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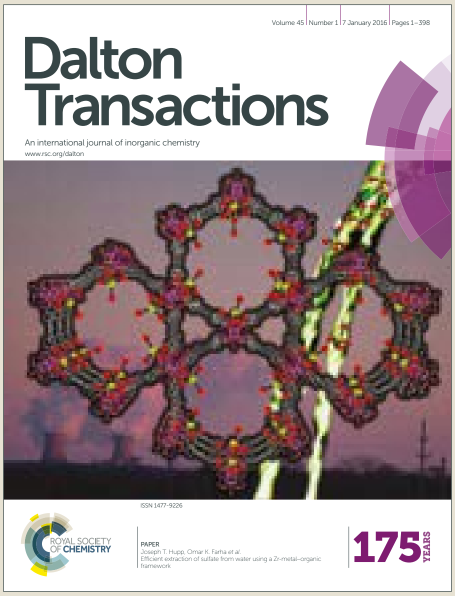

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COMMUNICATION

Intriguing C–H···Cu interactions in bis-(phenanthroline)Cu(I) redox mediators for dye-sensitized solar cells

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We have synthesized and characterized a series of bis-(phenanthroline)Cu(I) complexes of interest as redox mediators for dye-sensitized solar cells. This study led to the discovery of intriguing anagostic interactions between the hydrogen atom and the copper center as evidenced by X-ray diffraction studies on single crystal. Remarkably, an anagostic interaction was found between a H atom of a methyl group and a copper site.

An important challenge of humanity is to replace fossil fuels with renewable energy sources to answer the growing worldwide energy demand, minimizing negative environmental and climate effects. Indeed, sunlight remains the cleanest, the most abundant and the cheapest energy source. [1] Dye-sensitized solar cells (DSSCs)[2–5] are a realistic solution for harnessing the sun energy and converting it into electrical energy. [6]

The traditional redox mediator in DSSCs is the I^-/I_3^- couple as it presents ideal kinetic properties. However it has some disadvantages, e.g., I_2 in equilibrium with I_3^- is volatile, complicating long-term cell sealing, I_3^- is darkly colored and limits the light harvesting efficiency of the dye, the couple presents large photovoltage loss due to the non-optimal matching with the dye redox potential, and I_3^-/I^- is corrosive and corrodes most metals.[7] Therefore, during the recent years, there has been numerous efforts to search for new electron transfer mediators, in particular based on transition metal complexes.[7] In this context, copper complexes are particularly appealing, as they stand as promising efficient and cheap electron mediators for solar cells.[8]

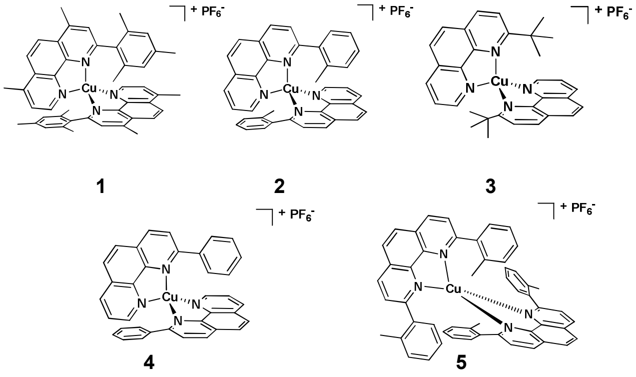

Fig.1. Chemical structures of the investigated Cu complexes.

The use of copper complexes with a distorted tetrahedral geometryin which the structural change between the Cu(I) and Cu(II) complexes is minimized, provides a promising strategy to electron mediators for DSSCs, allowing a very fast electron transfer and a redox potential of the Cu(I)/Cu(II) couple high enough to increase open-circuit voltage (V_{oc}) values.[9-11]

In this framework, we have synthesized a series of different copper complexes (**1-5**)[10-12] (see Fig.1, all with PF_6^- counterion), with phenanthrolines that bear, in α position, a substituent with different steric hindrance, in order to clarify its contribution in achieving simultaneously: (i) an appropriate redox potential; (ii) a distorted tetrahedral geometry; and (iii) an effective shield of the metal core.

