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# A tetrathiafulvalene-functionalized schiff base macrocycle: synthesis, electrochemical, and photophysical properties

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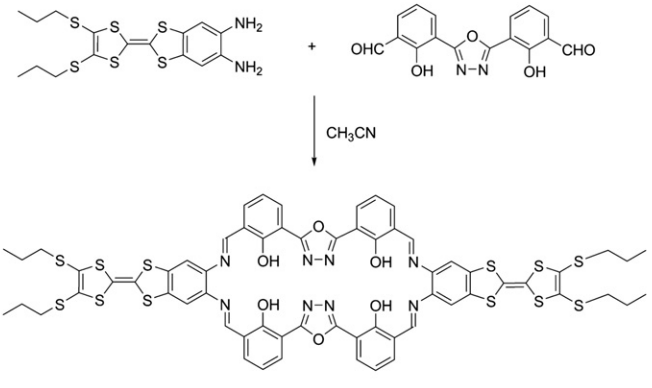
## ABSTRACT

Highly selective formation of 2+2 macrocycle **1** from 2,5-bis(3-formyl-2-hydroxyphenyl)-1,3,4-oxadiazole and a diamine-functionalized tetrathiafulvalene derivative is reported. Its electronic properties have been studied experimentally by the combination of electrochemistry and UV–vis–NIR spectroscopy. Particularly, its largely extended π-conjugation renders this novel macrocycle simultaneously a good multielectron donor and a strong chromophore, which is rationalized on the basis of density functional theory.

## 1. Introduction

Schiff base macrocycles, particularly those derived from salicylaldimines with $N_2O_2$ binding pockets, have become a topic of growing interest due to their highly tunable structures, ease of synthesis, and excellent metal complexing properties.[1,2] They have been designed for binding multiple metal centers and investigated mainly in the context of supramolecular chemistry, molecular magnetic materials, sensitizers, and catalysts. It has been amply demonstrated that these multimetallic complexes frequently exhibit intriguing magnetic, catalytic, or supramolecular behavior. Moreover, a broad variety of Schiff base macrocycles has been developed for metal biosites modeling.[3] Despite these appealing properties, much less attention has been placed on the development of suitably functionalized Schiff base macrocycles with fascinating electronic, optical, and coordinating properties for promising applications, for example, in cooperative recognition systems and molecular (opto) electronics.[4] We introduce here the Schiff base macrocycle **1** (Scheme 1) incorporating the 1,3,4-oxadiazole chromophore and tetrathiafulvalene (TTF) donor functionalities inside and outside of the cavity, respectively. Consequently, the actual annulation process renders this novel macrocycle simultaneously a good multielectron donor and a strong chromophore.



**1**

**Scheme 1.** Synthesis of the TTF-fused macrocycle **1**.

It is well known that a particularly appealing and characteristic aspect of TTF is its electron-rich π-system, which affords persistent cation radical and dication species upon oxidation, leading to the formation of mixed-valence systems.[5] Our combined interest in conducting magnets and molecular (opto)electronics led us to the synthesis, electrochemical, and spectroscopic investigations of a variety of TTF-fused donor–acceptor (D–A) systems showing photoinduced electron or energy transfer processes, further leading to long-lived charge-separated states.[6] As a continuation of this project, we have prepared the first TTF-fused multidentate

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1,3,4-oxadiazole-containing Schiff base macrocycle **1**. Particularly, it can potentially coordinate not only two M(II) ions with electron neutrality upon deprotonation of the phenol groups but also two additional metal ions in an MM′M′M fashion. Hence, the integration of two $N_2O_2$ and two 1,3,4-oxadiazole coordination sites is expected to be effective for the construction of fascinating supramolecular materials and sensors triggered by ligand coordination to the metal ion.[1,2,7] To the best of our knowledge, none of electronic properties of 1,3,4-oxadiazole-containing Schiff base macrocycles except for their synthesis has been reported.[8] In the present work, we describe an efficient one-step preparation of macrocycle **1** and present its electronic properties, which have been fully investigated experimentally and theoretically.

