDCl₃): δ = 1.86 (pent, ³J = 6.0 Hz, 4H, CH₂CH₂CH₂), 2.45 (br t, ³J = 4.3 Hz, 8H, NCH₂CH₂O), 2.51 (t, ³J = 6.0 Hz, 4H, CH₂CH₂CH₂N), 3.44 (t, ³J = 6.1 Hz, 4H, CH₂NH), 3.79 (t, ³J = 4.3 Hz, 8H, NCH₂CH₂O), 5.07 (s, 1H, N[⋯]C[⋯]CH), 5.39 (s, 1H, O[⋯]C[⋯]CH), 9.50 (br s, 2H, NH); ¹³C{¹H} NMR (75 MHz, CDCl₃) δ = 23.58 (s, CH₂CH₂CH₂), 43.30 (s, NCH₂CH₂O), 53.86 (s, CH₂CH₂CH₂N), 57.41 (s, NHCH₂), 66.68 (s, OCH₂), 80.41 (s, N[⋯]C[⋯]C), 99.12 (s, O[⋯]C[⋯]C), 156.86 (s, N[⋯]C), 172.80 (s, O[⋯]C); Anal. Calcd. for C₂₀H₃₂N₄O₄·1/3H₂O: C, 60.28; H, 8.26; N, 14.06. Found: C, 60.79; H, 8.36; N, 13.65.

2.2. Synthesis of Cu(II) complexes

Typically, the zwitterionic ligand (ca. 2 mmol) was dissolved in anhydrous dichloromethane (80 ml) and 0.5 equiv. Cu(acac)₂ was added to the solution. After the solution was stirred at room temperature for 3 h, the solvent was evaporated and the red, crystalline complex was isolated by filtration after precipitation from a mixture of dichloromethane and pentane.

14: Yield: 86%. (MALDI-TOF⁺): m/z : 622.3 [M + 1]⁺; Anal. Calcd. for C₂₈H₄₆CuN₈O₄·CH₂Cl₂: C, 49.25; H, 6.84; N, 15.84. Found: C, 49.13; H, 7.05; N, 15.87.

15: Yield: 89%. (MALDI-TOF⁺): m/z : 678.4 [M + 1]⁺; Anal. Calcd. for C₃₂H₅₄CuN₈O₄: C, 56.66; H, 8.02; N, 16.52. Found: C, 56.24; H, 7.98; N, 16.20.

16: Yield: 87%. (MALDI-TOF⁺): 622.3 [M + 1]⁺; Anal. Calcd. for C₂₈H₄₆CuN₈O₄·1/3CH₂Cl₂: C, 52.31; H, 7.23; N, 17.22. Found: C, 52.34; H, 7.39; N, 17.38.

17: Yield: 85%. (MALDI-TOF⁺): m/z : 570.2 [M + 1]⁺; Anal. Calcd. for C₂₄H₃₄CuN₄O₈: C, 50.56; H, 6.01; N, 9.83. Found: C, 50.16; H, 6.00; N, 9.65.

18: Yield: 90%. (MALDI-TOF⁺): m/z : 790.3 [M + 1]⁺; Anal. Calcd. for C₃₆H₅₄CuN₈O₈: C, 54.70; H, 6.89; N, 14.18. Found: C, 54.38; H, 7.00; N, 14.26.

19: Yield: 85%. (MALDI-TOF⁺): m/z : 846.5 [M + 1]⁺; Anal. Calcd. for C₄₀H₆₂CuN₈O₈: C, 56.75; H, 7.38; N, 13.24. Found: C, 56.90; H, 7.60; N, 12.59.

2.3. Physical measurements

λ_{\max} and ϵ in l/mol cm values of the compounds were determined in CH₂Cl₂ using an UV spectrophotometer. These values were obtained from measurements performed at three different concentrations.

Decomposition point (DP) and heat release (HR) were determined using a TA Instruments DSC Q100 apparatus, the compound being incorporated into a sealed aluminium pan. The analysis conditions were the following: temperature range from 25 to 400 °C, heating rate 10 °C/min, nitrogen flow of 50 ml/min. Values were determined from a single measurement. The dye melts and decomposes immediately in an irreversible process.

