

# Tuning metalloporphyrin and metallophthalocyanine redox potentials using ligand electrochemical ( $E_L$ ) and Hammett ( $\sigma_p$ ) parametrization<sup>☆</sup>

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## Abstract

A compilation and analysis of literature values for a number of iron and chromium tetraphenylporphyrins shows that there is a linear correlation between observed  $M^{III/II}$  potentials and the total contribution of the axial ligand electrochemical parameters,  $\Sigma E_L(L)$ . Substituted iron and chromium phthalocyanine adducts in different coordinating solvents indicate that the potential of the  $M^{III/II}$  redox couple is linearly dependent on  $\Sigma E_L(L)$  and on the total Hammett *para* substituent constant,  $\Sigma \sigma_p$ . The application of this electrochemical model to the design of metallomacrocycles possessing desired values of  $E_{1/2}$  is discussed.  
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**Keywords:** Metalloporphyrins; Metallophthalocyanines; Ligand electrochemical parameter; Hammett parameter

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## 1. Introduction

Porphyrins are the most commonly occurring biological tetrapyrrole macrocyclic ligands and have been the subject of extensive investigation and review [1–5]. In addition to the obvious interest in the biological properties of metalloporphyrins [6] there is also great interest in their catalytic behaviour [7–15]. Fused porphyrin arrays have emerged as potential molecular wires as well as non-linear optical (NLO) materials [16,17]. Porphyrin-type macrocycles have also shown merit in medicine as phototherapeutic agents and radiation enhancers, benefiting various medical fields, such as oncology, cardiology, and dermatology [18–20].

The metallophthalocyanines have long been of great importance in the pigment and dye industry and rank second only to azo colorants in terms of commercial use. Their very special physical and chemical properties make them suitable for numerous applications: ink jet printing, electrophotography, as colorants in colour filters for liquid crystal displays (LCD), electron transport materials for organic semiconductors, organic light emitting devices (OLEDs), photodynamic therapy of malignant tumours, odour removal, catalysts for many purposes, sensors, information recording (CD-R) and NLO devices [21–26].

One of the most fundamental objectives of modern chemistry is the correlation between the structure of compounds and their chemical reactivity. In this paper, we examine the relationship between ligand electrochemical and Hammett parameters with the observed potentials of several metalloporphyrins and phthalocyanines in solution and begin the process of designing molecules with specific electrochemical half-wave potentials,  $E_{1/2}$ . This design information can then be used to tune the redox properties of a given metal complex.

## 2. Hammett and $E_L(L)$ parameter relationships

The application of Hammett parameters [27] to the analysis of the electrochemical potentials of substituted porphyrins has an extensive and successful history [28–43]. The application to substituted metallophthalocyanines, while much less well developed, has also proven successful [34,35,44–46].

These relationships provide a means, in principle, to predict the redox potentials of a wide range of substituted porphyrins and phthalocyanines. However, other important factors are also at work. Very often these redox energies are quite solvent dependent and they will clearly be influenced by the nature of any axial ligands (donor solvents or additional ligands) bound to the central metal sites. Clearly they also depend on the identity, oxidation number, stereochemistry and spin state of the central metal ion [47].

Solvent effects have been explored in some depth [36,38,40–42,48–52] with the shifts in potential usually being related to the Gutmann donor number [53].

It should be possible to use ligand electrochemical parameter,  $E_L(L)$  theory [54–57] to rationalize the effects of an axial interaction through the  $E_L(L)$  value of the axial ligand. Macrocycles were specifically excluded in the initial study [54]

because  $E_L(L)$  parameters are intended to be independent of the metal centre to which they are attached. This cannot be the case for a macrocycle because the ‘hole’ size is a major factor in determining the interaction energy between macrocycle and central metal ion. However, for a given  $M(\text{Mac})$  species, one ought to be able to predict redox energies for a series of  $L_2M(\text{Mac})$  through use of  $E_L(L)$ . Preliminary analysis shows that this idea has promise for phthalocyanine chemistry [26]. One supposes that it will surely also be useful in metalloporphyrin chemistry, but this has not yet been demonstrated in the literature. Rather, previous attempts to correlate the effect of variation of axial ligand has focused upon the  $pK_a$  value of this ligand [41,42,50,58–60].