## 2. Results and discussion

The fused target macrocycle **1** was obtained in 72% isolated yield via the direct condensation reaction of 2,5-bis(3-formyl-2-hydroxyphenyl)-1,3,4-oxadiazole[9] with 5,6-diamino-2-(4,5-bis(propylthio)-1,3-dithio-2-ylidene)benzo[*d*][1,3]dithiole[6d] in a 1:1 M ratio in $CH_3CN$. A $^1H$ NMR study of **1** in $CD_2Cl_2$ and $CDCl_3$ shows, that all the resonances from the protons of the aromatic rings are almost invisible, while those from the protons of the propyl groups are quite weak and broad. To deplete the aggregation, a $^1H$ NMR experiment was performed in $CDCl_3$/TFA-$d_1$ (20:1). The CH=N protons of the salicylaldimine moiety and CH protons of benzene rings adjacent to the TTF units appear as singlets at 8.98 and 7.48 ppm, respectively, being consistent with a highly symmetric cyclic structure. The ESI mass spectrum shows a strong peak at *m*/*z* 1413.10, which agrees with the 2:2 macrocyclic structure confirmed also by elemental analysis. It is noteworthy that the reaction selectively affords the 2+2 compound in a relatively concentrated solution under mild and simple conditions, indicating that the desired macrocycle **1** is thermodynamically favored. Besides, the hydroxy groups of 2,5-bis(3-formyl-2-hydroxyphenyl)-1,3,4-oxadiazole play an important role in the selective formation of the 2+2 macrocycle, as demonstrated in analogous systems.[10]

The presence of two TTF units in macrocycle **1** should confer to this compound some interesting electrochemistry behavior. As expected, the voltammograms of macrocyle **1** let appear two successive reversible oxidation processes at 0.014 and 0.430 V (vs Fc/Fc$^+$), respectively (Fig. 1a). These oxidations are assigned to the two stable successive oxidation states of TTF as radical cation and dication species. The broader shape of the first oxidation wave suggests the presence of some intra and/or intermolecular interactions among the TTF moieties, as previously observed in the tris-TTF compound[6b] and related TTF oligomers.[11] However, an increase of the concentration induces a broadening of both oxidation waves and a diminution of the stability of generated species (Fig. 1b). This concentration dependence suggests that the interactions between both TTF units result mostly from intermolecular interactions, which is clearly evidenced by $^1H$ NMR experiments. In order to support this hypothesis, thin layer cyclic voltammetry experiments (TLCV) were carried out. Despite numerous attempts, the instability of the oxidized species, especially at low scan rate, did not improve the resolution and discern the first oxidation of each TTF unit. In fact, the TLCVs show only the degradation of our system starting from the first oxidation process. Nevertheless, the presence of some interactions between TTF units is confirmed by recording the UV–vis–NIR spectra upon chemical oxidation by a successive aliquot addition of an oxidant, such as $NOSbF_6$ (Figs. 2 and S1). As illustrated in Fig. 2, chemical oxidation leads to the gradual decreasing of the absorption band around 330 nm, and the concomitant emergence of new absorption bands characteristic for the formation of the cation-radical species (at

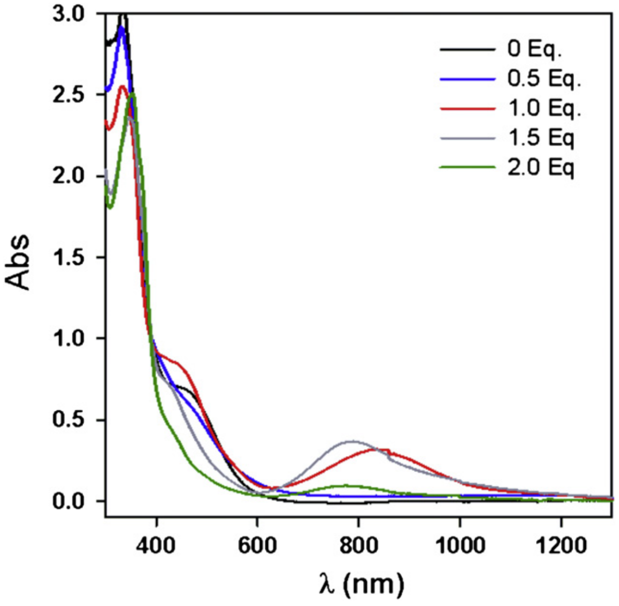

**Fig. 2.** Variation of the UV–vis–NIR absorption spectra of **1** ($2.0\times10^{-4}$ M) in $CH_2Cl_2$ upon successive addition of aliquots of $NOSbF_6$.

