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Exploring the Optical and Electrochemical Properties of Homoleptic versus Heteroleptic Diimine Copper(I) Complexes

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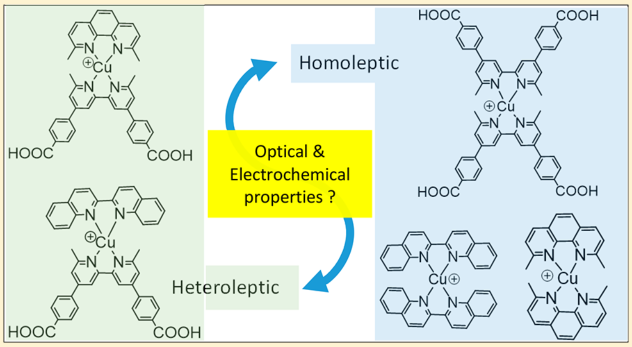

ABSTRACT: Due to ligand scrambling, the synthesis and investigation of the properties of heteroleptic Cu(I) complexes can be a challenging task. In this work, we have studied the optical and electrochemical properties of a series of homoleptic complexes, such as $[Cu(dbda)_2]^+$, $[Cu(dmp)_2]^+$, $[Cu(Br\text{-}dmp)_2]^+$, $[Cu(bcp)_2]^+$, $[Cu(dsbtmp)_2]^+$, $[Cu(biq)_2]^+$, and $[Cu(dap)_2]^+$ in solution, and those of their heteroleptics $[Cu(dbda)(dmp)]^+$, $[Cu(dbda)(Br\text{-}dmp)]^+$, $[Cu(dbda)(bcp)]^+$, $[Cu(dbda)(dsbtmp)]^+$, $[Cu(dbda)(biq)]^+$, $[Cu(dbda)(dap)]^+$ adsorbed on the surface of anatase TiO_2 (dbda = 6,6′-dimethyl-2,2′-bipyridine-4,4′-dibenzoic acid; dmp = 2,9-dimethyl-1,10-phenanthroline; Br-dmp = 5-bromo-2,9-dimethyl-1,10-phenanthroline; bcp = bathocuproine or 2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline; dsbtmp = 2,9-di(*sec*-butyl)-3,4,7,8-tetramethyl-1,10-phenanthroline; biq = 2,2′-biquinoline; dap = 2,9-dianisyl-1,10-phenanthroline). We show that the maximum absorption wavelengths of the heteroleptic complexes on TiO_2 can be reasonably predicted from those of the homoleptic complexes in solution through a simple linear relation, whereas the prediction of their redox properties is less trivial. In the latter case, two different linear patterns emerge: one including the ligands bcp, biq, and dap and another one including the ligands dmp, Br-dmp, and dsbtmp. We offer an interpretation of the data based on the chemical structure of the ligands. On one hand, ligands bcp, biq, and dap possess a more extended π-conjugated system, which gives a more prominent contribution to the overall redox properties of the ligand dbda. On the other hand, the ligands dmp, Br-dmp, and dsbtmp are all phenanthroline-based containing alkyl substituents and contribute less than dbda to the overall redox properties.

INTRODUCTION

Copper(I) coordination complexes with diimine ligands have been extensively studied due to their interesting and peculiar electrochemical and photochemical properties.[1,2] Cu(I) complexes bearing sterically hindered ligands, such as 2,9-substituted 1,10-phenanthroline and 6,6′-substituted 2,2′-bipyridine experience a geometric strain upon oxidation that destabilizes the Cu(II) state. The strain originates from the attempt to move from a pseudotetrahedral geometry, characteristic of Cu(I) coordination complexes, to a flattened square-planar geometry, typical of Cu(II) complexes. As a consequence, the redox potentials of such strained complexes can differ quite significantly from their equivalents made from unsubstituted ligands, which do not experience any strain upon oxidation and easily relax to a flattened geometry.[3,4] Another interesting feature of Cu(I) diimine complexes is their strong absorption of visible light that arises from metal-to-ligand charge transfer (MLCT), d−π^*, electronic transitions. This aspect and the possibility of having long-lived excited states[5−8] are peculiar properties that strongly resemble those of Ru(II) polypyridine complexes. For this reason, Cu(I) diimine complexes have been often regarded as a viable replacement of the latter.[9,6,10] Another well-known characteristic of the discussed Cu(I) complexes is their lability, which is due to a dynamic and reversible ligand association−dissociation mechanism.[8,11] In general, bis- and trisphenanthroline metal complexes have been limited to the general homoleptic

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structure [M(L′)$_n$] (e.g., for Cu(I), Fe(II), Fe(III)) because of rapid ligand exchange processes.[12] Only in the case of Ru(II,III) is the combination of different phenanthroline ligands L in mixed (heteroleptic) complexes [Ru(L′)$_2$(L′′)]$^{2+/3+}$ and [Ru(L′)(L′′)(L′′′)]$^{2+/3+}$ known because their exchange kinetics are slow.[13] This makes the synthesis and study of the properties of heteroleptic complexes, in particular, of Cu(I), very challenging. Jean-Pierre Sauvage, Nobel laureate in Chemistry 2016, introduced and extensively studied stable Cu(I) complexes based on catenate ligands: interlocked ring systems completely suppressing ligand scrambling.[14,15] Nevertheless, homoleptic and heteroleptic Cu(I) complexes based on catenate ligands are difficult to synthesize and to purify. A second approach to the synthesis of stable heteroleptic Cu(I) complexes relies on the use of particularly bulky ligands, which are too sterically hindered to form the corresponding homoleptic Cu(I) complexes, thus pushing the equilibrium in favor of the heteroleptic complex. Based on this strategy, mixed 1,10-phenanthroline derivatives and the bulky phosphine ligand POP (POP = bis[2-(diphenylphosphino)phenyl]ether) Cu(I) complexes have been synthesized.[16,17] Diimine ligands with particularly bulky substituents used for the same purpose were first introduced by Schmittel and colleagues,[18] and the strategy successfully led to the preparation of several heteroleptic Cu(I) complexes.[12,5,19,20] However, the requirement of sterically hindered ligands poses some limitations on the design of heteroleptic complexes that can be studied. An elegant alternative, which allows for more structural variety, is the realization of surface-immobilized heteroleptic Cu(I) complexes, was adopted by Housecroft and Constable.[21,22] Their approach consists of a stepwise, on-surface assembly of [Cu(L′)(L′′)]$^+$ complexes by soaking a TiO_2 substrate in a solution of L′ and then in a solution containing either [Cu(L′′)$_2$]$^+$ or a mixture of [Cu(NCCH$_3$)$_4$]$^+$ and L′′.[23,24] The method relies on ligand exchange between the surface-anchored L′ and [Cu(L′′)$_2$]$^+$ for the formation of the desired heteroleptic complex. The technique has led to the preparation of a substantial number of heteroleptic Cu(I) complexes, which for their absorption and electrochemical properties have been employed as light absorbers, or dyes, in dye-sensitized solar cells (DSSCs).[25,26] The performances of Cu(I) dyes in DSSCs have been promising and have attracted significant attention in the photovoltaic field, inspiring other research groups to further investigate the topic.[27−29] In addition, Cu(I) diimine complexes are being investigated not only as dyes but also as hole-transporting materials and redox mediators in DSSCs.[30−33] In this work, by using the approach of Housecroft and Constable, a series of heteroleptic Cu(I) complexes were assembled on the surface of TiO_2, and their optical and electrochemical properties, together with those of the corresponding homoleptic complexes, were systematically studied. Although ruthenium(II) diimine coordination complexes have been extensively studied in DSSC, the use of copper(I) complexes is relatively recent.[13,22] The goal of the present work is to provide a rationale of the correlation between the properties of the homoleptic and heteroleptic complexes and investigate the suitability of the latter as dyes and charge-transporting media for DSSCs.