It is the intent of this publication to show that  $E_L(L)$  parameter theory can indeed be used to rationalize the energies of  $L_2\text{MPc}$  and  $L_2\text{MPor}$  species as a function of varying axial ligand,  $L$ . Further, we investigate two-dimensional correlations for a series of substituted macrocyclic species  $L_2M(\text{R-Pc})$  and  $L_2M(\text{R-Por})$ . The longer term intent is to lead to a multi-dimensional analysis which would include solvent and which could then be used to design metalloporphyrin and metallophthalocyanine complexes with desired redox properties. Fundamental bonding information can also be extracted by analysing the coefficients modifying the Hammett and  $E_L(L)$  parameters. One can also explore their independence or otherwise, that is, whether variation of  $R$  in  $R\text{-Pc}$  modifies the interaction between metal and axial ligand. One might suppose that it will. Spin state also plays an important role which must be incorporated into the model.

Thus we explore whether the potentials of variously substituted metalloporphyrins and metallophthalocyanines can be described by a general equation:

$$E_{1/2} = f \sum E_L(L) + f' \sum \sigma_p + C \quad (1)$$

where  $f$  and  $f'$  are slope coefficients for the respective parameters. Some of the data has been extracted directly from the literature while other data points are new in this publication. Ideally one should use only electrochemically reversible or at least quasi-reversible potentials. Irreversible peak potentials may be essentially coincident with the true reversible potential but without a detailed electrochemical study, one cannot readily prove that assumption. Nevertheless, in view of the relative paucity of data in the literature, we temporarily include peak potentials when they apparently fit a regression set. They are identified as irreversible in the figures and should be treated with caution. There can also be problems being sure of the redox process which is being observed. With axially labile ligands, various equilibria can be set up with solvent, supporting electrolyte and any other ligands which may be added. One cannot assume that the observed redox processes are necessarily arising from the dominant species in solution, e.g. [36,50,52,59,61,62].

There are questions concerning the spin states of each redox partner. The  $\text{XFe}^{\text{III}}\text{TPP}$  species are high spin five-coordinate and remain high spin five-coordinate when they are reduced to  $[\text{XFe}^{\text{II}}\text{TPP}]^-$  [52,63,64]. It is probable that a solvent molecule coordinates weakly in the remaining axial site or displaces the group,  $\text{X}^-$ . Certainly there are rather large variations of potential (shifts of up to 0.3 V or

more) upon variation of solvent and correlating roughly with Gutmann donicity of the solvent [43]. There is no simple correlation with the  $E_L(L)$  parameter of the solvent because the data arise variously from equilibrium mixtures of  $XFeTPP$ ,  $X(sol)FeTPP$  and  $(sol)_2FeTPP$ . Thus the same (weakly coordinating) solvent should be used in considering the  $XFeTPP$  data. Data reported here were recorded in the non-donor solvent dichloromethane.

$E_{1/2}$  values for the di-pyridine species were taken from Table 1 [60]. These are the reduction potentials of  $TPPFeClO_4$  in  $CH_2Cl_2$ , containing 1.0 M of the corresponding substituted pyridine (R-py) wherefrom the redox potentials of the six-coordinate  $[(R-py)_2FeTTP]$  species can be derived. The  $E_{1/2}$  values for these species were found to be linearly related to the  $pK_a$  of the substituted pyridine. The six-coordinate  $L_2FeTPP$  species can be assumed to be low spin in both the  $Fe^{II}$  and  $Fe^{III}$  oxidation states. High spin six-coordinate  $Fe^{II}$  porphyrin species are very uncommon [63] and are not covered here.

The chromium tetraphenylporphyrin data involve  $L_2CrTPP$  and  $L(Cl)CrTPP$  species which are in equilibrium. Kadish and Bottomley analysed these data in depth to extract the appropriate  $E_{1/2}$  values which are reported here. Again there is a correlation between  $E_{1/2}[Cr^{III/II}]$  and the  $pK_a$  of substituted pyridines [58,59]. Similar equilibrium low temperature data from O'Brien and Sweigart [65] are also included.

Table 1 summarizes some preliminary regression data for a selection of phthalocyanine and tetraphenylporphyrin redox couples in Volts versus NHE. The quality of the fits can be visualized in Figs. 1–4 and the raw data from which these regressions are derived is shown in the Appendix.

