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COMMUNICATION

The corrole and ferrocene marriage: 5,10,15-triferrocenylcorrolato Cu

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Two synthetic routes have been defined for the preparation of 5,10,15-triferrocenylcorrole as Cu derivative. This complex has been characterized and the preliminary electrochemical investigation shows a strong interaction among the corrole and *meso* ferrocenyl substituents. The results obtained suggest that peculiar properties are gained combining the eccentric characteristic of ferrocenyl substitution on the corrole macrocycle.

Corrole is one of the first porphyrin analogs reported in the literature,¹ but its chemistry has not been studied in detail since the new century, when the corrole related researches witnessed a dramatic increase. The peculiar behavior of such a macrocycle is at the basis of this strong interest, but the impressive increase of corrole popularity has been allowed by the definition of simple synthetic methods for the preparation of *meso*-arylcorroles starting from commercially available pyrrole and arylaldehydes.² This synthetic advancement opened corrole studies to researchers not familiar with the lengthy and tedious pathway necessary for the preparation of β -alkylcorroles. In the first decade of the century different synthetic routes to corroles have been defined,³ making the *meso*-arylcorroles library now comparable to that of porphyrins. Among the different substituents, in the last few years great attention has been devoted to the combination of porphyrinoid macrocycle properties with those of ferrocenyl moieties.⁴ Among the different examples, *meso*-substituted porphyrins show interesting electrochemical features⁵ that found applications in several areas,⁶ while ferrocenyl axial-coordinated metal-subphthalocyanine or porphyrins received great attentions for their photophysical properties.⁷ Other sparse examples concerned the synthesis of di-substituted ferrocenyl units bearing two porphyrinoid macrocycles.^{8,9} In the corrole field, a macrocycle bearing one ferrocenyl group in the position 10 has been reported in the literature,⁹ but in this case electron-withdrawing pentafluorophenyl groups should be present at the other *meso* carbon atoms to stabilize the compound, counterbalancing the donor effect

of the ferrocenyl group. On the other hand, for both mono-ferrocenyl-substituted porphyrins⁸ and corrole,⁹ a single ferrocenyl substituent is not enough to allow a significant interaction between the two moieties, as observed when the number of ferrocenyl substituents at the *meso* position increases. Only when ferrocenyl groups occupy all the available *meso* positions, a compound with unique electronic properties to respect those of the separate units is obtained.^{4b,c,e}

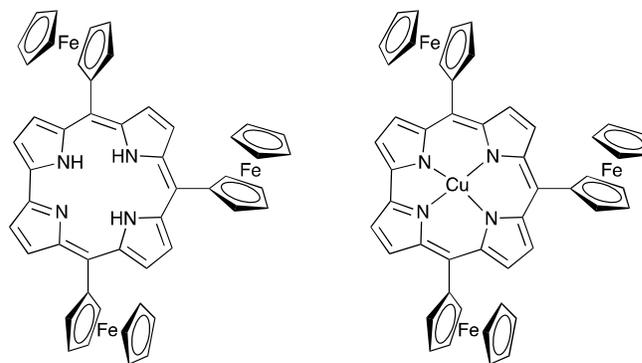


Fig. 1 Structure of H₃TFcC and its copper complex

For this reason, we focused our interest on the preparation of 5,10,15-triferrocenylcorrole, (H₃TFcC, Fig. 1), with the aim of coupling the well known “not-innocent” ligand character of the corrole backbone¹⁰ with the tendency of polynuclear transition metals to form mixed-valence states. Indeed, we believe that such a combination could lead to the formation of organic substrates with potential applications in the field of material chemistry. We initially attempted to define a method for the synthesis of H₃TFcC, by investigating two of the most general procedures^{3c,d} for *meso*-triarylcorrole preparation. Both methods should be slightly modified to allow the formation of