■ EXPERIMENTAL SECTION

General. All chemicals were purchased from Sigma-Aldrich and used as received unless noted otherwise. NMR spectra were recorded with a Bruker DRX 400 NMR or a Bruker DRX 500 NMR spectrometer operating at 400 and 500 MHz with respect to the ^{1}H nucleus, respectively. Chemical shifts were referenced to the residual solvent peak ($CHCl_3$ δ: 7.26 ppm for ^{1}H NMR and 77.16 ppm for ^{13}C NMR; CH_3CN δ: 1.94 ppm for ^{1}H NMR and 1.32 ppm for ^{13}C NMR). Coupling constants are given in hertz.

Synthesis of the Homoleptic Cu(I) Complexes. [Cu(dmp)$_2$]PF$_6$ was synthesized according to a previously reported procedure.[11] The dsbtmp ligand and the corresponding [Cu(dsbtmp)$_2$]PF$_6$ complex were prepared according to McCusker et al.[10] The [Cu(dap)$_2$]Cl complex was purchased from Sigma-Aldrich and used without further purification. The dbda ligand was synthesized according to the procedure reported by Colombo et al.[34] The Br-dmp ligand was synthesized according to Eggert et al.[35]

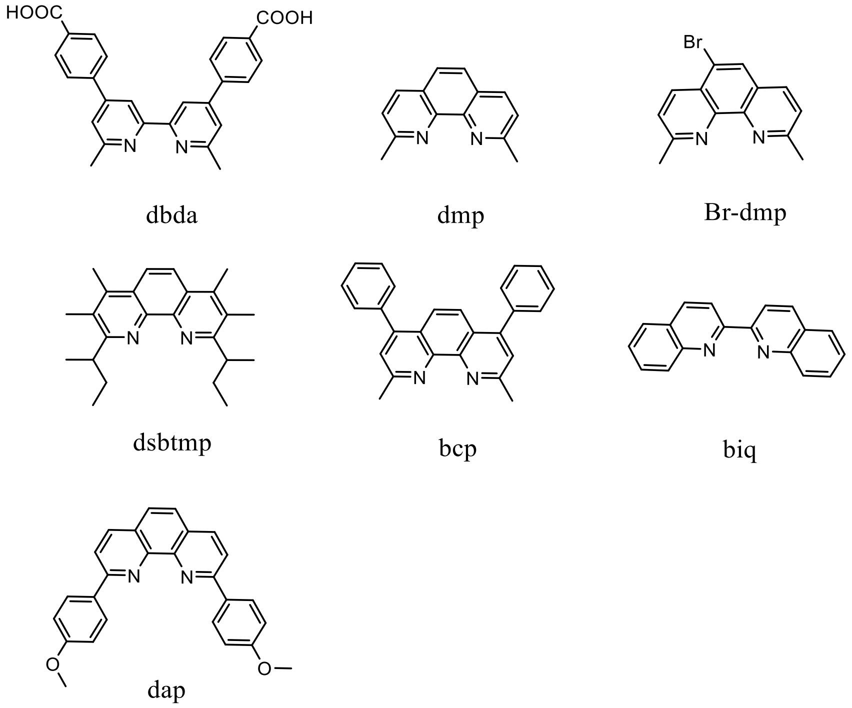
[Cu(biq)$_2$]TFSI Complex. A solution of copper(I) chloride (0.194 g, 1.96 mmol, 1.00 equiv) and 2,2′-biquinoline (1.505 g, 5.88 mmol, 3 equiv) in 50 mL of ethanol was stirred for 16 h at room temperature and under a nitrogen atmosphere. After complexation, 5.625 g of Li bis(trifluoromethanesulfonyl)imide (19.6 mmol, 10 equiv, LiTFSI) was added for counterion exchange. Further, the product was precipitated in water, filtered, and dried under reduced pressure. The resulting Cu(I) 2,2-biquinoline TFSI complex (Cu(biq)$_2$TFSI) was collected as a purple powder (1.525 g, 1.78 mmol; yield 91%).

[Cu(Br-dmp)$_2$]PF$_6$ Complex. In a round-bottomed flask, 5-bromo-2,9-dimethyl-1,10-phenanthroline (106 mg, 0.375 mmol) was dissolved in 2 mL of ethanol. A solution of Cu(CH$_3$CN)$_4$PF$_6$ (69 mg, 0.185 mmol) in acetonitrile (2 mL) was added to the reaction flask under strong stirring. The solution rapidly turned red and a precipitate started to form. The mixture was stirred for 30 min at room temperature, and then the solvent was removed under reduced pressure at 30 °C. The precipitate was dissolved in 1 mL of acetonitrile and moved to a centrifuge tube. The complex was precipitated by adding 30 mL of ethanol, and the precipitate was isolated as a dark red powder by being centrifuged at 5000*g* for 5 min. The complex was then dried under reduced pressure (126 mg, 0.165 mmol; yield 87%). ^{1}H NMR (CD_3CN, 500 MHz) δ: 8.82 (d, *J* = 8.2 Hz, 1H), 8.51 (d, *J* = 8.2 Hz, 1H), 8.46 (s, 1H), 7.92 (d, *J* = 8.0 Hz, 1H), 7.83 (d, *J* = 8.0 Hz, 1H), 2.41 (s, 3H), 2.39 (s, 3H) ppm. ^{13}C NMR (CD_3CN, 126 MHz) δ: 160.25 (s), 159.89 (s), 144.60 (s), 143.51 (s), 137.65 (s), 137.40 (s), 137.09 (s), 130.15 (s), 128.98 (s), 128.19 (s), 127.91 (s), 127.48 (s), 127.38 (s), 120.56 (s), 26.18 (s), 25.91 (s) ppm.

[Cu(bcp)$_2$]NO$_3$ Complex. The complex was synthesized from the preparation of [Cu(bcp)$_2$](NO$_3$)$_2$ and its subsequent reduction by L-ascorbic acid. In a round-bottomed flask, Cu(NO$_3$)$_2$·3H$_2$O (200 mg, 0.828 mmol) was dissolved in acetone (15 mL). Under stirring, a solution of bathocuproine (625 mg, 1.73 mmol) in dichloromethane (30 mL) was added to the reaction flask. The solution rapidly turned green, and a precipitate started to form. After a few seconds, while the solution was still green, 100 mL of diethyl ether was poured into the flask. The green precipitate formed was isolated by vacuum filtration and dried under reduced pressure (642 mg, 0.754 mmol; yield 90%). In a round-bottomed flask, the [Cu(bcp)$_2$](NO$_3$)$_2$ complex (350 mg, 0.411 mmol) was dissolved in acetonitrile (20 mL). To this was added an ethanol/water (1:1 volume ratio, 10 mL) solution of L-ascorbic acid (large excess), and the reaction solution turned red. The reaction was left stirring for 10 min. Subsequently, ethanol and acetonitrile were removed through rotary evaporation. Dichloromethane was added (30 mL), and the organic phase was extracted three times with water to remove any residue of L-ascorbic acid. The organic phase was then collected, dried with Na_2SO_4, and filtered before removal of the solvent by evaporation. The desired product was obtained as a dark red/brown powder (309 mg, 0.391 mmol; yield 95%). ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 8.05 (s, 4H), 7.76 (s, 4H), 7.55−7.65 (m, 20H), 2.61 (s, 12H) ppm.[36]

UV−Vis Absorption Spectroscopy. UV−visible absorption spectra were recorded using a double-beam UV−visible Cary 300 spectrophotometer. For the measurement of the absorption profiles of the homoleptic complexes and for the evaluation of the molar extinction coefficients, quartz (SUPRASIL) cuvettes were used.