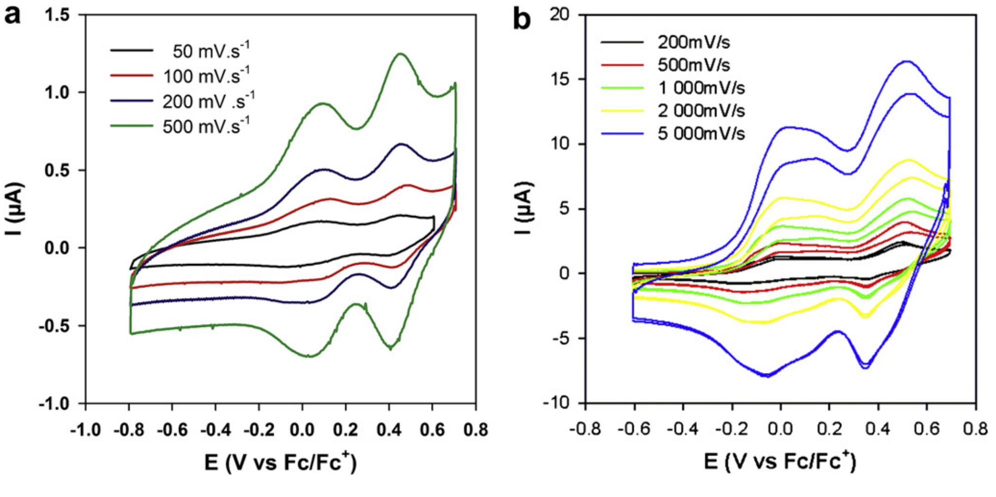

**Fig. 1.** Cyclic voltammograms of **1** (a: $2.83\times10^{-6}$ M, b: $1.4\times10^{-4}$ M) in $CH_2Cl_2$; 0.1 M $TBAPF_6$; on platinum electrode, as function of the scan rates.

460 nm and 840 nm). Moreover, a quite broad weak absorption band around 2200 nm occurs additionally and specifically for the generated $\mathbf{1}^{\bullet+}$ mixed-valence state (Fig. S1), which corroborates the fact that both TTF units are not oxidized at the same potential. Beyond 1.4 equiv of $NOSbF_6$, all absorption bands characteristic of the radical species decrease quickly while the band originally at 330 nm is restored and slightly red shifted (350 nm). Upon the addition of 1.5 equiv of $NOSbF_6$, a new absorption band around 800 nm suddenly appears, which decreases rapidly with the increasing amount of $NOSbF_6$. These observations indicate the instability of the diradical dication $\mathbf{1}^{2+}$ as demonstrated in TLCV.

The UV–vis–NIR spectrum of **1** (Fig. 3) shows a strong broad absorption band centered at 21,500 $cm^{-1}$ and a very strong band at 30,000 $cm^{-1}$ with a broad shoulder. To rationalize it, density functional theory (DFT) as well as time-dependent DFT calculations[12] of **1** (with methyl instead of propyl groups) were performed employing the B3LYP hybrid functional and the TZVP basis set of triple-ζ quality. All calculations were carried out with the TURBOMOLE V6.0 program package.[13] The important frontier molecular orbitals are given in Fig. 4.

The ground state geometry of macrocycle **1** was fully optimized without any symmetry restrictions. In the equilibrium structure, the two TTF subunits exhibit a boat-like conformation, whereas the macrocycle adopts a bowl geometry (Fig. S2). The electronically excited states were rationalized via a vertical TD-DFT calculation (see stick spectrum in Fig. 3). The lowest-energy electronic band comprises five different excitations with calculated energies and oscillator strengths $f_{calcd}$ ranging from 19,420 to 21,650 $cm^{-1}$ and 0.03–0.21, respectively. All of them involve one-electron excitations from one pair of degenerate π-orbitals HOMO and HOMO-1 to LUMO, LUMO+1, and LUMO+2, clearly reflecting the π-electron flow from the TTF into the macrocyclic subunits (Fig. 4). Consequently, these transitions have strong intramolecular charge-transfer (ICT) character and nicely correspond to the broad absorption band centered at 21,500 $cm^{-1}$. In contrast to CV and $^1H$ NMR experiments, the aggregation of **1** could not be clearly evidenced by the concentration-dependent UV–vis spectra (Fig. S3), very probably because of the presence of this strong and broad ICT band.