the target corrole in the range of 2-3% yield (see ESI), always observing the formation of the tetraferrocenylporphyrin (H_3TFcP) as byproduct.^{4e} The UV-Vis spectrum of the H_3TFcC fraction showed an intense absorbance at 434 nm and a weaker band at 780 nm, but it was impossible to obtain a resolved 1H NMR spectrum, because of many unresolved signals in the range 6.5-7.5 ppm. The presence of a sharp singlet at 15.7 ppm suggested the formation of an isocorrole species,^{10c} originated by the oxidation of the macrocycle. It is well known that corrole is easily oxidized and the electron-donating character of ferrocenyl groups further increases this characteristic, making the corrole free base not very stable, as also pointed out by the quick variation of the color of the solution from brown to green. Since the facile oxidation of H_3TFcC makes the free base not stable enough, we tried to increase the macrocycle robustness by coordination of the Cu ion (Fig. 1). Copper was inserted right after the oxidation step, by addition of a methanolic solution of $Cu(AcO)_2$ to the reaction mixture. This attempt was successful: the target corrole was obtained in an improved 6% yield, together with the corresponding porphyrin in a 6:4 ratio. The second band was the target $CuTFcC$, characterized by a slightly different UV-Vis spectrum (Fig. 2), with a Soret band and one Q-band located at 422 and 674 nm respectively.

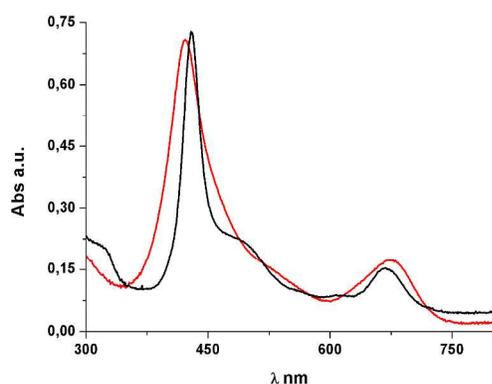


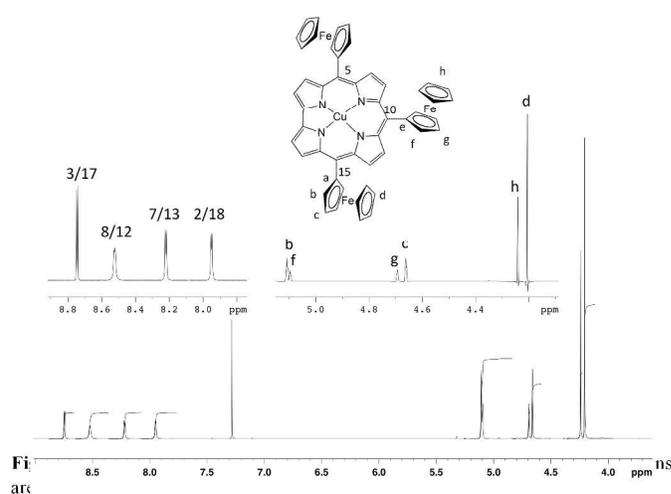
Fig. 2 Comparison between UV-Vis spectra of $CuTFcC$ (red line) and $CuTFcP$ (black line) in CH_2Cl_2 .

$CuTFcC$ has been characterized by NMR analysis (COSY, ROESY, HSQC, HMQC), HRMS and electrochemistry (cyclic voltammetry and differential pulse voltammetry).

High-resolution mass spectrum, showed the molecular peak, with the isotopic distribution impressively remarking the theoretical one (see ESI). The 1H NMR spectrum (Fig. 3), showed four doublets between 7.94 and 8.75 ppm (2 H each), which can be associated to the β -pyrrolic protons. Such a pattern is largely different with respect to other Cu-corrolates, which usually exhibit low-resolved, overlapped signals between 7 and 8 ppm, depending on the nature of substituents.¹¹

Cyclopentadienyl protons are splitted into two sets of resonances in a 2:1 ratio as expected for two different ferrocenyl (Fc) groups, namely adjacent and opposite Fc with respect to the pyrroles direct linked. The characteristic pattern

for monosubstituted ferrocenes was observed, consisting of three different signals, *i.e.* α (around 5.1 ppm) and β (around 4.7 ppm) hydrogens on the substituted rings and unsubstituted cyclopentadienyl (around 4.2 ppm). Data obtained for $CuTFcC$ represents a striking deviation from the classic behavior. The wide doublets separation (90 Hz), the large downfielding of the β -pyrrolic protons and the higher shielding recorded for the C-2 and C-18 protons with respect to what usually observed for triarylcorroles,¹² suggest a large influence of the cyclopentadienyl rings due to both steric hindrance and deshielding effect. The complete assignation was carried out using the bi-dimensional NMR analysis (COSY, ROESY, HSQC and HMBC, see ESI), which confirms the $CuTFcC$ structure. Moreover a spatial interaction between the unsubstituted ferrocenyl rings and β protons of the corrole ring was observed in the ROESY spectrum. In detail protons 3,7,13 and 17 interact with the cyclopentadienyl of ferrocenyl units in position 5 and 15, while the protons 8 and 12 interact with the ferrocene in position 10. To note no cross peaks, *e.g.* no interactions with β protons of the corrole ring, are visible for the β protons of substituted cyclopentadienyl rings. Together, these results indicate free rotation of ferrocenyl units (see ESI) as observed for the parent $TFcPs$.^{4e}