In many cases the number of redox potentials available is rather small and the regression coefficients should be taken as approximate. In this paper we are solely trying to establish that the methodology does work. Further experimental informa-

Table 1

Summary of regression data for phthalocyanine and tetraphenylporphyrin redox couples in volts versus NHE <sup>a</sup>

Redox process	$f[E_L(L)]$	$f'\sigma_p$	$C$	$R^2$	No. of species
$LFe^{III/II}(TPP)$ (HS)(HS)(HS)	1.56(0.19)	–	0.35(0.05)	0.96	5
$L_2Fe^{III/II}(TPP)$ (LS)	0.95(0.05)	–	–0.14(0.03)	0.97	11
$L_2Cr^{III/II}(TPP)$	0.56(0.04)	–	–0.74(0.02)	0.95	12
$L_2Cr^{III/II}(R-Pc)$	2.17(0.18)	0.21(0.07)	–0.51(0.06)	0.97	8
$L_2Fe^{III/II}(R-Pc)$ (LS)	1.01(0.09)	0.13(0.02)	0.39(0.04)	0.97	7
$L_2Cr^{II}(R-Pc^{-2/-3})$	1.06(0.08)	0.19(0.03)	–1.08(0.03)	0.99	5

<sup>a</sup> Coefficients  $f$  and  $f'$  for Eq. (1). In most cases the paucity of data points indicates that some caution should be exercised in using these data for predictive purposes.

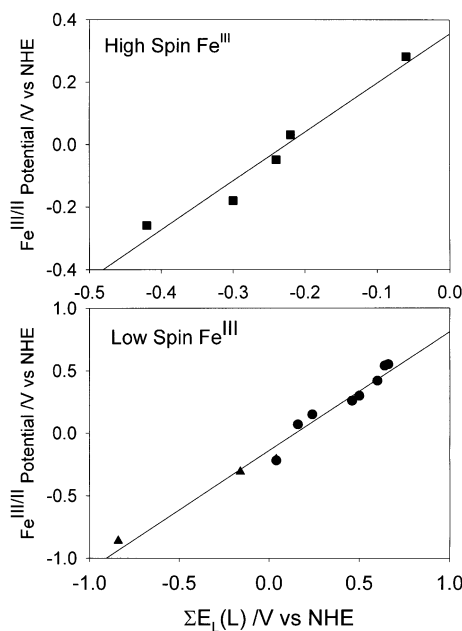


Fig. 1. Plots of the observed  $\text{Fe}^{III/II}$  potentials vs. NHE for high spin (upper graph, square) and low spin (lower graph, circles) iron tetraphenylporphyrin species. The data represented by triangles are derived from irreversible peak potentials and the value may not correspond to the true reversible potential (see text). See Appendix for details of solvent, etc., for all four Figures.

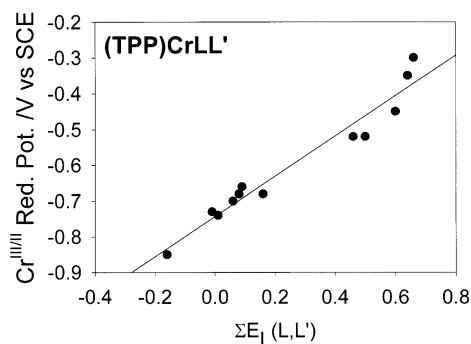


Fig. 2. Plot of the observed  $\text{Cr}^{III/II}$  potentials vs. NHE for chromium tetraphenylporphyrin species.

tion is certainly needed to establish the regression lines with greater certainty. As shown in the Appendix, a variety of solvents has been used by different authors and the scatter seen in some lines may be due to solvent effects which have not been

properly factored out. In most cases the connection to NHE is made through the use of an internal ferrocenium/ferrocene couple using corrections from the literature [44]. Of course some of the solvent effects seen previously [50], with donor solvents,