Moreover, the calculated transition at 25,923 $cm^{-1}$ with $f_{calcd}=0.44$ corresponds to a combination of the one-electron excitations from one pair of degenerate π-orbital HOMO-3 and HOMO-2 to LUMO and LUMO+1 and therefore bears ICT as well as macrocycle-localized π–π* characteristics. This electronic transition can be attributed to the shoulder around 28,000 $cm^{-1}$. The most intense absorption at 26,680 $cm^{-1}$ with $f_{calcd}=1.14$ is predicted to be a macrocycle-localized π–π* transition (HOMO-4 → LUMO), in fairly good agreement with the observed strong absorption band centered at 30,000 $cm^{-1}$.

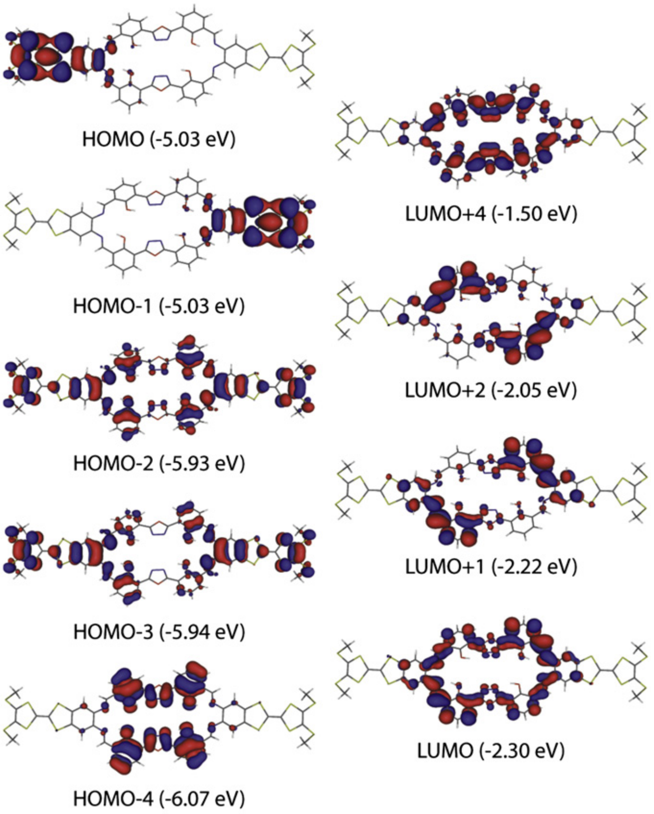

**Fig. 4.** Frontier molecular orbitals of macrocycle **1** (with methyl instead of propyl groups).

## 3. Conclusion

In conclusion, the macrocycle **1** combines two characteristics. On one hand, several electronic charge-transfer transitions originate from its inherent donor–acceptor nature. On the other hand, it acts as a redox-active compartmental ligand, for example, it has a potential ability to bind two or more metal ions in close proximity into two identical or different compartments. Specifically, molecular

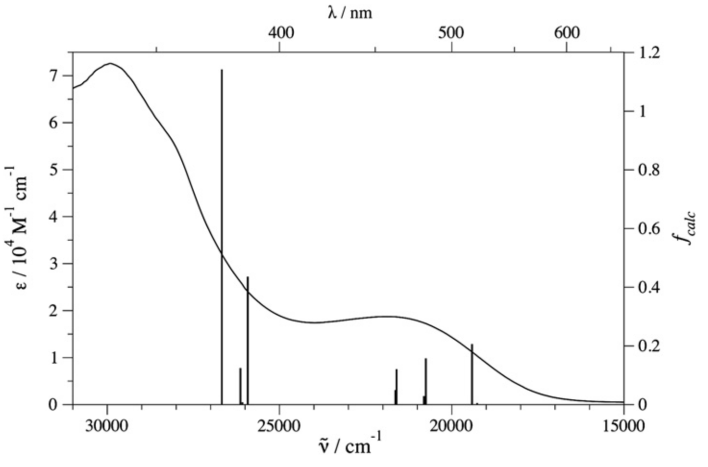

**Fig. 3.** Electronic absorption spectrum of macrocycle **1** together with the calculated $S_0 \rightarrow S_n$ transitions at the TD-B3LYP/TZVP level of theory.

systems having two or more redox-active centers in close proximity, capable of cooperative interactions, are of prime interest in the development of catalysts. As a consequence, considerable effort is currently devoted to the investigation of the coordination behavior of this promising ligand as well as of the role of 1,3,4-oxadiazole bridging groups in modulating the type and the extent of mutual interaction between the metal ions inside the adjacent chambers.