We have synthesized the proper phenanthroline ligand and the corresponding Cu(I) complex, with simple and fast reactions (Scheme 1). Ligands were prepared thanks to a reaction developed by Sauvage [13] as an effective and quick way to obtain 2-substituted and 2,9-disubstituted-1,10-phenanthrolines starting from commercially available 1,10-phenanthroline and organolithium reagents.[14]

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Electronic Supplementary Information (ESI) available: [visible absorption spectra, crystallographic data, atomic coordinates, thermal parameters and bond distances and angles, DFT method and geometries]. See DOI: 10.1039/x0xx00000x

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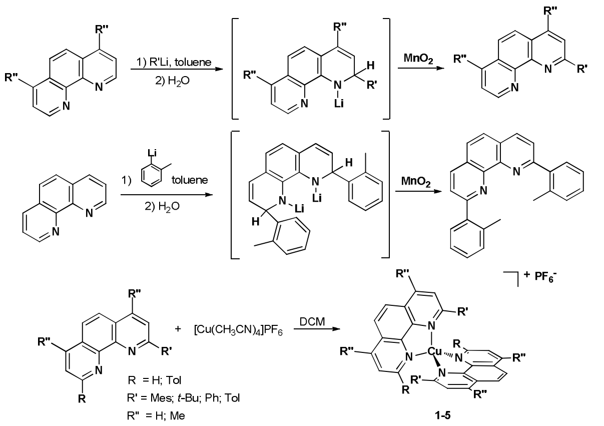

Scheme 1. Synthesis of ligands and complexes.

The reaction is a two-step addition-oxidation. The 2,9-disubstituted derivative is obtained using an excess of organolithium reagent in the first stage. In the second step re-aromatization is achieved treating the intermediate with activated manganese dioxide. In more details, copper complexes were prepared by reaction of the appropriate ligand with the stoichiometric amount of $[Cu(CH_3CN)_4][PF_6]$ (2:1) in the minimal amount of dichloromethane in order to favor the formation of the product that in some cases directly precipitates from the reaction environment in a pure form, avoiding the subsequent crystallization step. The starting white salt $[Cu(CH_3CN)_4][PF_6]$ was synthesized from Cu_2O according to literature[15] (Scheme 1).

The knowledge of metal complexes potentials is crucial to ascertain their applicability as redox mediators in DSSCs. Therefore the electrochemical properties of the copper coordination compounds were studied by cyclic voltammetry in acetonitrile, focusing on the electron transfer process centered on the metal core (see Fig. 2). In all complexes the anodic window showed one chemically reversible peak attributed to a Cu(I) to Cu(II) redox switching; a quite high electrochemical reversibility, i.e. a small potential difference between forward and backward peaks, indicative of a fast electron transfer occurs, is found in all the compounds indicating a limited rearrangement of the coordination sphere. The determination of the heterogeneous electron transfer rate constant, k_{heter}, can be a valuable parameter to quantitatively assess the impact of the steric bulkiness of α-substituents on the self-exchange rate.[16] For the sake of comparison bulky *tert*-butyl chains in compound **3** induce a *ca.* 20 times faster heterogeneous electron transfer toward glassy carbon electrode surface with respect to the unsubstituted bis(1,10-phenanthroline)copper complex; k_{heter}, being $9\cdot10^{-3}$ and $5\cdot10^{-4}$ cm s^{-1} respectively, with and without the bulky substituents, respectively. These values were estimated from charge transfer resistance, R_{ct}, by electrochemical impedance spectroscopy according to the following relationship:[17]

$$k_{\text{heter}} = \frac{RT}{F^2 R_{\text{ct}} C}$$

where R is the gas constant, T the absolute temperature, F the Faraday constant and C the concentration of the copper complex (in mol cm^{-3}).

The Cu(I)/Cu(II) half-wave potentials, $E_{1/2}$, are reported in Table 1. Electronic and steric effects of the substituents finely control the oxidation potentials.