Scheme 1. Ligands Employed for the Realization of the Homoleptic and Heteroleptic Cu(I) Complexes in This Study: 6,6′-Dimethyl-2,2′-bipyridine-4,4′-dibenzoic acid (dbda), 2,9-Dimethyl-1,10-phenanthroline (dmp), 5-Bromo-2,9-dimethyl-1,10-phenanthroline (Br-dmp), 2,9-Di(*sec*-butyl)-3,4,7,8-tetramethyl-1,10-phenanthroline (dsbtmp), 2,9-Dimethyl-4,7-diphenyl-1,10-phenanthroline (bcp), 2,2′-Biquinoline (biq), and 2,9-Dianisyl-1,10-phenanthroline (dap)



dbda dmp Br-dmp

dsbtmp bcp biq

dap

Emission Spectroscopy. We assembled the heteroleptic complexes on the surface of ZrO_2 substrates prepared in the same way as described for the TiO_2 in order to check their emission properties. However, no detectable emission was recorded.

Electrochemical Characterization. The electrochemical investigation was performed in a three-electrode electrochemical cell with a platinum net as the counter electrode and $Ag/AgNO_3$ (10 mM/acetonitrile) as the reference electrode. For the electrochemical measurements of the homoleptic complexes in solution, a glassy carbon disk (Ø = 3 mm) was used as the working electrode. For the electrochemical measurements of the copper complexes on TiO_2, a fluorine-doped tin oxide (FTO)-coated glass (Pilkington TEC15) with a mesoporous TiO_2 layer (area = 1.0 cm × 1.5 cm), on which the desired complex was assembled, was used as the working electrode. The scan rate used for all of the measurements was 100 mV/s. The supporting electrolyte used was a 0.1 M $[(n\text{-Bu})_4N]PF_6$ solution in acetonitrile. The measurements were performed using an Ivium Technologies vertex potentiostat; ferrocene (Fc) was used as an internal standard, and the redox potentials were reported vs $Fc^{+/0}$.

TiO_2 Substrate Preparation. For the absorption spectra of the complexes adsorbed on TiO_2, plain microscope slides (VWR) were cleaned in an ultrasonic bath for 30 min with ethanol. After being cleaned and dried, a slide was masked with tape (Scotch Magic Tape 810 (3M)) to leave an active area of 1.0 cm × 2.0 cm, which was then doctor-bladed with a TiO_2 paste (GreatCell Solar, 18NR-T). The mask was then removed, and the doctor-bladed substrate was placed in a furnace (Nabertherm Controller P320) for sintering in air with the following temperature program: 25 min to 325 °C (kept for 15 min), 15 min to 500 °C (kept for 30 min). After being cooled, the substrates were used for the self-assembly of the Cu(I) complexes.

The same procedure was used for the preparation of the substrates for the electrochemical experiments but replacing the microscope slides with an FTO substrate (TEC15).

Film Thickness Characterization. Measurements of the thickness of TiO_2 layers were made by means of a profilometer (Veeco Dektak 150).

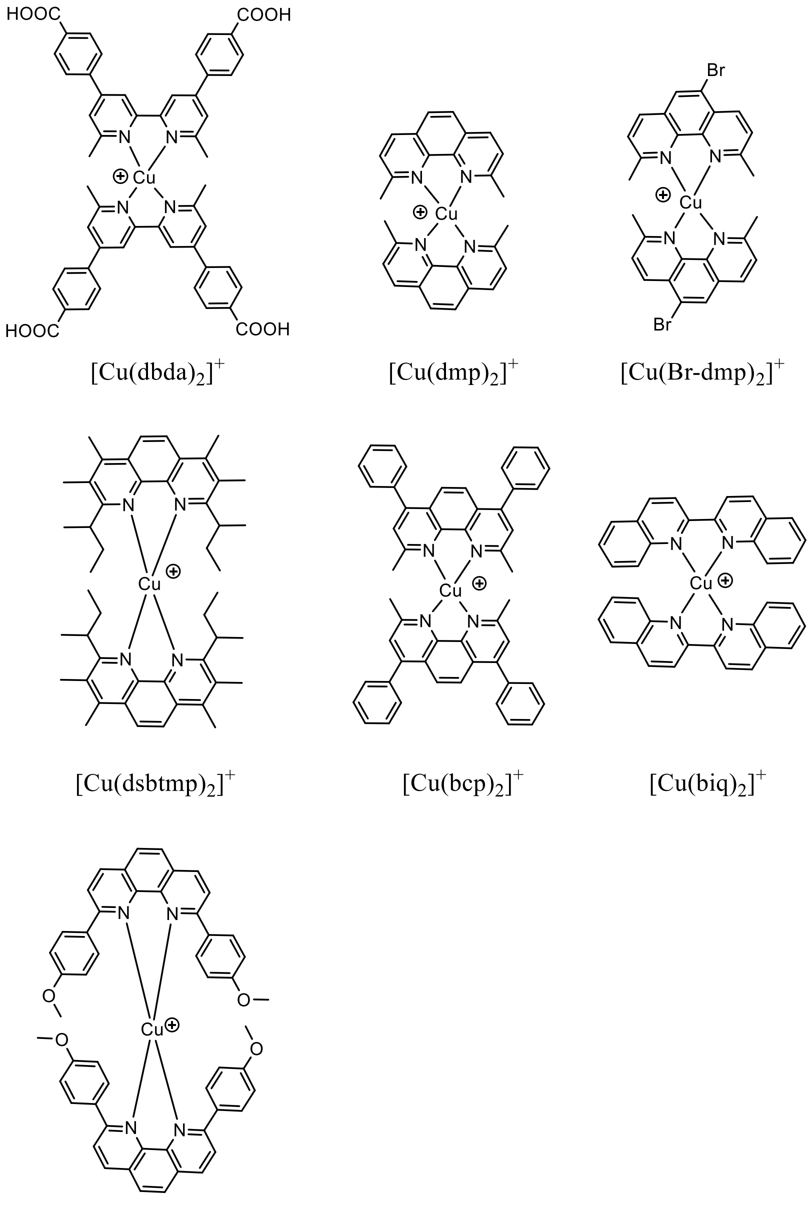
Self-Assembly of Complexes on TiO_2. The TiO_2 substrates (15 μm) were soaked in a 1.0 mM methanol solution of dbda for 24 h at room temperature. The electrodes were removed from the solution, washed with methanol, and dried with compressed air. The functionalized electrodes were then soaked at room temperature for 24 h in a 1 mM acetonitrile solution containing the desired homoleptic complexes $[Cu(dmp)_2]^+$, $[Cu(Br\text{-}dmp)_2]^+$, $[Cu(bcp)_2]^+$, $[Cu(dsbtmp)_2]^+$, $[Cu(biq)_2]^+$, and $[Cu(dap)_2]^+$ or in a methanol solution containing 1 mM $[Cu(CH_3CN)_4]PF_6$ and 2 mM dbda. The electrodes were finally removed from the solution and washed with acetonitrile.

■ RESULTS AND DISCUSSION

Scheme 1 displays the ligands used for the generation of homoleptic and heteroleptic complexes in this study.

