View Article Online

Dalton Transactions

Accepted Manuscript

This article can be cited before page numbers have been issued, to do this please use: X. Liang, M. Li, J. Mack, K. Lobb and W. Zhu, *Dalton Trans.*, 2018, DOI: 10.1039/C8DT02510J.



This is an Accepted Manuscript, which has been through the Royal Society of Chemistry peer review process and has been accepted for publication.

Accepted Manuscripts are published online shortly after acceptance, before technical editing, formatting and proof reading. Using this free service, authors can make their results available to the community, in citable form, before we publish the edited article. We will replace this Accepted Manuscript with the edited and formatted Advance Article as soon as it is available.

You can find more information about Accepted Manuscripts in the **author guidelines**.

Please note that technical editing may introduce minor changes to the text and/or graphics, which may alter content. The journal's standard <u>Terms & Conditions</u> and the ethical guidelines, outlined in our <u>author and reviewer resource centre</u>, still apply. In no event shall the Royal Society of Chemistry be held responsible for any errors or omissions in this Accepted Manuscript or any consequences arising from the use of any information it contains.



rsc.li/dalton

YAL SOCIETY CHEMISTRY

Dalton Transactions Accepted Manuscript

Dalton Transitions

ARTICLE

Received 00th January 20xx, Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

www.rsc.org/

Iron(III)Porphyrin Electrocatalyzed Enantioselective Carbon-Chloride Bond Cleavage of Hexachlorocyclohexanes (HCHs): A Combined Experimental Investigation and Theoretical Calculation

Xu Liang,^{*a, b} Minzhi Li,^a John Mack,^{*c} Kevin Lobb^c and Weihua Zhu^{*a, b}

The enantioselective electrocatalysis of α -, β -, γ - and δ -hexachlorocyclohexanes (HCHs) by *tetrakis*-pentafluorophenyl-Fe(III)porphyrin is described. The first example of the combined use of electrochemical measurements and theoretical calculations to determine the mechanism of the enantioselective C–Cl bond cleavage of the electrocatalysis is reported. The electrochemical measurements demonstrate that the reactivity of the HCHs follows the order γ -HCH > α -HCH > δ -HCH > β -HCH. Steric considerations and a molecular orbital theory approach can be used to rationalize the enantioselective nature of the catalysis based on the ease of approach of each Cl atom to the central Fe(I) ion and a considerations of the nodes on the C–Cl bonds that weaken these bonds in a manner that results in bond cleavage and the formation of an Fe–Cl bond.

Introduction

Organochlorides are organic compounds that contain at least one covalent C-Cl bonds have been used in a wide range of applications in the past decades, and the level of agriculture has also been enhanced significantly^[1]. Unfortunately, organochlorides often do not degrade completely in the environment, so despite restrictions being placed on their use in agriculture in many countries, they are still present around the world at significant concentrations as a ubiquitous contaminant in soils and waters^[2]. Recent advances in the study of the carcinogenic properties of organochlorides have demonstrated the need for new techniques to enable the efficient removal of organochlorides. It has been reported that microorganisms can be used to degrade organochlorides, but the formation of further organochloride products and the low efficiency of the degradation has limited further progress with this method^[3]. Recently, the focus of research in this field has moved to C-Cl bond cleavage through photocatalysis^[4] chemical catalysis^[5] and electrochemical catalysis^[6], and several related results have been described on catalyst preparation, structure-property relationships, reaction

intermediates and the mechanism of the degradation processes^[7]. Electrocatalysis with macrocyclic transition metal complexes, such as metallophthalocyanines (MPcs)^[8] and metalloporphyrins^[9] is particularly attractive due to the highly efficient and facile procedures that are involved and the low cost. Typically, when a phthalocyanine is used, a central divalent metal ion is reduced electrochemically to form a $[M^{I}Pc(-2)]^{-}$ species, so it can react with alkyl halides (R-X) to form a σ -bond and a M^{III}-macrocycle, since this results in the release of a chloride ion through the cleavage of a C-Cl bond. For example, the tunable modulation of C-CI bond cleavages can be achieved by changing the macrocyclic $\operatorname{core}^{[10]}$, various substituents. metal center and even magnetic nanomaterials^[11]. Additionally, the full dechlorination of a toxic organochloride, DDT, was successfully carried out through a molecular electrochemical process in 2017^[12]. Further, as well-known organochloride derivatives. hexachlorocyclohexanes (HCHs) describes any of several polyhalogenated organic compounds consisting of a cyclohexane ring with one chlorine and one hydrogen attached to each of the carbon atoms, and there are many isomers for this structure, which differ by the stereochemistry of the Cl atoms^[13].