## 4. Experimental section

### 4.1. Equipment

$^1$H and $^{13}$C NMR spectra were obtained on a Bruker AC 300 spectrometer operating at 300.18 and 75.5 MHz, respectively: chemical shifts are in parts per million and referenced to TMS via the lock signal of the solvent. The following abbreviations were used s (singlet), d (doublet), t (triplet), and m (multiplet). Elemental analyses were performed on an EA1110 Elemental Analyzer CHN Carlo Erba Instruments. Mass Spectrum was recorded with an FTMS 4.7 T BioAPEX II for the MALDI ionization method while HRMS data was obtained with an LTQ Orbitrap XL for ESI (electrospray ionization) mode. UV–vis absorption spectrum of **1** in $CH_2Cl_2$ was recorded on a Perkin–Elmer Lambda 900 spectrometer at room temperature.

### 4.2. Electrochemistry

Dichloromethane (HPLC grade, Acros), $CH_3CN$ (HPLC grade, Aldrich), and tetra-*n*-butylammonium hexafluorophosphate (TBAP, electrochemical grade, Fluka was recrystallised from ethanol).

Cyclic voltammetry (CV) was performed in a three-electrode cell equipped with a platinum millielectrode, a platinum wire counter-electrode, and a silver wire used as a quasi-reference electrode. The electrochemical experiments were carried out under a dry and oxygen-free atmosphere ($H_2O<1$ ppm, $O_2<1$ ppm) in $CH_2Cl_2$ with TBAP (0.1 M) as the supporting electrolyte. The voltammograms were recorded on an EGG PAR 273 A potentiostat with positive feedback compensation. Based on repetitive measurements, absolute errors on potentials were estimated to be $\approx\pm5$ mV.

Concerning the evolution of UV–vis–NIR spectra after successive addition of $NOSbF_6$ aliquots, the experiments were carried out on a Varian Cary 5E spectrophotometer in a 1 mm quartz cell using a solution of **1** ($2\times10^{-4}$ M) in $CH_2Cl_2$ and a solution of $NOSbF_6$ ($6\times10^{-3}$ M) in $CH_3CN$.

### 4.3. Materials

Unless otherwise stated, all reagents were purchased from commercial sources and used without additional purification. 5,6-Diamino-2-(4,5-bis(propylthio)-1,3-dithio-2-ylidene)-benzo[*d*][1,3] dithiole[6d] and 2,5-bis[2-hydroxy-3-(*trans*-1-propeny1)phenyl]-1,3,4-oxadiazol[8] were prepared following the literature procedures. Air- and/or water-sensitive reactions were conducted under nitrogen using dry solvents.

*4.3.1. 2,5-Bis(3-formyl-2-hydroxyphenyl)-1,3,4-oxadiazole.* A solution of 2,5-bis[2-hydroxy-3-(*trans*-1-propenyl)phenyl]-1,3,4-oxadiazol (300 mg, 0.90 mmol)[8] in dioxane (25 mL) was treated with water (9.5 mL), sodium periodate (885.4 mg, 4.14 mmol), and a 2.5% solution of osmium tetroxide in *tert*-butanol (0.71 mL, 0.10 mmol). The mixture was stirred at room temperature for 2 h, and then water (50 mL) was added to the suspension which was kept at 0 °C for 0.5 h. The resulting white solid was filtered off and washed with water (50 mL) to give the analytically pure product as a white powder. Yield 200 mg (72%). $^1$H NMR (DMSO-$d_6$) $\delta$: 7.31 (d, $J$=7.8 Hz, 1H), 8.02 (dd, $J$=7.8 , 1.8 Hz, 1H), 8.28 (dd, $J$=7.8 , 1.8 Hz, 1H), 10.33 (s, 1H), 11.33 (s, 1H). $^{13}$C NMR (DMSO-$d_6$) $\delta$: 111.4, 120.5, 123.3, 134.6, 135.4, 158.6, 161.9, 192.6. Anal. Calcd for $C_{16}H_{10}N_2O_5\cdot0.5H_2O$: C, 60.19; H, 3.47; N, 8.77. Found C, 60.56; H, 3.30; N, 8.69. HRMS (ESI): $[M+H]^+$ calcd 311.0668; found 311.0669.