2.4. Test procedure

The following method was used to check the solubility and filterability of dyes for opto-electronic applications. All operations were carried out under a hood and the safety precautions contained in the safety data sheets of the products have to be followed. The temperature has to be kept between 20 and 22 °C during the manipulation, and the solvent was stored in the room at least 24 h before test run begins. The solvent 2,2,3,3-tetrafluoropropanol (TFP) should not contain more than 200 ppm of water; if this is not the case, it must be redistilled until this value is reached.

A sample was prepared from 0.40 g of dye and 20 ml of TFP. It was stirred for 12–15 h on a magnetic plate without heating. The resulting solution was filtered using a 10 ml syringe equipped with a 200 nm pore size PTFE-filter (diameter 13 mm). Filtration Ranking (three categories by filterability): (i) a compound is class A when 10 ml of the solution are filtered with one filter with virtually no stop of smooth filtration (max time allowed for complete filtration is 30 s); (ii) a compound is class B when around 5–6 ml of the solution are filtered with one filter with virtually no stop of smooth filtration and the remaining solution can still be filtered, by applying increased pressure; (iii) a sample is class C when filtration occurs dropwise as the solution passes through the filter.

3. Results and discussion

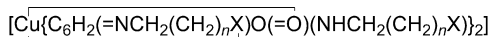
3.1. Ligand synthesis

The first member of the zwitterionic benzoquinone-monoimine family (molecule **2**) was prepared in 2002 by following a multi-step procedure [8]. More recently, we have extended this class of molecules by using a transamination reaction which allows the introduction of additional functionalities, as in **6** and **8–10** [9,10]. Accordingly, the zwitterions $[C_6H_2(\overset{\ominus}{N}HR)_2(\overset{\oplus}{O})_2]$ **7** ($R = -(CH_2)_3NMe_2$) and **11** ($R = -(CH_2)_3N \rightleftharpoons O$) can now be prepared in high yield by the smooth reaction at room temperature in water and under aerobic conditions between diaminoresorcinol and a large excess of the corresponding primary amines RNH_2 (see Section 2).

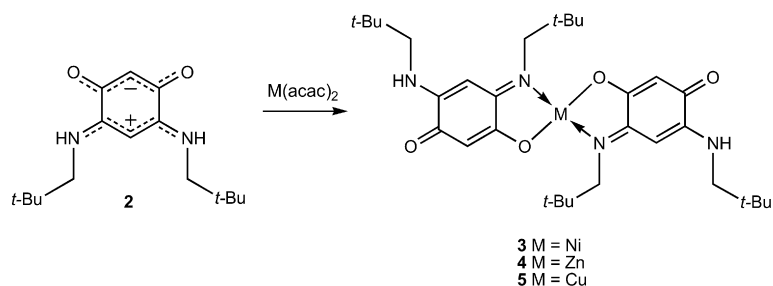
3.2. Synthesis of the metal complexes

It has been shown that the metallation reaction of ligands with no coordinating arm, such as zwitterion **2**, leads to the formation of square planar complexes **3–5** which are almost *insoluble* (Scheme 1) [21].