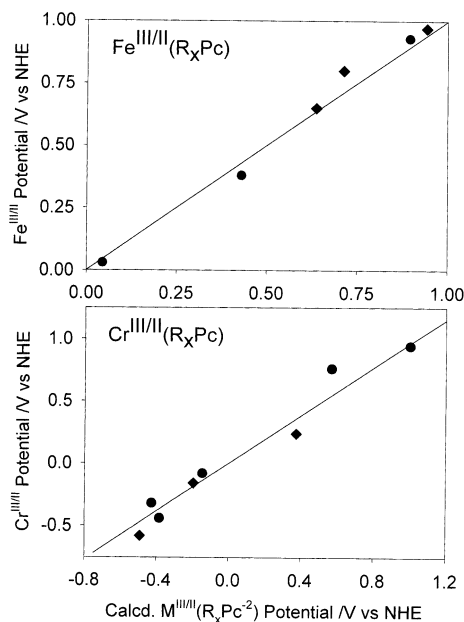


Fig. 3. Plots of the observed  $\text{Fe}^{\text{III/II}}$  (upper) and  $\text{Cr}^{\text{III/II}}$  (lower) potentials vs. NHE, for substituted metallophthalocyanines ( $\text{M}(\text{R}_x\text{-Pc})$ ) versus the calculated potentials according to Eq. (1) and the coefficients in Table 1. The data presented in circles are for  $\text{R} = \text{H}$ , while those represented as diamonds are for  $\text{R}$ -substituted phthalocyanines.

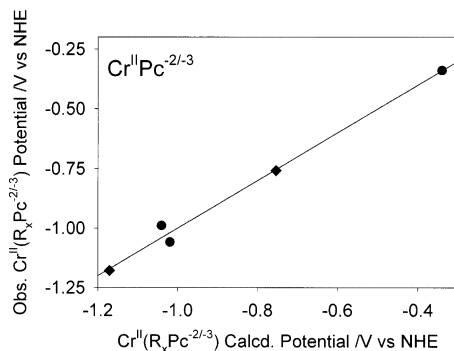


Fig. 4. Plot of the observed phthalocyanine ring reduction  $\text{Cr}^{\text{II}}(\text{R}_x\text{Pc}^{-2/-3})$  potentials versus the potentials calculated according to Eq. (1) in V vs. NHE.

are due simply to the donor solvent occupying an axial site and this will, at least partially, be corrected for via the  $E_L(L)$  parameter of the solvent.

### 3. Summary of results

It is clear from the high regression coefficients shown in Table 1 and the data illustrated in Figs. 1–4, that the general principle of using ligand electrochemical and Hammett parameters to define various redox potentials exhibited by  $L_2M(R-Mac)$  species ( $R-Mac$  = phthalocyanines and porphyrins, but probably more generally includes other macrocycle species) is valid. We hope therefore that this will stimulate others in the field to assemble appropriate collections of data.

With such limited data, it is premature to discuss the trends observed in Table 1 in depth. However, some comments are worthwhile as a means to encourage further work in the field. The Hammett coefficient does not change a great deal and is of similar magnitude to those previously observed [44]. The  $E_L(L)$  coefficient however is quite variable and conveys useful information about the extent of interaction between axial ligand and metal centre. Recall that large coefficients,  $> 1$ , infer that the axial ligand forms a more stable complex with the higher oxidation state ion than with the lower oxidation state ion [54], relative to the  $Ru^{III}/Ru^{II}$  ratio, and vice versa for small coefficients,  $< 1$ .

The coefficient of  $E_L(L)$  is substantially larger for the  $Cr^{III/II}Pc$  couple than it is for the  $Fe^{III/II}Pc$  couple. To conclude that  $Cr^{III}Pc$  binds axial ligands more strongly than low spin  $Fe^{III}Pc$  seems improbable; more likely the larger value for the  $Cr^{III/II}Pc$  couple reflects greater relative binding by low spin  $d^6$   $Fe^{II}$  than low spin  $d^4$   $Cr^{II}$ .

Although these results are preliminary, it is clear that a combined analysis using the Hammett  $\sigma_p$  values to model the substituents, and  $E_L(L)$  parameters to model the axial ligands, is a useful procedure both to design metalloporphyrins or metallophthalocyanines with desired redox properties, and to extract new bonding information therefrom. Studies are in hand to expand the database.

### 4. Web site and supporting information

The data used to construct the Figures and regressions can be found in the Appendix and are also tabulated on our Web site [<http://www.chem.yorku.ca/profs/lever/>] by following the links to this paper.