*4.3.2. TTF-fused macrocycle (**1**).* A solution of 2,5-bis(3-formyl-2-hydroxyphenyl)-1,3,4-oxadiazole (18.6 mg, 0.06 mmol) and 5,6-diamino-2-(4,5-bis(propylthio)-1,3-dithio-2-ylidene)-benzo[*d*][1,3] dithiole[6d] (25.9 mg, 0.06 mmol) in acetonitrile (6 mL) was refluxed for 1 h under $N_2$. The resulting precipitate was filtered off, washed with hot acetonitrile and methanol, and dried under high vacuum to afford analytically pure product as a dark-brown powder. Yield 30.6 mg (72%). $^1$H NMR ($CDCl_3$/TFA-$d_1$ (20:1)) $\delta$: 0.94 (t, 12H), 1.56–1.63 (m, 8H), 2.74 (t, 8H), 7.35 (t, $J$=7.5 Hz, 4H), 7.48 (s, 4H), 7.94 (d, $J$=7.5 Hz, 4H), 8.29 (d, $J$=7.5 Hz, 4H), 8.98 (s, 4H). Selected IR data (KBr, cm$^{-1}$): 3434, 2921, 1621, 1467, 1256, 1022, 748. Anal. Calcd for $C_{64}H_{52}N_8O_6S_{12}\cdot3CH_3OH$: C, 53.29; H, 4.27; N, 7.42. Found C, 53.14; H, 4.01; N, 7.32. MS (MALDI-TOF): $[M+H]^+$ calcd 1413.07; found 1413.10.

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## Supplementary data

Supplementary data associated with this article can be found in online version at doi:10.1016/j.tet.2011.01.011. These data include MOL files and InChIKeys of the most important compounds described in this article.