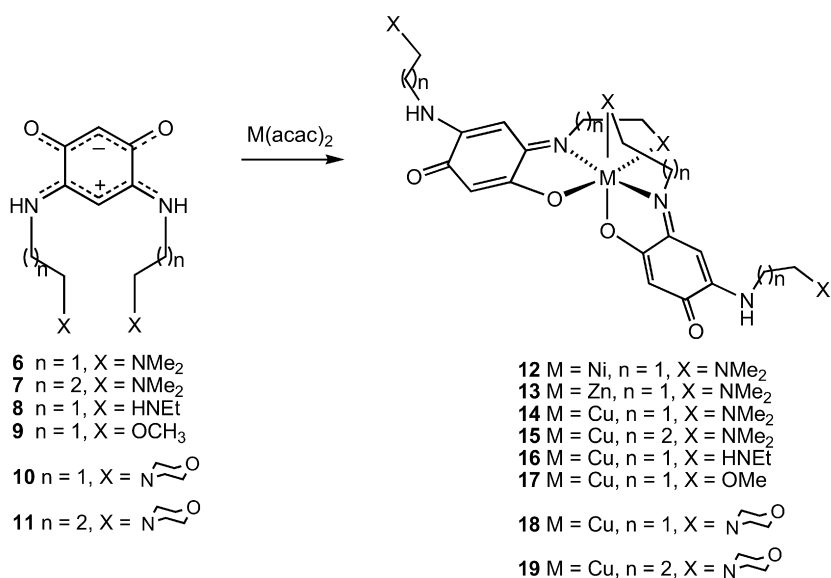
In contrast, the metallation of ligand **6**, which bears a coordinating amine moiety, affords high yields of the octahedral and *soluble* complexes **12** [22] and **13** [9] (Scheme 2). Similarly, reactions of ligands **6–11** at room temperature with $Cu(acac)_2$ in a 2:1 ligand/metal ratio leads to the complexes



14–19 (Scheme 2). As expected, the new ligands **7** and **11** show better coordination abilities than **2** ($R = t\text{-Bu}$). We assume for the Cu(II) complexes **14–19** an octahe-



Scheme 1.



Scheme 2.

dral coordination geometry by analogy with their analogues **12** and **13** which were fully characterised, including by X-ray diffraction [9,22].

3.3. Physical properties

All the data are listed in Table 1.

3.3.1. Thermal decomposition

Although the thermal behaviour of a molecule is closely related to its molecular structure (ligand vs. complex, nature of the metal centre and/or the N-substituent), its decomposition is difficult to predict (endothermic vs. exothermic process and/or sharpness of the peaks).

Measurements on the organic dyes **2**, **6**, **8** and **9** showed a thermal decomposition at lower temperatures than required for optical recording application (>200 °C). In contrast, the presence of a metal centre such as Zn in complex **13** led to a much better thermal stability than that of its corresponding organic ligand **6** (melting at 210 vs. 191 °C) (Table 1). However, although the temperature was above 200 °C for **13**, its decomposition is not exothermic, as required, and occurs with melting (Fig. 1). We also examined the thermal properties of the analogous nickel and copper complexes (**12** and **14**) to study the influence of the metal centre on thermal stability. Although **12** presents the highest melting temperature (249 °C, see Table 1), only **14** revealed upon decomposition under nitrogen atmosphere an exothermic reaction above 200 °C, which is a key point for this type of application (Fig. 1). Therefore, we decided to focus on the synthesis of copper complexes.

Table 1
Physical properties

Compound	λ_{\max} (nm)	ϵ (l/mol cm)	Decomp. temp. (°C)	HR (w/g)	Filterability
2	340	31500	213(m)	<i>m</i> *	C
3	–	–	–	–	Insoluble
4	–	–	–	–	Insoluble
5	–	–	–	–	Insoluble
6	348	13500	191(md)	0.5	B
8	350	59000	167(m)	<i>m</i>	A
9	348	29000	145(m)	<i>m</i>	A
12	363	67000	249(m)	<i>m</i>	C
13	335	33000	210(m)	<i>m</i>	A
14	347	55000	231(d)	2	A
15	351	55000	207(d)	1	A
16	349	55000	222(d)	2	A
17	365	54000	221(d)	0.5	C
18	372	60000	231(d)	2.8	A
19	371	69000	215(d)	1.7	A

*m**: melting without decomposition.