The 2,2′-bipyridine derivative dbda was selected as the anchoring ligand as it is able to anchor to the surface of TiO_2 through the carboxylic acid moieties.[37,34] The ancillary ligands (dmp, Br-dmp, dsbtmp, bcp, biq, and dap) were chosen with the scope of having a reasonable variability of different steric, electronic, and redox properties deriving from the different types and positions of the substituents and from the flexibility of the structures. The 2,9-dimethyl-1,10-phenanthroline (dmp) ligand, or neocuproine, is one of the most basic and studied building blocks for the synthesis of sterically hindered copper(I) complexes due to the presence of methyl groups in the 2,9-positions of phenanthroline.[38−41] The 5-bromo-2,9-dimethyl-1,10-phenanthroline (Br-dmp) ligand is a simple variation of dmp having an electron-withdrawing substituent, bromine, in the 5-position on the phenanthroline core. The 2,9-di(*sec*-butyl)-3,4,7,8-tetramethyl-1,10-phenanthroline (dsbtmp) ligand was selected due to its ability to more efficiently screen the metal center from solvent interactions due to the bulky alkyl *sec*-butyl groups, rendering reversible

Scheme 2. Molecular Structures of the Homoleptic Cu(I) Complexes Investigated[a]



$[Cu(dbda)_2]^+$ $[Cu(dmp)_2]^+$ $[Cu(Br\text{-}dmp)_2]^+$

$[Cu(dsbtmp)_2]^+$ $[Cu(bcp)_2]^+$ $[Cu(biq)_2]^+$

$[Cu(dap)_2]^+$

[a] Note that the $[Cu(Br\text{-}dmp)_2]^+$ complex is obtained as a racemic mixture.

redox chemistry, as well as impressive thermodynamic and photochemical stability in solution.[10] The well-known bathocuproine (bcp) ligand was employed, as well, and it can be regarded as a slightly modified version of dmp in which additional phenyl groups are present in the 4,7-positions of the phenanthroline unit. The 2,2′-biquinoline framework (biq) was chosen in order to introduce a variation in terms of both electronic properties and geometric flexibility from the rest of the series, which is based on a rigid central phenanthroline building block.[42] Finally, we wanted to include a ligand with bulky aromatic substituents in the 2,9-positions of phenanthroline, and therefore, 2,9-dianisyl-1,10-phenanthroline (dap) was selected.[15]

Scheme 2 shows the homoleptic Cu(I) complex involved in this study.

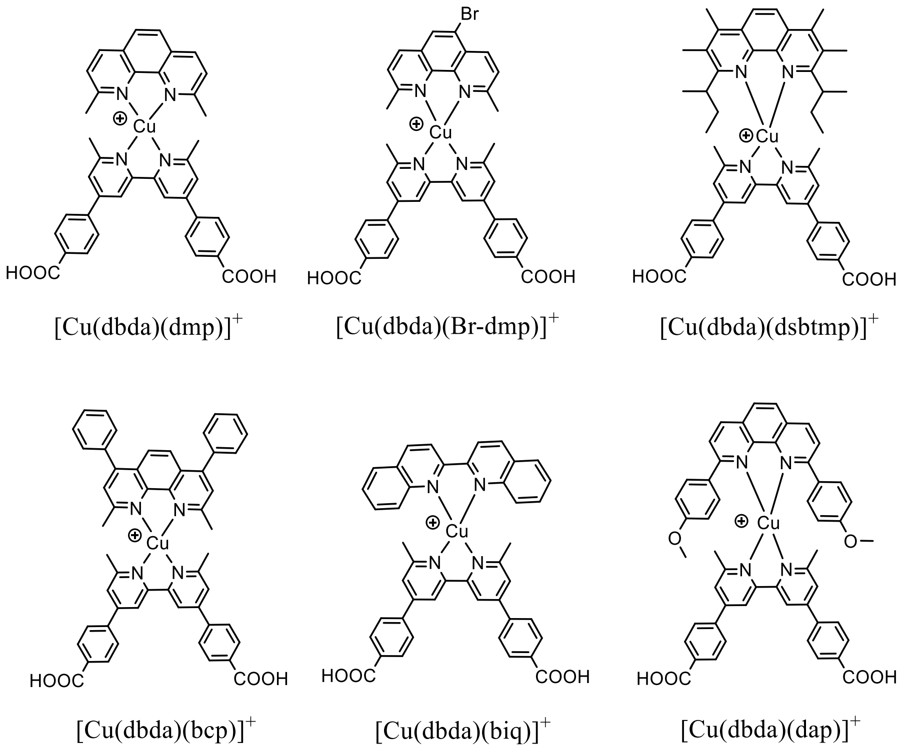
Scheme 3 displays the molecular structure of the heteroleptic Cu(I) complexes involved in this study.

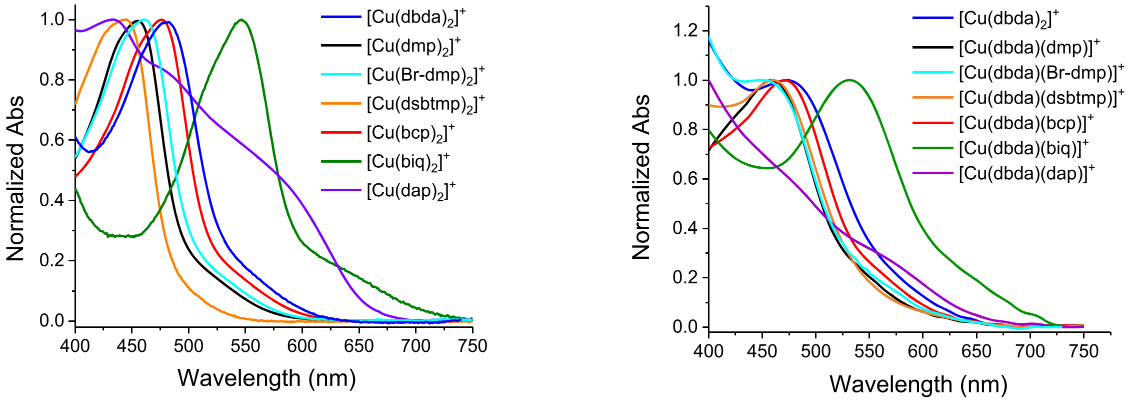
Due to the lability of the copper complexes, it is not possible to obtain the heteroleptic species displayed in Scheme 3 with a high degree of purity in solution. Indeed, ligand scrambling (eq 1) quickly leads to mixtures in which the heteroleptic complex and the two respective homoleptic complexes coexist in equilibrium in various amounts dependent on the kinetics and thermodynamic stability of the involved species.

$$2[Cu(L')(L'')]^+ \rightleftharpoons [Cu(L')_2]^+ + [Cu(L'')_2]^+ \qquad (1)$$

For this reason, the formation of the pure heteroleptic complexes was carried out by employing a surface-assembly technique previously described by Housecroft and Constable.[21,22,43] The method employs a substrate with a layer of a metal oxide, in our case, mesoporous anatase TiO_2, which is

Scheme 3. Molecular Structures of the Surface-Assembled Heteroleptic Cu(I) Complexes Investigated





(a) (b)