^a School of Chemistry and Chemical Engineering, Jiangsu University, Zhenjiang 212013, P. R. China.E-mail: <u>liangxu@ujs.edu.cn</u> (to X. Liang); <u>sayman@ujs.edu.cn</u> (to W. Zhu), Tel&Fax: +86-511-8879-1928.

^{b.} State Key Laboratory of Coordination Chemistry, Nanjing University, Nanjing 210000, P. R. China.

^c Department of Chemistry, Rhodes University, Grahamstown 6140, South Africa. Email: j.mack@ru.ac.za (to J. Mack), Tel: +27-46-603-7234.

[†] Electronic Supplementary Information (ESI) available: additional electrochemical and GC-MS data, and structural characterization and theoretical calculation data. See DOI: 10.1039/x0xx00000x

DOI: 10.1039/C8DT02510J Journal Name

ARTICLE

HCHs have been used as models for analyzing the effects of the different geometries of the large Cl atoms and dipolar bonds on the stability of different cyclohexane conformations, such as α -, β -, γ -, and σ -HCHs (**Scheme 1**) are the four most



Scheme 1 Chemical Structure of α -, β -, γ -, and σ -HCHs, a-type bonds were highlighted by red color.

abundant isomers in nature, but the reactivity of these enantiomers is quite different due to the differing arrangements in the axial and equatorial (a- and e-) type bonds



Figure 1 Reductive electrochemical measurement of **1** in the absence (black) and/or presence 1.0 eq of α - (red), β - (blue), γ - (green), and σ - (purple) HCH (left), and plot of i_p/i_{p0} vs the ratio of [HCHs]/[Fe^{III}CIPor], where i_p and i_{p0} are derived from cathodic peak currents in the cyclic voltammograms for the 3rd reduction steps.

in the chair conformer cyclohexane system. The reaction mechanism for the C–Cl bond cleavage reaction during molecular electrochemical catalysis with reduced metalloporphyrin anion species is still not fully understood. In this study, the first example of a combined experimental

investigation and theoretical calculation of enantioselective C–Cl bond cleavage through electrochemical processes is reported. $(TF_5PP)Fe(III)Cl(1)$, an iron porphyrin containing used strongly electron-withdrawing substituents *meso*-aryl rings, is to explore the reaction mechanism in depth.

Experimental

General

solvents All reagents and for electrochemical measurements were of commercial spectroscopically pure grade and were used without further purification except where noted. Cyclic voltammetry measurements were carried out in a three-electrode cell using a Chi-730D electrochemistry station. A glassy carbon disk electrode was used as the working electrode, and the counter and reference electrodes were platinum mesh and a saturated calomel electrode (SCE), respectively. An "H" type cell with a fritted glass layer to separate the cathodic and anodic sections of the cell was used for bulk electrolysis. Both the working and reference electrodes were placed in one compartment while the counter electrode was in the other cell compartment. An Agilent HP6890 GC gas chromatography system with an HP5975-MSD detector was used to separate and identify the products of reductive dechlorination. The catalvtic experimental and the methods used for conditions removing tetrabutylammonium perchlorate (TBAP) from the electrolysis solution prior to the GC-MS measurements are described in the literature.

Computational methods

DFT calculations were carried out for both the dianionic species of **1** and the α -, β -, γ - and δ -HCH isomers by using the Gaussian 09 software package^[14] at the MN12-L/6-31G(d)^[15] and BP86/LANL2DZ/6-31G(d)^[16] level of theory. Transition states were identified by using semi-empirical PM6 calculations^[17] for MN12-L/6-31G(d) optimized structures of the dianionic species of **1** and the α -, β -, γ - and δ -HCH isomers, since several attempts to use a DFT approach proved to be too computationally expensive.