The intriguing features of $CuTFcC$ were confirmed by electrochemical techniques. Five reversible electrochemical processes were detected by cyclic voltammetry (CV) and differential pulse voltammetry (DPV) in $PhCN/TBAP$ 0.1M, as visible in Fig. 4. As summarized in table 1, one out of two reduction processes detected is ascribable to the corrole ring, while the other is due to the couple $Cu(III/II)$. In the anodic region of the window, the oxidation of Fc groups occurs with a 2:1 ratio, *i.e.* chemically equivalent Fc groups are oxidized simultaneously. Oxidations of non-equivalent Fc groups are sharply separated by 170 mV, even using the usual electrolyte tetrabutylammonium perchlorate. In the same experimental conditions, the parent $CuTFcP$ (see ESI) revealed a broad oxidation peak due to 4 single-electron oxidations much close

in potential.^{4b,d} Such a difference is reasonably due to the lower symmetry of corrole that renders Fc groups chemically non-equivalent. The apparent lack of electronic communication, which prevents the differentiation of opposite Fc groups, could be ascribed to different factors (distortion of the core, the use of a coordinating electrolyte, solvent) and will be investigated in a separate paper.

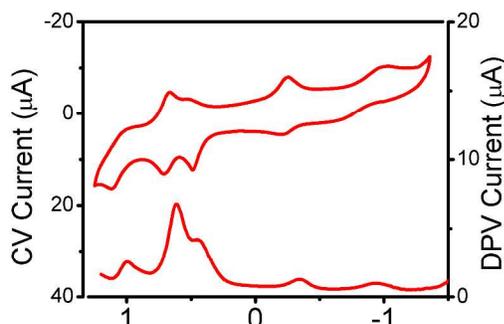


Fig. 4 Cyclic voltammogram (CV) and Differential Pulse Voltammogram (DPV) of CuTFcC with five electrochemical processes clearly visible.

Moreover, the presence of five reversible, well defined and separate electrochemical processes in a small potential window (2 Volts), indicates that this molecule is a very promising candidate as active species in several applications, such as molecular memory devices.¹³

Table 1 Potential of the electrochemical processes in CuTFcC

Process	Potential (V vs SCE)	Attribution
1	1.02	1 st Core oxidation
2	0.62	Fc ⁺ /Fc <i>cis</i>
3	0.45	Fc ⁺ /Fc <i>trans</i>
4	-0.34	Cu ^{III} /Cu ^{II}
5	-0.98	1 st Core Reduction

In conclusion, we prepared the novel CuTFcC by adapting two different methodologies usually exploited for the preparation of *meso*-triarylcorroles. The good stability of the copper derivative allowed its detailed characterization and its possible exploitation in the field of material chemistry. The main variations in the electronic properties to respect the well-studied analogous TFcP can be related to the lower symmetry of the corrole ring, which allows to distinguish two sets of ferrocenyl groups, with the electronic communication becoming significantly different. As a consequence, in the visible absorption spectrum, Soret and Q bands are broadened to respect the analogous porphyrin transitions (Fig. 2), while the differentiation of the ferrocenyl groups provides a better resolution of the redox processes with respect to the parent CuTFcP.

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Notes and references

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†Electronic Supplementary Information (ESI) available: Experimental details, UV-Vis, mass and NMR spectra. See DOI: 10.1039/c000000x/1 A. W. Johnson and I. T. Kay, *J. Chem. Soc.*, 1965, 1620.

2 a) R. Paolesse, L. Jaquinod, D. J. Nurco, S. Mini, F. Sagone, T. Boschi and K. M. Smith, *Chem. Commun.* 1999, 1307. b) Z. Gross, N. Galili and I. Saltsman, *Angew. Chem. Int. Ed.* 1999, **38**, 1427.