Figure 1. Normalized absorption spectra of the homoleptic Cu(I) complexes $[Cu(dmp)_2]^+$, $[Cu(Br\text{-}dmp)_2]^+$, $[Cu(dsbtmp)_2]^+$, $[Cu(bcp)_2]^+$, $[Cu(biq)_2]^+$, and $[Cu(dap)_2]^+$ in acetonitrile solution and $[Cu(dbda)_2]^+$ in methanol solution (a). Normalized absorption spectra of $[Cu(dbda)_2]^+$ and the heteroleptics complexes adsorbed on the surface of TiO_2 (b). Note: It is not possible to record the absorption spectrum of $[Cu(dbda)_2]^+$ in acetonitrile due to its low solubility.

first dipped into a solution of an anchoring ligand (dbda) and later into a solution of the selected homoleptic complex. During the first step, through its carboxylic moieties, dbda strongly binds to the surface of TiO_2, providing a coordination site for the formation of the heteroleptic complex, which, due to ligand exchange, forms at the immersion of the substrate into the homoleptic complex solution (eq 2).

$$TiO_2{:}L' + [Cu(L'')_2]^+ \leftrightharpoons TiO_2{:}[Cu(L')(L'')]^+ + L'' \tag{2}$$

By binding one ligand onto the TiO_2 surface, ligand scrambling (eq 1) is inhibited. However, this method implies that all investigation of the properties of the heteroleptic complexes must be carried out on the surface of TiO_2.

The optical properties of the homoleptic and heteroleptic copper complexes were investigated, and their UV−vis absorption spectra are shown in Figure 1.

Table 1 summarizes the optical parameters of the homoleptic and heteroleptic complexes.

Within the series of the homoleptic complexes in solution, we observe the following trend of the maximum absorption wavelength when going from lower to higher energies: $[Cu(biq)_2]^+$, $[Cu(dbda)_2]^+$, $[Cu(bcp)_2]^+$, $[Cu(Br\text{-}dmp)_2]^+$, $[Cu(dmp)_2]^+$, $[Cu(dsbtmp)_2]^+$, and $[Cu(dap)_2]^+$. The $[Cu(biq)_2]^+$ complex formed from a biquinoline ligand has the maximum absorption wavelength of its MLCT band, which perfectly matches the one reported in the literature,[42] and the

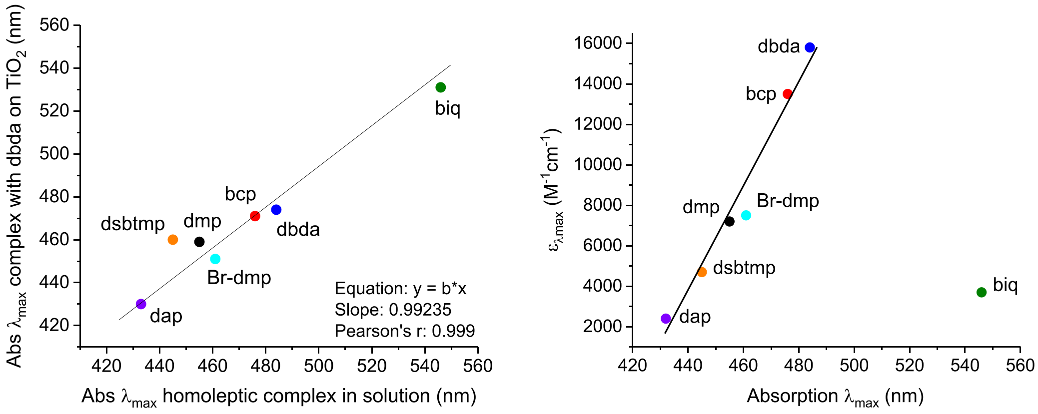
Table 1. Main Optical Parameters of the Cu(I) Complexes Investigated in Solution and on TiO_2

complex	λ_{max} abs (nm)	$\varepsilon_{\lambda_{max}}$ (M^{-1} cm^{-1})	E_{0-0} (eV)[f]
$[Cu(dbda)_2]^+(PF_6)^-$	484[a]	15800[a,d]	2.27
$[Cu(dmp)_2]^+(PF_6)^-$	455[b]	7200[b]	2.45
$[Cu(Br\text{-}dmp)_2]^+(PF_6)^-$	461[b]	7500[b]	2.43
$[Cu(dsbtmp)_2]^+(PF_6)^-$	445[b]	4700[b]	2.55
$[Cu(bcp)_2]^+(NO_3)^-$	476[b]	13500[b]	2.35
$[Cu(biq)_2]^+(TFSI)^-$	546[b]	3700[e]	2.07
$[Cu(dap)_2]^+(Cl)^-$	433[b]	2400[b]	1.88
$[Cu(dbda)_2]^+$ on TiO_2	474		2.15
$[Cu(dbda)(dmp)]^+$ on TiO_2	459		2.30
$[Cu(dbda)(Br\text{-}dmp)]^+$ on TiO_2	451		2.23
$[Cu(dbda)(dsbtmp)]^+$ on TiO_2	460		2.25
$[Cu(dbda)(bcp)]^+$ on TiO_2	471		2.25
$[Cu(dbda)(biq)]^+$ on TiO_2	531		1.95
$[Cu(dbda)(dap)]^+$ on TiO_2	430[c]		1.88

[a] In methanol. [b] In this work, measured in acetonitrile. [c] Predicted value according to the equation in Figure 3. [d] According to Colombo et al.[34] [e] According to Jahng et al., in acetonitrile.[42] [f] Calculated from the onset of the absorption spectrum.

absorption profile is substantially red-shifted compared to the other homoleptic complexes. The observed red shift is attributable to the extended conjugation of the 2,2′-biquinoline ligand compared to that of the bipyridine- or phenanthroline-based ligands.[28] Indeed, despite the single bond connecting the two quinoline units of the ligand, which could allow for structural distortion, dihedral angles in the crystal structure of the complex show that the ligands are extremely flat, thus indicating full conjugation.[44] The $[Cu(dbda)_2]^+$ and $[Cu(bcp)_2]^+$ complexes have ligands based on, respectively, a bipyridine and a phenanthroline core with aromatic substituents connected via single bonds, allowing for free rotation, thus partially disrupting the conjugated system and resulting in more blue-shifted absorption maxima. On the other hand, the $[Cu(Br\text{-}dmp)_2]^+$, $[Cu(dmp)_2]^+$, and $[Cu(dsbtmp)_2]^+$ complexes do not contain any aromatic substituent on the phenanthroline core, resulting in a further blue shift of the absorption maxima within the series. In particular, the absorption maximum of $[Cu(dsbtmp)_2]^+$ appears at higher energy than the one of $[Cu(Br\text{-}dmp)_2]^+$ and $[Cu(dmp)_2]^+$ due to a near-perfect tetrahedral ligand arrangement around the Cu(I) center in the ground state. The degree of steric restriction imposed by the *sec*-butyl substituents is high, and the complex undergoes a minimal distortion in the lowest energy triplet state.[10] The absorption spectra of $[Cu(dap)_2]^+$ has the most blue-shifted absorption maximum in the series, but an interesting aspect is the large width of the MLCT bands over the range of 400−650 nm. These features are characteristic of a system with 2,9-diaryl substituents, and the absorption spectrum therefore cannot be rationalized on the sole basis of the conjugation degree of the dap ligand.[45,46,30] The low-energy shoulder in the 550−600 nm range has been attributed to a molecular distortion of the complex from the ideal D_{2d} into an approximate C_2 symmetry, which is further distorted in comparison to the approximate D_2 geometry induced by the 2,9-dialkyl substituents.[47,48] The conclusion came from the work of McMillin and Sauvage, who have shown that the solid-state absorption spectrum of $[Cu(dpp)_2]^+$ (dpp = 2,9-diphenyl-1,10-phenanthroline) is essentially the same as the solution-state spectrum.[47,15,49] Finally, the HOMO−LUMO gap of the complexes in solution ranges from 1.88 eV of $[Cu(biq)_2]^+$ to 2.55 eV of $[Cu(dsbtmp)_2]^+$.

