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Mononuclear and dinuclear heteroleptic Cu(I) complexes based on pyridyl-triazole and DPEPhos with long-lived excited-state lifetimes

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ABSTRACT

A mononuclear and two dinuclear heteroleptic Cu(I) complexes have been successfully prepared, using the chelating bis [(2-diphenylphosphino)phenyl] ether (DPEPhos) and pyrid-2′-yl-*1H*-1,2,3-triazole as $N^{\wedge}N$ chelating ligands. They show good luminescence in solution at room temperature with long-lived excited states. Furthermore, bimolecular quenching experiments of these new complexes with the catalyst Ni(cyclam)Cl$_2$ encourage the use of such compounds as photosensitizers for the photoreduction of carbon dioxide.

1. Introduction

Nowadays the reduced availability of materials and their recyclability are raising enormous interest in the research community. Furthermore, the exploitation of environmentally sustainable – so called ‘*green*’ – resources has become very important. Light can be considered a ‘green’ reagent; definitely when it comes directly from the sun, but also if it comes from artificial sources. Photons are ‘green’ in view of the fact that they do not leave any waste products [1].

The development of molecules that can absorb electromagnetic radiation to deliver a certain function is thus a central research question. In particular, photosensitizers based on organometallic complexes [2] have shown promising results in diverse catalytic reactions [3–6] as well as in solar energy conversion [7–9]. Copper(I) complexes represent an appealing alternative to expensive photosensitizers based on ruthenium (II), iridium (III) or rhenium(I) [10,11]. In fact, copper is more abundant in the earth's crust and is therefore cheaper. Moreover, Cu(I) complexes are of easy preparation. Being a *d10* nucleus, metal centred electronic transitions cannot occur and the excited state of a copper(I) complex is normally a metal-to-ligand charge-transfer state (MLCT). Nevertheless, in the excited state they suffer from a Jahn–Teller flattening distortion from the pseudo-tetrahedral geometry in the ground state, which allows Lewis bases to form adducts and to deactivate the excited state of the copper(I) complex [12,13]. Steric hindrance imposed by the ligands in the coordination sphere avoids this distortion to a certain extent and therefore increases the excited state lifetime and the photoluminescence quantum yield. Lability of the ligands might also complicate the development of such compounds. In fact it has been found that heteroleptic Cu($P^{\wedge}P$) ($N^{\wedge}N$) complexes, where $P^{\wedge}P$ is a chelating diphosphine and $N^{\wedge}N$ is a 1,10-phenanthroline derivative, undergo an exchange of ligands in solution, affording homoleptic Cu($N^{\wedge}N$)$_2$ and Cu($P^{\wedge}P$)$_2$ complexes, which are more favoured [14]. In the solid state, these drawbacks are somehow limited and the utilisation of Cu(I) complexes in light-emitting devices (OLEDs or LEECs) has attracted a strong interest [15–18]. The pioneering work of Sauvage and co-workers with Cu(dap)$_2$Cl [19] as photoredox catalyst was published in 1987 [20], but apart from some contemporary publications [21], only recently have Cu(I) complexes been applied as photoredox catalysts or photosensitizers (PS) [22–32]. In artificial photosynthesis [33,34] the photosensitizer absorbs the luminous radiation and transfers

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the energy to a catalyst, which then activates the small molecule (usually either water or carbon dioxide). The characteristics that a PS should have are the following: good absorption in the visible light region, long-lived excited state, and high stability. There are still very few Cu(I)-based PS applied to artificial photosynthesis; nevertheless, they are quite promising [35–40]. We are interested in the development of new PS based on copper(I), which can be used in the homogeneous reduction of CO_2. In this work three heteroleptic Cu(I) coordination compounds based on pyrid-2′-yl-*1H*-1,2,3-triazole ligand and bis [(2-diphenylphosphino)phenyl] ether (DPEPhos) are presented. The dinuclear complexes have been prepared using the pyrid-2′-yl-*1H*-1,2,3-triazole as chelating unit, as in mononuclear complex **1H**, bridged by a phenyl ring, substituted in *meta* (**2H**) or in *para* (**3H**) positions. A methyl group *alpha* to the nitrogen atom of the pyridine increases the steric hindrance in the excited state, allowing an increase in the quantum yield in solution of such complexes. In the dinuclear complexes **2H** and **3H**, this effect is more pronounced. The long lifetime of the excited states and their good emission in solution make these complexes very appealing for application as PSs. As a preliminary test, a Stern–Volmer bimolecular quenching experiment was conducted with the three complexes and Ni(cyclam)Cl_2 [41], a known catalyst in the reduction of CO_2 [42].

2. Experimental section

2.1. General information and materials

The starting materials were purchased from commercial suppliers and used without further purification. Solvents for synthesis were purified according standard procedure, if necessary. Dichloromethane was dried over CaH_2 and freshly distilled before each reaction. All air- and water-sensitive experiments were carried out in standard glassware under an inert Ar atmosphere, using standard vacuum line techniques. Tetrakis (acetonitrile)copper(I) tetrafluoroborate was synthesized according to literature procedures.

Warning! Azides and nitrogen-rich compounds can be explosive. Handle with care!

^1H NMR (300 MHz, 500 MHz) and $^{13}C\{H\}$ NMR (150 MHz) spectra were recorded with a Bruker Avance III spectrometers operating at 298 K in the Fourier transform mode. Chemical shifts are reported in δ units (ppm) using residual $CHCl_3$ (^1H δ 7.26 ppm, ^{13}C δ 77.00) as reference.