## References and notes

1. (a) Borisova, N. E.; Reshetova, M. D.; Ustynyuk, Y. A. *Chem. Rev.* **2007**, *107*, 46; (b) Leung, A. C. W.; Hui, JK.-H.; Chong, J. H.; MacLachlan, M. J. *Dalton Trans.* **2009**, 5199; (c) Jiang, J.; MacLachlan, M. J. *Chem. Commun.* **2009**, 5695; (d) Akine, S.; Nabeshima, T. *Dalton Trans.* **2009**, *47*, 10395; (e) Radecka-Paryzek, W. *Can. J. Chem.* **2009**, *87*, 1; (f) Frischmann, P. D.; MacLachlan, M. J. *Comments Inorg. Chem.* **2008**, *29*, 26.
2. (a) Wezenberg, S. J.; Kleij, A. W. *Angew. Chem., Int. Ed.* **2008**, *47*, 2354; (b) Wong, W.-K.; Yang, X.-P.; Jones, R. A.; Rivers, J. H.; Lynch, V.; Lo, W.-K.; Xiao, D.; Oye, M. M.; Holmes, A. L. *Inorg. Chem.* **2006**, *45*, 4340; (c) Yang, X.-P.; Jones, R. A. *J. Am. Chem. Soc.* **2005**, *127*, 7686; (d) Frischmann, P. D.; Gallant, A. J.; Chong, J. H.; MacLachlan, M. J. *Inorg. Chem.* **2008**, *47*, 101; (e) Ray, A.; Pilet, G.; Gómez-García, C. J.; Mitra, S. *Polyhedron* **2009**, *28*, 511; (f) Gupta, K. C.; Sutar, A. K. *Coord. Chem. Rev.* **2008**, *252*, 1420.
3. (a) Hanzlik, R. P. *Inorganic Aspects of Biological and Organic Chemistry*; Academic: New York, NY, 1976; (b) Mascharak, P. K. *Coord. Chem. Rev.* **2002**, *225*, 201; (c) Okawa, H.; Furutachi, H.; Fenton, D. E. *Coord. Chem. Rev.* **1998**, *174*, 51; (d) Singh, D. P.; Grover, V.; Kumar, R.; Jain, K. *J. Enzyme Inhib. Med. Chem.* **2010**, *25*, 445.
4. (a) Boden, B. N.; Abdolmaleki, A.; Ma, C. T.-Z.; MacLachlan, M. J. *Can. J. Chem.* **2008**, *86*, 50; (b) Katsiaouni, S.; Dechert, S.; Brückner, C.; Meyer, F. *Chem. Commun.* **2007**, 951; (c) Tamburini, S.; Sitran, S.; Peruzzo, V.; Vigato, P. A. *Eur. J. Inorg. Chem.* **2009**, *1*, 155; (d) Galbraith, E.; Kelly, A. M.; Fossey, J. S.; Kociok-Koehn, G.; Davidson, M. G.; Bull, S. D.; James, T. D. *New J. Chem.* **2009**, *33*, 181; (e) Arnold, P. L.; Patel, D.; Blake, A. J.; Wilson, C.; Love, J. B. *J. Am. Chem. Soc.* **2006**, *128*, 9610; (f) Kitchen, J. A.; Brooker, S. *Dalton Trans.* **2010**, *39*, 3358.
5. (a) Segura, J. L.; Martín, N. *Angew. Chem., Int. Ed.* **2001**, *40*, 1372; (b) Lorcy, D.; Bellec, N.; Fourmigué, M.; Avarvari, N. *Coord. Chem. Rev.* **2009**, *253*, 1398; (c) Canevet, D.; Sallé, M.; Zhang, G.; Zhang, D.; Zhu, D. *Chem. Commun.* **2009**, 2245.
6. (a) Goze, C.; Leiggener, C.; Liu, S.-X.; Sanguinet, L.; Levillain, E.; Hauser, A.; Decurtins, S. *ChemPhysChem* **2007**, *8*, 1504; (b) Jia, C.-Y.; Liu, S.-X.; Tanner, C.; Leiggener, C.; Sanguinet, L.; Levillain, E.; Leutwyler, S.; Hauser, A.; Decurtins, S. *Chem. Commun.* **2006**, 1878; (c) Goze, C.; Dupont, N.; Beitler, E.; Leiggener, C.; Jia, H.; Monbaron, P.; Liu, S.-X.; Neels, A.; Hauser, A.; Decurtins, S. *Inorg. Chem.* **2008**, *47*, 11010; (d) Jia, C.-Y.; Liu, S.-X.; Tanner, C.; Leiggener, C.; Neels, A.; Sanguinet, L.; Levillain, E.; Leutwyler, S.; Hauser, A.; Decurtins, S. *Chem.—Eur. J.* **2007**, *13*, 3804; (e) Loosli, C.; Jia, C.-Y.; Liu, S.-X.; Haas, M.; Dias, M.; Levillain, E.; Neels, A.; Labat, G.; Hauser, A.; Decurtins, S. *J. Org. Chem.* **2005**, *70*, 4988; (f) Wu, J. C.; Liu, S.-X.; Keene, T. D.; Neels, A.; Mereacre, V.; Powell, A. K.; Decurtins, S. *Inorg. Chem.* **2008**, *47*, 3452.
7. (a) Shimakoshi, H.; Takemoto, H.; Aritome, I.; Hisaeda, Y. *Tetrahedron Lett.* **2002**, *43*, 4809; (b) Akine, S.; Utsuno, F.; Nabeshima, T. *Chem. Commun.* **2010**, *46*, 1029; (c) Yuan, Z.-L.; Zhang, Q.-L.; Liang, X.; Zhu, B.-X.; Lindoy, L. F.; Wei, G. *Polyhedron* **2008**, *27*, 344.

8. Pérez, M. A.; Bermejo, J. M. *J. Org. Chem.* **1993**, *58*, 2628.
9. It was obtained by a new procedure and fully characterized, giving the same analytical data as reported in the literature, Ref. 8. In this case, a highly improved yield has been obtained.
10. Houjou, H.; Lee, S.-K.; Hishikawa, Y.; Nagawa, Y.; Hiratani, K. *Chem. Commun.* **2000**, 2197.
11. (a) Iyoda, M.; Hasegawa, M.; Miyake, Y. *Chem. Rev.* **2004**, *104*, 5085; (b) Jia, H.-P.; Liu, S.-X.; Sanguinet, L.; Levillain, E.; Decurtins, S. *J. Org. Chem.* **2009**, *74*, 5727.
12. (a) Treutler, O.; Ahlrichs, R. *J. Chem. Phys.* **1995**, *102*, 346; (b) Bauernschmitt, R.; Ahlrichs, R. *Chem. Phys. Lett.* **1996**, *256*, 454.
13. Ahlrichs, R.; Bär, M.; Häser, M.; Horn, H.; Kölmel, C. *Chem. Phys. Lett.* **1989**, *162*, 165.