A first noticeable feature which characterizes all of the absorption spectra of the complexes adsorbed on TiO_2 with respect to those in solution is a broadening of the absorption band related to the MLCT transition. This phenomenon is well-known in the dye-sensitized solar cell field, which has for a long time studied dyes adsorbed on semiconductor surfaces.[50,51] This effect is manifested in the absorption spectra of the homoleptic complex $[Cu(dbda)_2]^+$ in solution and on TiO_2: although originating from the same compound, the absorption spectrum on the semiconductor surface is broader than the one recorded in solution. Moreover, the maximum absorption wavelength of $[Cu(dbda)_2]^+$ on TiO_2 is slightly blue-shifted compared to the maximum recorded in solution.



(a) (b)

Figure 2. Maximum absorption wavelengths of the homoleptic complexes in acetonitrile solution (abscissa) and of the corresponding complexes formed on the surface of TiO_2 with dbda as the anchoring ligand (ordinate) (a). Molar extinction coefficient measured in acetonitrile, at the maximum absorption wavelength ($\varepsilon_{\lambda_{max}}$), for the homoleptic complexes, as a function of the absorption λ_{max} itself (b). The point related to the dap ligand on the ordinate of graph (a) is a prediction based on the fitted linear model obtained from the rest of the data.

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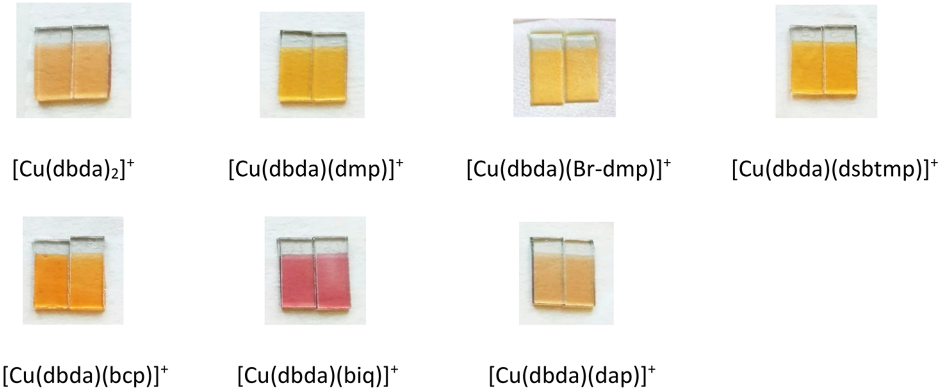


$[Cu(dbda)_2]^+$ $[Cu(dbda)(dmp)]^+$ $[Cu(dbda)(Br\text{-}dmp)]^+$ $[Cu(dbda)(dsbtmp)]^+$

$[Cu(dbda)(bcp)]^+$ $[Cu(dbda)(biq)]^+$ $[Cu(dbda)(dap)]^+$

Figure 3. Doctor-bladed TiO_2 substrates showing the colors of the self-assembled Cu(I) complexes investigated.

The difference can most likely be attributed to the different chemical environment experienced by the complex in solution in contrast to being adsorbed on TiO_2. Finally, it has been observed for a number of compounds that aggregation, that is, stacking of compound molecules not directly adsorbed on the surface of TiO_2, can cause spectral broadening and shifts toward either higher or lower energies.[52,53] When going from lower energy to higher energy, the maximum absorption wavelengths of the complexes on TiO_2 follow a similar trend as the homoleptic complexes in solution: $[Cu(dbda)(biq)]^+$, $[Cu(dbda)_2]^+$, $[Cu(dbda)(bcp)]^+$, $[Cu(dbda)(dmp)]^+ \approx [Cu(dbda)(dsbtmp)]^+$, $[Cu(dbda)(Br\text{-}dmp)]^+$, and $[Cu(dbda)(dap)]^+$. Once again, the complex involving the biq ligand, $[Cu(dbda)(biq)]^+$, shows an absorption profile which is considerably red-shifted compared to the rest of the series and that is closer to the maximum absorption wavelength of $[Cu(biq)_2]^+$ rather than that of $[Cu(dbda)_2]^+$. We can thus assume that the ligand biq has a dominant impact on the optical properties of the heteroleptic complex. Following the same trend observed for the homoleptic complexes in solution, $[Cu(dbda)_2]^+$ adsorbed on TiO_2 shows the second highest absorption wavelength. We also note that the absorption of the $[Cu(dbda)(bcp)]^+$ complex is only slightly blue-shifted compared to its corresponding homoleptic complexes in solution. When compared to their respective homoleptic complexes in solution, the $[Cu(dbda)(dmp)]^+$ and $[Cu(dbda)(dsbtmp)]^+$ complexes seem to display a contribution slightly higher than that of the phenanthroline ligands. In contrast to the trend observed for the homoleptic complexes in solution, the absorption maxima of $[Cu(dbda)(Br\text{-}dmp)]^+$ is located at higher energy with respect to those of $[Cu(dbda)(dmp)]^+$ and $[Cu(dbda)(dsbtmp)]^+$. The absorption spectrum of the complex $[Cu(dbda)(dap)]^+$ was difficult to analyze, as we cannot detect any marked transition in the range of 400−450, where we would expect to find the maximum absorption wavelength corresponding to the MLCT transition located at 433 nm in solution for $[Cu(dap)_2]^+$. However, considering the reduced steric hindrance around the Cu(I) center in $[Cu(dbda)(dap)]^+$ in contrast to $[Cu(dap)_2]^+$, the absorption profile of the first complex may differ considerably from the latter one.[54,31] Finally, the HOMO−LUMO gaps of the complexes adsorbed on TiO_2 ranges from 1.88 eV of $[Cu(biq)_2]^+$ to 2.30 eV of $[Cu(dbda)(dmp)]^+$.

Figure 2a shows the correlation between the maximum absorption wavelengths of the homoleptic and heteroleptic complexes. Figure 2b shows the molar extinction coefficient of the homoleptic complexes, calculated at the maximum absorption wavelength, as a function of the absorption maximum itself.

Interestingly, the distribution of the absorption wavelengths (Figure 2a) can be described with a linear pattern that allows us with reasonable accuracy to predict the maximum absorption wavelength of a hypothetical heteroleptic complex formed with dbda absorbed on the surface of TiO_2. In general, we expect the properties of the copper complexes under examination to be derived from two different contributions. The first one is the electronic contribution originating from the electron-withdrawing or -donating ability of the ligands. The second one is the geometrical contribution, which derives from the steric hindrance of the groups located around the metal center as well as the flexibility of the ligand. The fact that, despite the different ground-state geometries of the complexes studied, we can describe the data in Figure 2a with a linear equation suggests that the electronic properties dominate the maximum absorption wavelength. Interestingly, the molar extinction coefficient of the homoleptic complexes in solution shows a linear dependence to the maxima absorption wavelengths. The sole complex that does not follow the trend is $[Cu(biq)_2]^+$, which has a surprisingly low molar extinction coefficient.

Figure 3 shows a picture of the TiO_2 substrate with the self-assembled complexes in this study.

Subsequently, the redox behavior and properties of the homoleptic and heteroleptic complexes was investigated by cyclic voltammetry (CV) and differential pulse voltammetry (DPV). Figure 4 shows the CVs of the homoleptic complexes in solution.