### Acknowledgements

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## Appendix A. Additional information of figures

For  $M^{III/II}(TPP)$  plots, data are reported as follows: (axial ligands)  $[\Sigma E_L(L)$  (V versus NHE), observed potential (V versus NHE), calculated potential (V versus NHE), experimental conditions]. For  $M^{III/II}(R-Pc)$  plots, data are reported in a similar format, but with slight modification: {peripheral Pc substituent; when not indicated assume remaining substituents are H} (axial ligands)  $[\Sigma E_L(L)$  (V versus NHE),  $\Sigma \sigma_p$ , observed potential (V versus NHE), calculated potential (V versus NHE), experimental conditions]. Literature references are indicated at the end of each entry. These data are presented in tabular form as supporting information for this paper on our web site — <http://www.chem.yorku.ca/profs/lever>

**Figure 1:**  $LFe^{III/II}(TPP)$  (HS)–(F<sup>−</sup>) [−0.42, −0.26, −0.31, (a)]; (N<sub>3</sub><sup>−</sup>) [−0.30, −0.18, −0.12, (a)]; (Cl<sup>−</sup>) [−0.24, −0.05, −0.02, (a)]; (Br<sup>−</sup>) [−0.22, 0.03, 0.01, (a)]; (SCN<sup>−</sup>) [−0.06, 0.28, 0.26, polarogram in DMF]. (a) in CH<sub>2</sub>Cl<sub>2</sub> [52,64].  $L_2Fe^{III/II}(TPP)$  (LS)–(F<sup>−</sup>)<sub>2</sub> [−0.84, −0.86, −0.94, irreversible, in DMSO]; (MeIm/Cl<sup>−</sup>) [−0.16, −0.31, −0.29, irreversible process,  $E_{p,c}$  reported]; (CN<sup>−</sup>)<sub>2</sub> [0.04, −0.22, −0.10, original potential corrected to NHE from Ag/AgNO<sub>3</sub> reference]; (NO<sub>2</sub><sup>−</sup>)<sub>2</sub> [0.04, −0.21, −0.10, in DMF,  $E_{p,c}$  reported]; (MeIm)<sub>2</sub> [0.16, 0.07, 0.01]; (Im)<sub>2</sub> [0.24, 0.15, 0.09, polarogram in DMF, average of  $E_{1/2}$  taken for TPPFe(Im)<sub>2</sub>·X, X = Cl<sup>−</sup>, OAc<sup>−</sup>, SCN<sup>−</sup>; (4-CH<sub>3</sub>py)<sub>2</sub> [0.46, 0.26, 0.30, (b)]; (py)<sub>2</sub> [0.50, 0.30, 0.34, (b)]; (4-OAcpy)<sub>2</sub> [0.60, 0.42, 0.43, (b)]; (4-CNpy)<sub>2</sub> [0.64, 0.54, 0.47, (b)]; (3,5-Cl<sub>2</sub>py)<sub>2</sub> [0.66, 0.55, 0.49, (b)]. (b) TPPFeClO<sub>4</sub> in CH<sub>2</sub>Cl<sub>2</sub>, 1.0 M substituted py [52,60,62,64,66,67].

**Figure 2:**  $L_2Cr^{III/II}(TPP)$ –(MeIm/Cl<sup>−</sup>) [−0.16, −0.85, −0.83, in CH<sub>2</sub>Cl<sub>2</sub> at −91°C]; (4-CH<sub>3</sub>py/Cl<sup>−</sup>) [−0.01, −0.73, −0.75, (c)]; (py/Cl<sup>−</sup>) [0.01, −0.74, −0.74, (c)]; (4-OAcpy/Cl<sup>−</sup>) [0.06, −0.70, −0.71, (c)]; (4-CNpy/Cl<sup>−</sup>) [0.08, −0.68, −0.70, (c)]; (3,5-Cl<sub>2</sub>py/Cl<sup>−</sup>) [0.09, −0.66, −0.69, (c)]; (MeIm)<sub>2</sub> [0.16, −0.68, −0.65, in CH<sub>2</sub>Cl<sub>2</sub>]; (4-CH<sub>3</sub>py)<sub>2</sub> [0.46, −0.52, −0.48, (d)]; (py)<sub>2</sub> [0.50, −0.52, −0.46, (d)]; (4-OAcpy)<sub>2</sub> [0.60, −0.45, −0.41, (d)]; (4-CNpy)<sub>2</sub> [0.64, −0.35, −0.38, (d)]; (3,5-Cl<sub>2</sub>py)<sub>2</sub> [0.66, −0.30, −0.37, (d)]. (c) cyclic differential pulse voltammogram in EtCl<sub>2</sub>, 1.0 M substituted py. (d) in EtCl<sub>2</sub>, 1.0 M substituted py [58,59,65].