2.2. Synthesis

2.2.1. Ligand 1

(a) *Synthesis 6-methyl-2-phenylethynyl-pyridine*. Under Argon atmosphere, in 20 ml of dry diisopropylamine the reagents were dissolved as following: 2-bromo-6-methylpyridine (1.0 ml, 1.511 g, 8.7 mmol); ethynylbenzene (0.96 ml, 0.897 g, 8.5 mmol). Then the catalyst $Pd(PPh_3)Cl_2$ (62.2 mg, 0.089 mmol) and the co-catalyst CuI (40.0 mg, 0. 21 mmol) were added. The reaction was heated to 80 °C until the starting materials are not present anymore in the reaction mixture (almost after 4 h). A white precipitate was filtered out and the solvent was removed under reduced pressure. The residue was purified by column chromatography in silica gel. Eluent was CH_2Cl_2:C_6H_{12} (50:50). The product is yellow oil. Yield: 1.2 g (71.3%). ^1H NMR (300 MHz, 298 K,$CDCl_3$) δ: 7.60–7.55 (m, 2H), 7.51 (d, 1H), 7.36–7.28 (m, 4H), 7.07 (d, 1H), 2.56 (s, 3H).

(b) *Synthesis 5-(6′methyl-pyrid-2′-yl)-4-phenyl-1H-1,2,3-triazole.* In 25 ml of dry N,N-dimethylformamide, 6-methyl-2-phenylethynyl-pyridine (1.2 g, 6.2 mmol) was dissolved. Trimethylsilylazide was added (2.5 ml, 2.17 g, 19 mmol) was added and the reaction temperature was set to 110 °C. Trimethylsilylazide was added more than once, so that in total other 20 mmol were added. The reaction stirred for 2 days. The solvent was removed by reduced pressure. The residue was purified by column chromatography in silica with CH_2Cl_2:CH_3OH (98:2) as eluent. A sticky very viscous orange oil was obtained. Yield: 1.105 g, (75%). ^1H NMR (300 MHz, 298 K,$CDCl_3$) δ: 7.68–7.64 (m, 2H); 7.54 (t, *J*=7.7 Hz, 1H), 7.38 (m, 4H), 7.12 (d, *J*=7.6 Hz, 1H); 2.56 (s, 3H).

2.2.2. Ligand L2

(a) *-Synthesis meta-bis((6‘-methyl-pyrid-2‘-yl)ethynyl)benzene.* Under Argon atmosphere, in 25 ml of dry diisopropylamine the reagents were dissolved as following: 2-bromo-6-methylpyridine (0.45 ml, 0.678 g, 4.0 mmol); 1,3-diethynylbenzene (0.24 ml, 0.228 g, 1.8 mmol). Then the catalyst $Pd(PPh_3)Cl_2$ (12 mg, 0.017 mmol) and the co-catalyst CuI (5.2 mg, 0.027 mmol) were added. The reaction was heated to 80 °C until the starting materials are not present anymore in the reaction mixture (almost after 6 h). Solvent was removed under reduced pressure. The residue was dissolved in CH_2Cl_2 and washed with water. The aqueous phases were extracted with 3 × 10 ml DCM. The organic phases were washed with brine and dried over Na_2SO_4. The residue solvent was removed and the product was purified by column chromatography in silica gel. Eluent was CH_2Cl_2:CH_3OH (99:1). Yield: 0.480 g (88%). ^1H NMR (300 MHz, 298 K,$CDCl_3$) δ: 7.819 (s, 1H), 7.59 (m, 4H), 7.36 (d, *J*=7.8 Hz, 3H), 7.14 (d, *J*=7.8 Hz,2H), 2.60 (s, 6H).

(b) *-Synthesis meta-bis(5’-(6’‘-methyl-pyrid-2’‘-yl)1H-1,2,3-triazol-4’-yl)benzene.* In 10 ml of N,N-dimethylformamide, *meta*-bis((6‘-methyl-pyrid-2‘-yl)ethynyl)benzene (0.420 g, 1.36 mmol) was dissolved. Trimethylsilylazide (0.73 ml, 0.633 g, 5.5 mmol) was added and the reaction temperature was set to 110 °C. The reaction stirred for 1 day. The solvent was removed by reduced pressure. The residue was purified by column chromatography in silica with CH_2Cl_2:CH_3OH (98:2) as eluent. Yield: 170 mg, (32%). ^1H NMR (300 MHz, 298 K,$CDCl_3$) δ: 7.97 (s, 1H); 7.57 (m, 4H), 7.45 (d, *J*=7.8 Hz, 2H), 7.10 (d, *J*=7.6 Hz, 2H); 2.52 (s, 6H).

2.2.3. Ligand L3

(a) *-Synthesis para-bis((6‘-methyl-pyrid-2‘-yl)ethynyl)benzene.* Under Argon atmosphere, in 10 ml of dry diisopropylamine the reagents were dissolved as following: 2-bromo-6-methylpyridine (99 µl, 0.15 g, 0.89 mmol); 1,4-diethynylbenzene (0.056 g, 0.44 mmol). Then the catalyst $Pd(PPh_3)Cl_2$ (2.3 mg, 0.003 mmol) and the co-catalyst CuI (5.1 mg, 0.027 mmol) were added. The reaction was heated to 80 °C until the starting materials are not present anymore in the reaction mixture (almost after 6 h). Solvent was removed under reduced pressure. The residue was dissolved in CH2Cl2 and the not soluble fraction was filtered out. The solution was recrystrallized by slow evaporation of the solvent. Yield: 0.32 g (72.7%). ^1H NMR (300 MHz, 298 K,$CDCl_3$) δ: 7.56 (m, 6H); 7.35 (d, 2H); 7.12 (d, 2H); 2.58 (s, 6H).