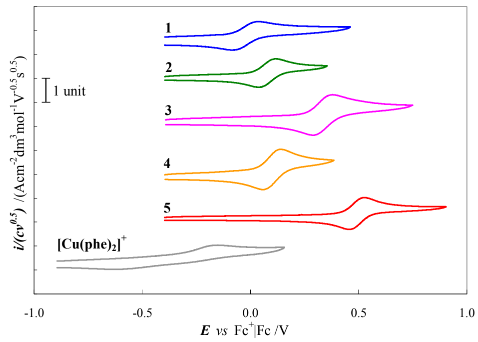

Fig. 2 Cyclovoltammetric, CV, patterns of Cu-based complexes **1-5**, in acetonitrile with 0.1 M $TBAPF_6$ on glassy carbon electrode at 0.2 Vs^{-1}.

Table 1. Oxidation half-wave potential, $E_{1/2}$, in acetonitrile.

Complex	1	2	3	4	5
$E_{1/2}$ *vs* $Fc^+|Fc$ /V	-0.02	0.09	0.34	0.10	0.50

$[Cu(1,10\text{-phenanthroline})_2][PF_6]$ shows $E_{1/2}$ = -0.38 V

Table 2. Visible absorption spectra of **1-5** complexes in acetonitrile.

Complex	λ (nm)	10^3 ε ($M^{-1}cm^{-1}$)
1	445	4.4
2	455	4.6
3	356 426	2.1 2.2
4	437	4.6
5	470	4.5

In agreement with a previous work,[10] complex **5** with 2,9-disubtituted phenanthrolines exhibits $E_{1/2}$ positively shifted with respect to the 2-substituted analogue (complex **2**) due to an increased steric hindrance around the copper atom that progressively destabilizes the electrogenerated Cu(II) product that is forced to maintain a geometry similar to the preferred Cu(I) one.

Remarkably, all 2-substituted complexes (**3** being borderline) have redox potentials suitable for energetic application as electron mediators in DSSCs, being thermodynamically able to regenerate many common photosensitizers with oxidation potentials higher than 0.30-0.35 V *vs* $Fc^+|Fc$.

Electronic absorption spectra of the investigated copper complexes were recorded in acetonitrile (see Table 2 and ESI). They follow the pattern reported in literature, with a MLCT band between 426 and 470 nm,[18] associated with charge transfer from Cu(dπ) to phenanthroline (π*) orbitals. The extinction coefficients of the MLCT band decrease with increasing steric bulk at position 2, with compound **3** possessing the weakest visible absorption (2200 M^{-1} cm^{-1}). To verify the influence of various substituents in α position of the phenanthrolines on the distorted tetrahedral geometry of the corresponding complexes, we have prepared crystals of complexes **2**-**4** suitable for X-ray characterization using a simple double layer procedure (slow diffusion in CH_3CN/hexane).[‡] The structures are displayed in Figs. 3 to 6, for compounds **1** to **4**. The structure of **5** has also been determined but is not detailed here because it is already known.[12a] Unexpectedly, the synthesized complexes show a "peculiar" interaction between a hydrogen of a C-H bond (of the CH_3 or of a CH of phenanthroline or of a tolyl ring ring) and the copper site, as shown in Table 3.

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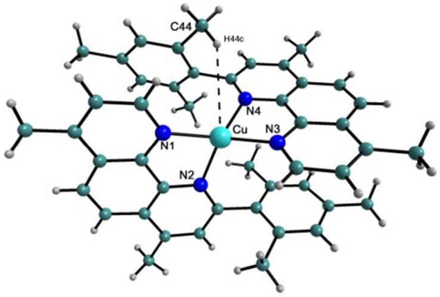

Fig.3 Structure of the cation in (**1**) (see ref. 11)

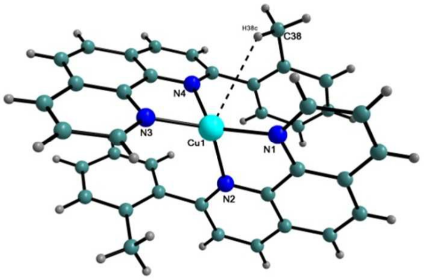

Fig.4 Structure of the cation in (**2**)