**Figure 3:**  $L_2Fe^{III/II}(R-Pc)$  (LS)–{H}<sub>16</sub> (py/OH<sup>−</sup>) [−0.34, 0, 0.03, 0.04, presumably electrogenerated from [PcFe]<sub>2</sub>O]; {H}<sub>16</sub> (CN<sup>−</sup>)<sub>2</sub> [0.04, 0, 0.38, 0.43, [PcFe<sup>III</sup>(CN)<sub>2</sub>]<sup>−</sup> in acetone]; {SO<sub>3</sub><sup>−</sup>}<sub>4</sub> (DMF)<sub>2</sub> [0.06, 1.4, 0.65, 0.64, TsPcFe<sup>II</sup> in DMF]; {CH<sub>3</sub>}<sub>8</sub> (py)<sub>2</sub> [0.50, −1.36, 0.80, 0.71, OMePcFe<sup>II</sup> in py]; {H}<sub>16</sub> (py)<sub>2</sub> [0.50, 0, 0.93, 0.90, PcFe<sup>II</sup> in py]; {Cl}<sub>16</sub> (DMF)<sub>2</sub> [0.06, 3.68, 0.97, 0.94, Cl<sub>16</sub>PcFe<sup>II</sup> in DMF]; {H}<sub>16</sub> (MeCN)<sub>2</sub> [0.68, 0, 0.98, 1.08, PcFe<sup>II</sup> in MeCN] [35,68–73].  $L_2Cr^{III/II}(R-Pc)$ –{*t*-Bu}<sub>4</sub> (DMF)<sub>2</sub> [0.06, −0.80, −0.58, −0.54, TBuPcCr<sup>III</sup>OH in DMF]; {H}<sub>16</sub> (CN<sup>−</sup>)<sub>2</sub> [0.04, 0, −0.32, −0.42, Na[PcCr<sup>III</sup>(CN)<sub>2</sub>] in acetone]; {H}<sub>16</sub> (DMF)<sub>2</sub> [0.06, 0, −0.44, −0.38, PcCr<sup>III</sup>OH in DMF]; {H}<sub>16</sub> (NCS<sup>−</sup>/4-Phpy) [0.17, 0, −0.08, −0.14, titration of K[PcCr<sup>III</sup>(NCS)<sub>2</sub>] with 4-Phpy in acetone]; {SO<sub>3</sub><sup>−</sup>}<sub>4</sub> (DMF)<sub>2</sub> [0.06, 1.4, −0.16, −0.09, TsPcCr<sup>III</sup> in DMF]; {*t*-Bu}<sub>4</sub> (4-CH<sub>3</sub>py)<sub>2</sub> [0.46, −0.80, 0.24, 0.33, titration of TBuPcCr<sup>III</sup>OH with 4-CH<sub>3</sub>py in DMF]; {H}<sub>16</sub> (py)<sub>2</sub> [0.50, 0, 0.76, 0.58, PcCr<sup>II</sup> in py]; {H}<sub>16</sub> (PrCN)<sub>2</sub> [0.70, 0, 0.94, 1.02, PcCr<sup>III</sup>OH in PrCN] [70,74,75].

**Figure 4:**  $L_2Cr^{II}(R-Pc^{-2/-3})$ –{*t*-Bu}<sub>4</sub> (DMF)<sub>2</sub> [0.06, −0.80, −1.18, −1.17, (e)]; {H}<sub>16</sub> (CN<sup>−</sup>)<sub>2</sub> [0.04, 0, −0.99, −1.04, (e)]; {H}<sub>16</sub> (DMF)<sub>2</sub> [0.06, 0, −1.06, −1.02,



(e)];  $\{\text{SO}_3^-\}_4$  (DMF) $_2$  [0.06, 1.4,  $-0.76$ ,  $-0.76$ , (e)];  $\{\text{H}\}_{16}$  (PrCN) $_2$  [0.70, 0,  $-0.34$ ,  $-0.34$ , (e)]. (e) conditions as in  $\text{L}_2\text{Cr}^{\text{III/II}}(\text{R-Pc})$  [70,74,75].

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