Results and discussions

Electrochemical Characterization

Tetrakis-pentafluorophenyl-Fe(III)porphyrin (1) was selected for study, since the electron withdrawing mesosubstituents stabilize electrogenerated anion radical species that can be used to catalyze the C-Cl bond cleavage of HCHs electrochemical catalysis. Reductive through cvclic voltammetry (CV) measurements were carried out for (TF₅PP)Fe(III)Cl in DMF containing 0.1 M TBAP as a supporting electrolyte at room temperature (Figure 1). Three reversible processes are observed at -0.04, -0.85 and -1.35 V, with metal and porphyrin ring reduction steps leading to the formation of a [Fe¹Por]²⁻ species. As has been reported previously, reduced metalloporphyrin π -anions generally

Published on 23 July 2018. Downloaded by Nagoya Daigaku on 7/30/2018 2:42:23 PM

Published on 23 July 2018. Downloaded by Nagoya Daigaku on 7/30/2018 2:42:23 PM



enhance the rate of electrochemical reactions^[9]. Upon addition of 1.0 eq of hexchlorocyclohexane (HCH), little or no change is observed in the CV measurements for β -HCH. When σ -, α - and γ -HCHs were used, however, which have one, two and three a-type C-Cl bond, respectively, there is a stepwise increase in the peak current, and this clearly illustrates that there is a relationship between the intensity of the electrochemical response and the number of a-type bonds. An increase in the reduction peak current for the [Fe^lPor]⁻/[Fe^lPor]]²⁻ process is observed as a function of increasing HCHs concentration (**Figure 1**, right), where i_{p} and i_{p0} are the measured cathodic peak currents obtained from the CV of the porphyrin in the presence and absence of different concentration of HCHs. The order of the i_p/i_{p0} ratio in DMF solutions containing the same concentration of **1** is γ -HCH > α -HCH > σ -HCH > β -HCH. This also provides evidence that the observed trends in the reaction rates between the doubly reduced [Fe¹Por]²⁻ species and the different HCHs is related to which isomers contain the largest number of a-type C-Cl bonds.

Spectroelectrochemical Characterization

In situ spectroelectrochemical measurements were also out. The [Fe^lPor]²⁻ dianion carried species was electrogenerated from [Fe^{III}CIPor] in the presence of four different types of HCH, and the spectral changes were monitored to provide a better understanding of the mechanism of the C-Cl bond cleavage. The UV-visible absorption spectra of the electrochemical reduced [Fe'Por] anion are shown in Figure 2. The controlled potential was set at -1.05V so that **1** can be completely reduced to the $[Fe^{I}Por]^{2-1}$ species^[18]. The progress of the catalytic reaction was monitored by measuring the UV-visible spectra as a function of time. The [Fe^lPor]⁻ species has a single Soret band at 423 nm in DMF and three visible region bands at 500, 566, and 630 nm,

while the doubly reduced [Fe^lPor]⁻ anion has a split Soret band at 384 and 423 nm in the absence of HCHs as shown in Figure 2, along with an additional broad absorption band at 590 nm in the Q band region. Similar spectral transformations were observed upon addition of 5.0 eq of β -HCH, and this indicates that there is no significant interaction between β -HCH and doubly reduced [Fe[']Por]⁻ anion under these reaction conditions. Interestingly, significant spectral changes were observed upon the addition of 5.0 eq of γ -HCH. There is a decrease in the intensity of the Soret band at 423 nm, and a shoulder band absorption is observed at 440 nm. When α - and σ -HCHs were used instead, similar spectral changes were observed, but the intensity of the shoulder band weakens so that γ -HCH > α -HCH > σ -HCH. This can be attributed to the decrease in the number of a-type C-Cl bonds in the HCH system.



Figure 3 Time-dependent distribution of electrochemical catalyzed C–Cl bond cleavage of HCHs in DMF during controlled-potential reduction of (a) α -HCH at –1.70 V; (b) isomeric distribution of trichlorobenzenes for the α -HCH electrolysis; (c) γ -HCH at –1.70 V; (d) isomeric distribution of trichlorobenzenes in γ -HCH electrolysis.

Controlled-Potential Bulk Electrolysis

Controlled-potential bulk electrolysis was carried out in DMF solution containing $1 (2.0 \times 10^{-4} \text{ M})$, 0.1 M TBAP and 15.0 eq α -, β -, and γ -HCH (3.0 × 10⁻³ M). The bulk electrolysis potential was set at -1.70 V which is sufficient to generate the triply reduced dianion species [Fe¹Por]²⁻ and also to reduce the anticipated homogeneously generated σ -bonded [Fe^{III}Por]⁺-HCH products. After 6 h of electrolysis, no change was observed by GC-MS when β -HCH was used as the starting material, while in contrast, α - and γ -HCH had disappeared from solution within 5 and 4 h, respectively (Figure 3). The of pentachlorocyclohexane (PCCH), presence tetrachlorocyclohexadiene (TCDN) and trichlorobenzene (TCB) and their geometric isomers was confirmed as intermediates or final products of the C–Cl bond cleavage reaction of α -HCH (Figure 3). In contrast, TCDN was not observed when γ -HCH was used instead. The distribution of the geometric isomers of Published on 23 July 2018. Downloaded by Nagoya Daigaku on 7/30/2018 2:42:23 PM