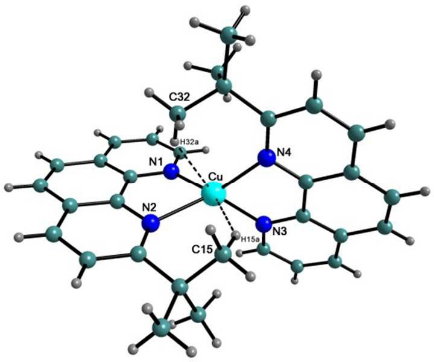

Fig.5 Structure of the cation in (**3**)

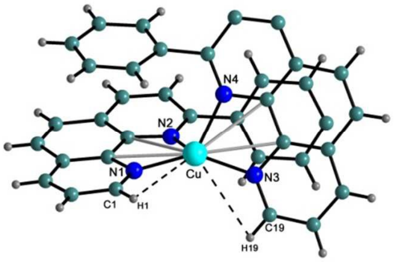

Fig.6 Structure of the cation in (**4**)

Table 3. Shortest Cu···H distances in Å in the synthesized complexes

Complex[a]	Shortest Cu…H distances (Å)	H belongs to:
1 (ref 11)	3.18	CH_3 of mesityl ring
2	3.05	CH_3 of tolyl ring
3	2.49; 2.53	CH_3 of tertbutyl
4	3.11;(3.27)	CH of phenanthroline (CH_3 of phenyl ring)
5 (ref. 12a)	2.72; 2.86	CH of tolyl ring

[a] In the complex $[Cu(1,10\text{-phen})_2][PF_6]$[19] the shortest Cu…H distance is 3.203 Å.

These interactions awoke our curiosity because in the literature there is some controversy regarding the agostic and anagostic interaction in copper complexes.[20] The strength, nonpolar nature, and low polarizability of C-H bonds make that they are generally considered as chemically inert. However, significant interactions between C-H bonds of σ-bound alkyl groups and metal atoms can occur.[18,21] The origin of the agostic interaction lies in the identification in the 1960s of hydridic H atoms in transition metal complexes by Trofimenko.[22] The term agostic was proposed in 1983 by Brookhart and Green in their seminal contribution[23] for a case in which a C–H group interacts with a transition metal with the formation of a two-electron three-center bond. In that case, the metal centre behaves like a Lewis acid. The term anagostic was coined in 1990 by Lippard and co-workers to distinguish sterically enforced M···H-C contacts (M=Pd, Pt) in square-planar transition metal d^8 complexes from attractive agostic interactions.[24] In this case, the availability of an empty orbital is not required. Today the theme of agostic and anagostic interactions remains a hot topic, as evidenced, for example, in a recent paper on anagostic interactions under pressure.[25] It is evident that the assignment of an agostic or anagostic interaction requires caution.[26] In the case of an ephedrine copper complex, for example, an interaction initially described as agostic[27] was next disputed by other authors. [20]

In the investigated complexes the Cu···H lengths, superior to 2.3 Å,[28] preclude any agostic bonds; in fact as far as bond lengths are concerned agostic interactions are characterized by relatively short M–H distances (1.8–2.3 Å) whereas anagostic interactions are characterized by relatively longer M-H distances (2.3-2.9 Å).The shortest bonds between a H atom of a methyl group (complex **3**) or of a CH in *ortho* position of tolyl group (complex **5**) and copper can be consequently attributed to anagostic interactions. To our knowledge, this is the first time that an anagostic interaction is found between a H atom of a methyl group and a copper site, as happened for complex **3**.