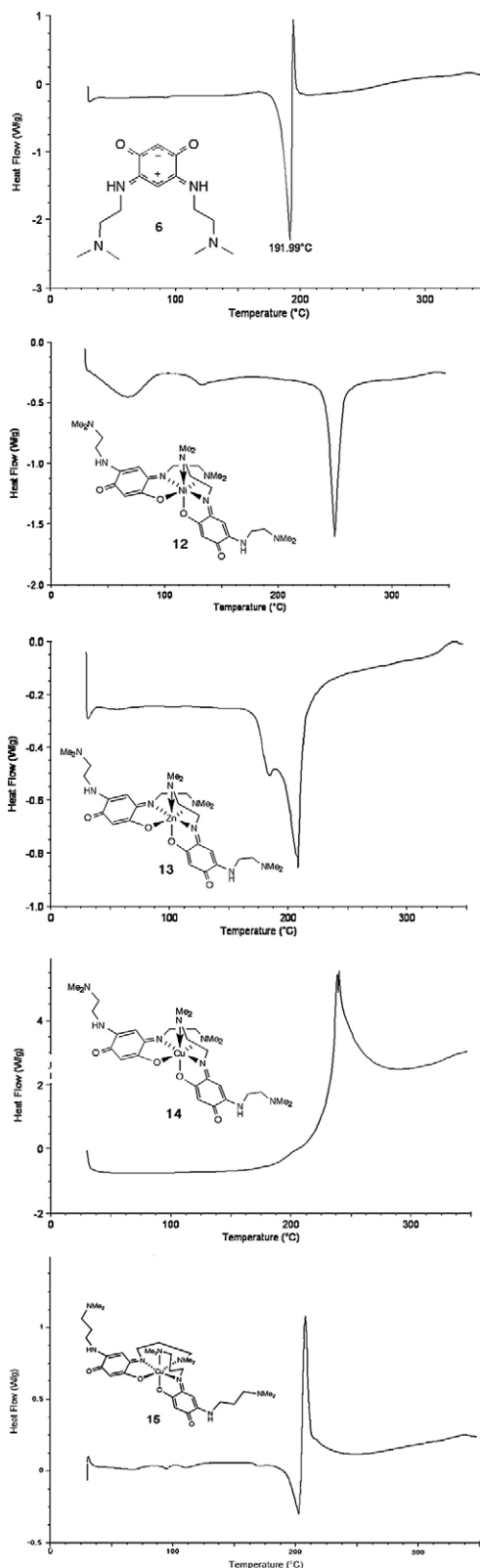


Fig. 1. Thermal decomposition of ligand **6** and complexes **12**–**15**.

Consistent with the data for **14**, compounds **15–19** revealed also an exothermic thermal decomposition at temperatures above 200 °C, which make them good candidates for optical recording (Table 1). Interestingly, the presence of a longer coordination side arm, as in **15** compared to **14** (one more CH₂ group), led to a sharper decomposition which makes it a better candidate, although this decomposition occurs at a lower temperature (207 vs. 231 °C for **15** and **14**, respectively) (Fig. 1).

3.3.2. Solubility

Dyes used for recordable compact discs or DVDs are generally applied as solutions by spin-coating on an injected polycarbonate substrate. The preferred solvent for a smooth application (homogeneous groove filling) is 2,2,3,3-tetrafluoropropanol (TFP). When this solvent is evaporated at high rotation speed, only a thin layer of dye remains on the polymer. Non-soluble crystals or solid impurities are usually eliminated by a pre-filtering system on industrial manufacturing lines, causing then the interruption of the production flow. For this reason, a control of solubility as well as of filterability of all the dyes synthesised must be effected. The square planar compounds **3–5** were *insoluble* in TFP. In contrast, all octahedral complexes (owing to the presence of coordinating arms) were *soluble*. Inorganic dyes **13–16**, **18** and **19**, and ligand **8** and **9** revealed the highest solubility and the best filterability (class A, Table 1).

3.3.3. Absorption

Except for **2** and **13**, all the complexes and organic dyes showed an absorption maximum very close to the required range (350–450 nm) for potential blue ray optical application (Table 1). Interestingly, the presence of a metal centre does not strongly modify the absorption by comparison with the free ligand.

4. Conclusion

We have prepared novel copper complexes for potential application in optical recording. The following key parameters have been identified: (i) the presence of additional coordinating arms on the quinonoid ligand leads to octahedral complexes with increased solubility, (ii) the presence of Cu(II) as a metal centre leads to a favourable exothermic thermal behaviour, (iii) the presence of quinonoid moieties results in the optical absorption to be in the desired range. A comparison of the data for such dyes revealed that complexes **14–**

16, **18** and **19** are the best candidates. They are currently under investigations for the preparation of thin films in the blue laser technology.

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