All of the homoleptic complexes exhibit one distinctive quasi-reversible redox process ($\Delta E_p \sim 85$−90 mV), related to the oxidation of Cu(I) to Cu(II). Moving from more negative toward more positive potentials, the following order is found: $[Cu(dap)_2]^+$, $[Cu(bcp)_2]^+$, $[Cu(dmp)_2]^+$, $[Cu(Br\text{-}dmp)_2]^+$, $[Cu(biq)_2]^+$, and $[Cu(dsbtmp)_2]^+$. Table 2 summarizes the redox potentials estimated from the CVs in Figure 4.

The dap ligand possesses bulky anisyl substituents at the 2,9-positions of 1,10-phenanthroline which are, from a chemical perspective, the most reactive positions of the core. This implies that the electron-donating inductive effect on the phenanthroline unit is strong, thus making the homoleptic complex $[Cu(dap)_2]^+$ easier to oxidize with respect to the other complexes. Being located in the 4,7-positions of 1,10-phenanthroline, the phenyl groups of bcp do not have an electron-donating effect as strong as that of the anisyl groups in dap. Therefore, the homoleptic complex $[Cu(bcp)_2]^+$ is

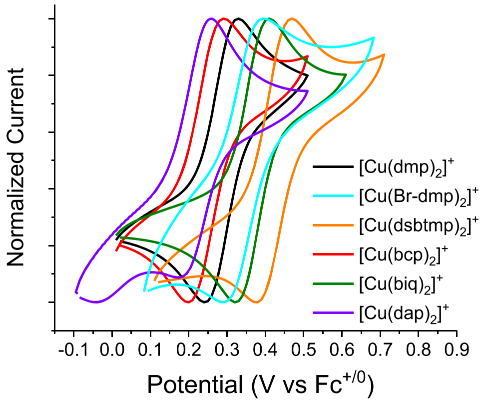


Figure 4. Cyclic voltammograms of the homoleptic Cu(I) complexes formed with the ligands dmp, Br-dmp, bcp, dsbtmp, biq, and dap in acetonitrile (0.1 M [(n-Bu)$_4$N]PF$_6$). All of the observed oxidative waves are quasi-reversible. It should be noted that, due to its very low solubility in acetonitrile, the CV of [Cu(dbda)$_2$]$^+$ in solution could not be obtained.

Table 2. Main Electrochemical Parameters Obtained from the CVs of the Homoleptic Complexes Investigated

complex	$E_{1/2}$ (V vs Fc$^{+/0}$)[a]	ΔE_p (mV)
[Cu(dmp)$_2$]$^+$(PF$_6$)$^-$	0.285	90
[Cu(Br-dmp)$_2$]$^+$(PF$_6$)$^-$	0.345	90
[Cu(dsbtmp)$_2$]$^+$(PF$_6$)$^-$	0.425	90
[Cu(bcp)$_2$]$^+$(NO$_3$)$^-$	0.245	90
[Cu(biq)$_2$]$^+$TFSI	0.365	90
[Cu(dap)$_2$]$^+$(Cl)$^-$	0.205	85

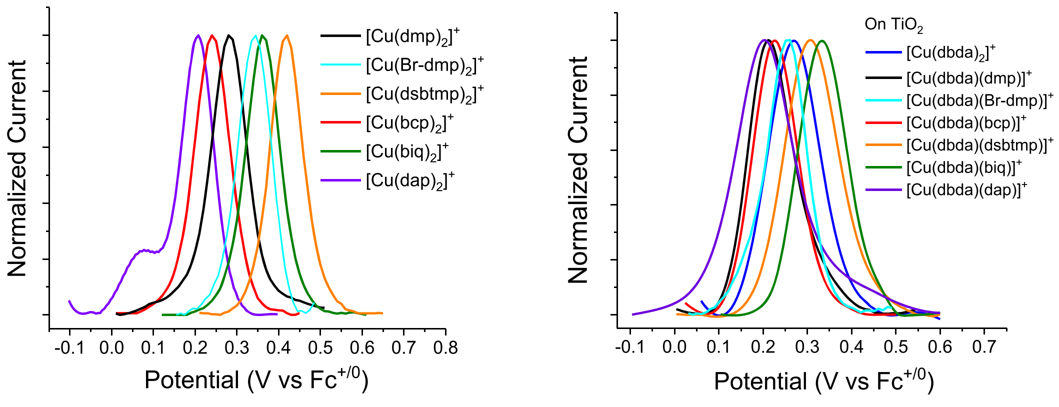
[a] The redox potentials of the complexes are reported vs Fc$^{+/0}$. The redox potentials of the complexes already known in literature are in agreement with the currently reported values.[10,8,42,46,55]

slightly harder (~40 mV) to oxidize than [Cu(dap)$_2$]$^+$. Moving along the series, we find [Cu(dmp)$_2$]$^+$, which is even more difficult (~40 mV) to oxidize than [Cu(bcp)$_2$]$^+$ as, with respect to ligand bcp, ligand dmp is lacking the electron-donating contribution of the phenyl substituents. With respect to [Cu(dmp)$_2$]$^+$, [Cu(Br-dmp)$_2$]$^+$ is more difficult to oxidize (~60 mV) due to the presence of the electron-withdrawing bromine substituent on the Br-dmp ligand. The positive redox potential of complexes [Cu(biq)$_2$]$^+$ and [Cu(dsbtmp)$_2$]$^+$ cannot simply be explained in terms of the electronic inductive effects of the ligands, and geometrical factors must be taken into account. It has been clearly shown by Jahng et al. that ligands with a more flexible core, such as the 2,2′-biquinoline (biq), as opposed to a more rigid phenanthroline core, lead to a more distorted Cu(I) geometry that is more difficult to oxidize.[42] For this reason, we find the redox potential of [Cu(biq)$_2$]$^+$ to be even slightly more positive than the one of [Cu(Br-dmp)$_2$]$^+$. Finally, [Cu(dsbtmp)$_2$]$^+$ exhibits a minimal degree of geometrical distortion upon oxidation due to the very bulky *sec*-butyl groups,[10] thus destabilizing the Cu(II) formation and being the most difficult homoleptic complex to oxidize of the ones investigated.

Due to the resistivity of the TiO$_2$ layer, we could not obtain clear cyclic voltammograms from the series of the complexes adsorbed on TiO$_2$. However, we have been able to obtain clear differential pulse voltammograms of both the homoleptic complexes in solution and the complexes on TiO$_2$, which are displayed in Figure 5.

The DPVs of the homoleptic complexes in solution show, as expected, redox potentials identical to those estimated from their respective CVs. All of the redox potentials determined from the DPVs in Figure 5 are reported in Table 3.

When moving from more negative toward more positive potentials, we found the following order of the Cu(I) complexes adsorbed on TiO$_2$: [Cu(dbda)(dap)]$^+$, [Cu(dbda)(dmp)]$^+$ ≈ [Cu(dbda)(bcp)]$^+$, [Cu(dbda)(Br-dmp)]$^+$, [Cu(dbda)$_2$]$^+$, [Cu(dbda)(dsbtmp)]$^+$, [Cu(dbda)(biq)]$^+$. The order is similar to the one previously observed for the homoleptic complexes, with a few exceptions. The heteroleptic complex [Cu(dbda)(dap)]$^+$, due to the electron-donating effect of the anisyl substituents in the dap ligand, remains the easiest one to oxidize. Interestingly, its redox potential is identical to the one of the homoleptic [Cu(dap)$_2$]$^+$ in solution, implying that the properties are dominated by the dap ligand rather than by dbda. Considering the homoleptic series, the [Cu(dbda)(dmp)]$^+$ and [Cu(dbda)(bcp)]$^+$ complexes present inverted order of the redox potentials: dmp makes the heteroleptic complex slightly easier to oxidize than bcp. However, it should be pointed out that the difference between the redox potential is quite small (~20 mV). This behavior cannot be explained solely on the basis of the effect exerted by



(a) (b)

Figure 5. Differential pulse voltammograms of the homoleptic complexes formed with the ligands dmp, Br-dmp, bcp, dsbtmp, biq, and dap in acetonitrile solution (a) and of the complexes assembled with dbda adsorbed on the surface of TiO$_2$ (b).