3 a) R. Paolesse, S. Nardis, F. Sagone and R. G. Khoury, *J. Org. Chem.* 2001, **66**, 550. b) D. T. Gryko and B. Koszarna, *Org. Biomol. Chem.* 2003, **1**, 350. c) R. Paolesse, A. Marini, S. Nardis, A. Froiio, F. Mandoj, D. J. Nurco, L. Prodi, M. Montalti and K. M. Smith, *J. Porphyrins Phthalocyanines* 2003, **7**, 25. d) B. Koszarna and D. T. Gryko, *J. Org. Chem.* 2006, **71**, 3707.

4 a) R. Sharma, P. Gautam, S. M. Mobin and R. Misra, *Dalton Trans.* 2013, **42**, 5539. b) V. N. Nemykin, G. T. Rohde, C. D. Barrett, R. G. Hadt, C. Bizzarri, P. Galloni, B. Floris, I. Nowik, R. H. Herber, A. G. Marrani, R. Zaroni and N. M. Loim, *J. Am. Chem. Soc.* 2009, **131**, 14969. c) V. N. Nemykin, G. T. Rohde, C. D. Barrett, R. G. Hadt, J. R. Sabin, G. Reina, P. Galloni and B. Floris, *Inorg. Chem.* 2010, **49**, 7497. d) G. T. Rohde, J. R. Sabin, C. D. Barrett and V. N. Nemykin, *New J. Chem.* 2011, **35**, 1440. e) C. H. Devillers, A. Milet, J.-C. Moutet, J. Pécaut, G. Royal, E. Saint-Aman and C. Bucher, *Dalton Trans.* 2013, **42**, 1196. f) V. N. Nemykin, P. Galloni, B. Floris, C. D. Barret, R. G. Hadt, R. I. Subbotin, A. G. Marrani, R. Zaroni and N. M. Loim, *Dalton Trans.* 2008, 4233.

5 a) A. Auger and J. C. Swarts, *Organometallics* 2007, **26**, 102. b) V. N. Nemykin, P. Chen, P. V. Solntsev, A. A. Purchel and K. M. Kadish, *J. Porphyrins Phthalocyanines* 2012, **16**, 793.

6 a) J. P. Herney, T. Dransfield and J. Rochford, *Tetrahedron Lett.* 2012, **53**, 4700. b) S. J. Dammer, P. V. Solntsev, J. R. Sabin and V. N. Nemykin, *Inorg. Chem.* 2013, **52**, 9496.

7 a) G. Bonded, P. V. Solntsev, J. R. Sabin, S. J. Dammer, N. N. Gerasimchuk and V. N. Nemykin, *Chem. Commun.* 2010, **46**, 6581. b) P. V. Solntsev, K. L. Spurgin, J. R. Sabin, A. A. Heikal and V. N. Nemykin, *Inorg. Chem.* 2012, **51**, 6537. c) D. González-Rodríguez, T. Torres, M. M. Olmstead, J. Rivera, M. A. Herranz, L. Echegoyen, C. A. Castellanos and D. M. Guldi, *J. Am. Chem. Soc.* 2006, **128**, 10680.

8 M. A. Bakar, N. N. Sergeeva, T. Juillard and M. O. Senge, *Organometallics* 2011, **30**, 3225.

9 D. T. Gryko, J. Piechowska, J. S. Jaworki, M. Galezowski, M. Tasiar, M. Cembor and H. Butenschon, *New J. Chem.* 2007, **31**, 1613.

10 a) A. Ghosh, T. Wondimagegn and A. B. J. Parusel, *J. Am. Chem. Soc.* 2000, **122**, 5100. b) F. A. Walker, S. Licoccia and R. Paolesse, *J. Inorg. Biochem.* 2006, **100**, 810. c) S. Nardis, G. Pomarico, F. R. Fronczek, M. G. H. Vicente and R. Paolesse, *Tetrahedron Lett.* 2007, **48**, 8643.

11 a) I. H. Wasbotten, T. Wondimagegn and A. Ghosh, *J. Am. Chem. Soc.* 2002, **124**, 8104. b) C. Brückner, R. P. Briñas and J. A. Krause Bauer, *Inorg. Chem.* 2003, **42**, 4495.

12 Y. S. Balazs, I. Saltsman, A. Mahammed, E. Tkachenko, G. Golubkov, J. Levine and Z. Gross, *Magn. Reson. Chem.* 2004, **42**, 624.

13 J. S. Lindsey and D. F. Bocian, *Acc. Chem. Res.* 2011, **44**, 638