DFT calculations were performed on all cations (see the ESI for technical details) to verify that the existence of "short" C–H•••Cu distances is not induced by crystal packing effects. We have found the following distances: for complex 1, 2.74 Å (between Cu and the H of the CH_3) for complex **2**, 2.60 Å (between Cu and H of CH_3 of tolyl ring); for complex **3**, 2.37 and 2.69 Å (between Cu and the H of the CH_3 of tertbutyl); for complex **4**, 2.90 and 3.20 Å (respectively between Cu and H of phenyl ring, and between Cu and H of phenantroline); and for complex **5**, 2.36 and 2.41 Å (between Cu and the H of the tolyl ring). Concerning complex **4**, different H atoms are involved in the shortest C–H•••Cu contact: in the X-ray structure the closest H atom belongs to the phen ligand whereas in DFT calculations the closest H atom belongs to the phenyl group: this difference is likely due to crystal packing effects that tune the dihedral angle between the phenyl ring and the phenantroline. As

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expected, the smallest distances obtained through DFT are in complexes **3** and **5** which is consistent with the solid-state results. This hints that the XRD finding should pertain in other environment than the crystals.

The anagostic interactions evidenced in the present work protect the copper site and improve the stability of the structure by further minimizing the change of geometry between Cu (I) and Cu (II). This protection is of crucial importance for the design of efficient redox couples for DSSCs. Therefore our complexes, whose potential can be easily tuned by adequate substituents on the phenanthrolines, have a great potential as redox couple of an electron transfer mediator electrolyte in DSSC applications, along with a proper dye with adequate HOMO and LUMO levels, where the HOMO level lies under the potential of the redox couple. In this framework, we underline that the most popular redox couple, I^-/I_3^-, has several limitations (see Introduction), and, in particular it presents a too negative redox potential (–0.28 V *vs* $Fc^+|Fc$ in acetonitrile, converted from 0.35 V *vs* NHE)[29] that precludes its use in DSSCs relying on some of the most promising dyes that have a relatively high potential. Copper complexes, and specifically complex **3**, are expected to be adequate redox mediators (along with the related Cu(II) complex) for DSSCs upon combination with organic dyes such as C218 [30a], LEG4 [30b] or Y123.[30c]

It is known that copper complexes, which versatile coordination chemistry has significant influence over their optical and redox properties,[26] are of great interest as catalysts because the use of complexes deriving from earth-abundant elements is desirable from the standpoint of scalability and sustainability. Besides, agostic[31] or anagostic[32] interactions are often used to activate inert C-H bonds, facilitating new reactions. For example, recently the catalytic activity of bis(pyrazolyl)borate copper complexes toward carbenoide insertion into N-H bonds was reported.[31] In this system weak intramolecular C-H···Cu interactions are of great importance and act as a switch which is turned “on” if interacting with the substrate and “off” if eliminating the product and regenerating the weak interaction.[31] Moreover the steric hindrance of groups in the positions 2,9 of 1,10-phenanthroline copper (I) complexes plays an important role in the regioselective addition of CBr_4 to styrene, substituted phenyl rings leading to a better catalytic activity then methyl groups.[33] The complexes investigated in the present work are therefore of potential interest for such catalysis studies.

In summary we have fully characterized variously substituted 1,10-phenanthroline copper(I) complexes. Their crystal structure, determined by single-crystal X-ray analysis, confirms a distorted tetrahedral geometry and reveals interesting anagostic interactions for complexes **3** and **5**. Clearly the investigated copper complexes are excellent candidates as electron transfer mediators for DSSCs and are appealing for catalysis studies.

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‡ X-ray crystallographic data in CIF format for **2**-**4** have been deposited with the Cambridge Crystallographic Data Centre, CCDC 1564905-1564907.

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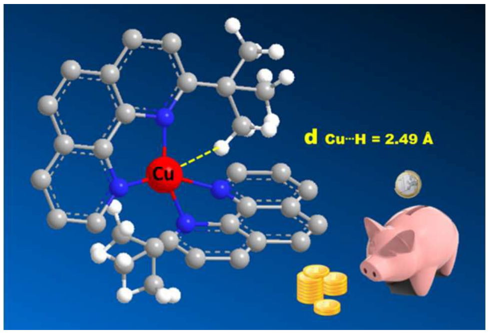

For the first time an anagostic interaction is found between a H atom of a methyl group and a copper site in bis-2-tertbutyl(phenanthroline)Cu(I) complex.