Table 3. Redox Potentials Obtained from the DPVs of the Homoleptic and Heteroleptic Complexes Shown in Figure 5

complex	$E_{1/2}$ (V vs $Fc^{+/0}$)[a]	LUMO (V vs $Fc^{+/0}$)[b]
$[Cu(dmp)_2]^+(PF_6)^-$	0.285	−2.17
$[Cu(Br\text{-}dmp)_2]^+(PF_6)^-$	0.345	−2.08
$[Cu(dsbtmp)_2]^+(PF_6)^-$	0.425	−2.10
$[Cu(bcp)_2]^+(NO_3)^-$	0.245	−2.10
$[Cu(biq)_2]^+$TFSI	0.365	−1.70
$[Cu(dap)_2]^+(Cl)^-$	0.205	−1.67
$[Cu(dbda)_2]^+$ on TiO_2	0.270	−1.90
$[Cu(dbda)(dmp)]^+$ on TiO_2	0.215	−2.10
$[Cu(dbda)(Br\text{-}dmp)]^+$ on TiO_2	0.255	−1.98
$[Cu(dbda)(dsbtmp)]^+$ on TiO_2	0.305	−1.95
$[Cu(dbda)(bcp)]^+$ on TiO_2	0.225	−2.00
$[Cu(dbda)(biq)]^+$ on TiO_2	0.335	−1.60
$[Cu(dbda)(dap)]^+$ on TiO_2	0.205	−1.70

[a] The redox potentials of the complexes are reported vs $Fc^{+/0}$. [b] Estimated from the E_{0-0} values reported in Table 1 and the $E_{1/2}$ (HOMO) vs $Fc^{+/0}$ determined by DPV.

the ligands dmp and bcp, which would otherwise lead to the same pattern observed for the homoleptic complexes. The heteroleptic complex $[Cu(dbda)(Br\text{-}dmp)]^+$ follows the trend of the homoleptic series, and the contribution of the Br-dmp ligand is more difficult to oxidize than $[Cu(dbda)(dmp)]^+$ and $[Cu(dbda)(bcp)]^+$. The complexes $[Cu(dbda)(dsbtmp)]^+$ and $[Cu(dbda)(biq)]^+$ show an inverted trend with respect to expectations based on the homoleptic series. In particular, the redox potential of the complex $[Cu(dbda)(dsbtmp)]^+$ significantly differs from the one of the homoleptic $[Cu(dsbtmp)_2]^+$, which can reasonably be explained in terms of steric hindrance of the ligand. In the homoleptic complex, the presence of the *sec*-butyl groups on both ligands freezes the complex in a pseudotetrahedral geometry both in the Cu(I) and in the Cu(II) states, therefore destabilizing the Cu(II) state, making Cu(I) particularly difficult to oxidize. However, in the heteroleptic complex, one of the dsbtmp ligands is replaced by dbda, which contains methyl groups instead of the *sec*-butyl ones. This allows for a higher degree of freedom in the flattening distortion upon the oxidation of Cu(I), resulting in a less destabilized Cu(II) state and a more negative redox potential.

In order to get more insights into the ligand contribution, a graph showing the correlation between the redox potentials of the homoleptic and the heteroleptic complexes is shown in Figure 6.

A first noticeable aspect is that, unlike the results reported in Figure 2, the data do not show one simple trend. This is not surprising, as the electron transfer processes investigated relies on a diffusion mechanism and, consequently, there is time for structural rearrangement, allowing geometrical factors to influence the oxidation to Cu(II). We suggest that two different patterns emerge from the data in Figure 6. The first pattern includes the complexes originating from the ligands dap, bcp, and biq. These ligands have a structurally extended π-system in common, which seems to give a predominant contribution over dbda ligand in determining the properties of the heteroleptic complexes. The second pattern includes the ligands dmp, Br-dmp, and dsbtmp. These ligands have alkyl substituents on the 1,10-phenanthroline core, and they lack aromatic substituents. Therefore, in this case, the more π-conjugated ligand dbda seems to play a larger role.

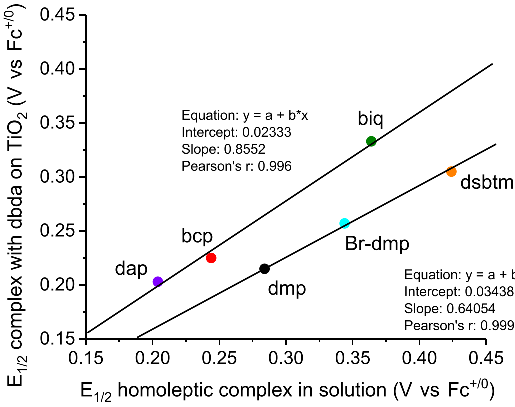


Figure 6. Redox potentials determined from the DPVs of the homoleptic complexes in acetonitrile solution (abscissa) and of the complexes assembled on the surface of TiO_2 with dbda as the anchoring ligand (ordinate).

■ CONCLUSION

A new diimine copper(I) complex, $[Cu(Br\text{-}dmp)_2]^+$, has been synthesized and characterized. Moreover, the optical and electrochemical properties of a series of homoleptic Cu(I) complexes, $[Cu(dbda)_2]^+$, $[Cu(dmp)_2]^+$, $[Cu(Br\text{-}dmp)_2]^+$, $[Cu(dsbtmp)_2]^+$, $[Cu(bcp)_2]^+$, $[Cu(biq)_2]^+$, and $[Cu(dap)_2]^+$, have been evaluated and compared to those of their corresponding heteroleptic complexes $[Cu(dbda)(dmp)]^+$, $[Cu(dbda)(Br\text{-}dmp)]^+$, $[Cu(dbda)(dsbtmp)]^+$, $[Cu(dbda)(bcp)]^+$, $[Cu(dbda)(biq)]^+$, and $[Cu(dbda)(dap)]^+$. The heteroleptic complexes have been prepared on the surface of TiO_2 by using a self-assembly technique. The observed properties of the complexes can be rationalized considering electronic and steric effects of the ligands. The first is related to the electronic inductive effect dependent on the degree of conjugation and electron-withdrawing or -donating character of the ligands, whereas the steric effects are associated with how the substituents in the 2,9-positions of the 1,10-phenanthroline or 6,6′ of the 2,2′-bipyridine destabilize the Cu(II) state with respect to the Cu(I) one. We have shown that, although the optical properties can be fairly described and predicted by a single linear relationship, the interpretation of the redox properties is less trivial. We have explained these observations based on the fact that the optical properties mostly depend on the electronic effect of the ligands, whereas the electrochemical properties are influenced by both electronic and steric contributions. Moreover, the results suggest that the assembled heteroleptic complexes can be used as dyes for DSSCs.

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Notes

The authors declare no competing financial interest.

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