DOI: 10.1039/C8DT02510J Journal Name



Figure 4 A transition state for the higher energy ring flip conformation of δ -HCH involving the abstraction of a Cl by proximal C–Cl bond cleavage (**A**). The favoured pathway for Fe–Cl bond formation for steric reasons involves the approach of an a-type Cl atom to the central Fe ion of the porphyrin ring is illustrated by using the highest energy conformation of δ -HCH (**B**), while that of an e-type Cl atom is not possible (**C**). This is illustrated with the structure of β -HCH.

trichlorobenzenes could be determined by GC-MS through comparison with standard samples, and the 1,2,4trichlorobenzene was confirmed to be present at a higher ratio (**Figure 3** and **Figure S1**, see ESI⁺). Finally, in order to confirm whether trichlorobenzenes are the final C–CI bond cleavage products, reductive electrochemical measurements were carried out in DMF containing 0.1 M TBAP (**Figure S2**, see ESI⁺). Little to no electrochemical changes were observed for all of the reductive electrochemical measurements of [Fe^{III}CIPor] **1** upon addition of 1.0 eq of 1,3,5-, 1,2,4- and 1,2,3trichlorobenzenes, and this indicates that the electrochemical catalyzed C–CI bond cleavage reactions stop at this point due to the greater stability aromatic sp² hybridized C(sp²)–CI bond (**Figure S2**, see ESI⁺).

Quantum Chemical Calculations

A series of modelling calculations were carried out to study the interaction between the $[Fe^{I}Por]^{2^{-}}$ species and the various HCH conformations to identify transition states (**Table 1**). Details for these transition states including the results of normal coordinate analyses and Cartesian coordinates are provided as supplemtary information (**Table S1**, see ESI⁺). Low spin resulting in a singly occupied $3d_z^2$ MO on the central Fe^I ion was assumed, since DFT calculations indicated that this provides an energetically favored triplet multiplicity for the ring and metal reduced $[Fe^{I}Por]^{2^{-}}$ species. Various DFT methods including MN12-L and BP86/LANL2DZ/6-31G(d) mixed basis based scans of HCHs, demonstrated that the increasing proximity of CI to the porphyrin Fe center resulted in a marked weakening of both local and remote C–CI bonds, sometimes resulting in extremely low or barrierless transitions in which the Cl atom is lost. The reason for this is clear. The $3d_{z2}$ electron density is distributing in a highly antibonding LUMO and is hence weakening one or more C-Cl bonds. Raised energy transitions at the semi-empirical PM6 level make it possible for transition states to be identified for C-Cl bond cleavage in close proximity to the Fe atom (Figure 4, top). An a-type Cl atom is most suitable for this for steric reasons, in particular an a-type chlorine with no adjacent e-type chlorine atoms. Although the approach of e-type C-Cl bonds is less favored for steric reasons, it is also possible when there is either none or only one adjacent e-type C-Cl bonds. As shown in the bottom left part of Figure 4, the abstraction of an axial chlorine atom from the highest energy conformation of δ -HCH can be readily achieved in this manner, but a similar approach is not possible in the case of β -HCH due to hindered access of the e-type Cl atom to the central Fe¹ ion (Figure 4, bottom right). This provides an obvious reason why there is no electrochemical reaction when β -HCH is used under the same reaction conditions.

Transition State and Energy Calculation

The essential requirement for the formation of a pentachlorocyclohexyl radical is the release of a Cl radical (representative atomic spin densities are provided in the ESI⁺) through an interaction with the singly occupied $3d_{22}$ orbital of the Fe(I) ion, so the approach of the C-H bond to the iron center to form an unstable Fe-C bond is also possible if the adjacent Cl atom is transferred to the porphyrin ring (Figure 5). The formation of a positively charged carbon atom is required on the porphyrin ring after the subsequent abstraction of the chlorine atom to complete this pathway, but in terms of energetics the simple abstraction of a chlorine atom by the iron center is generally more energetically favorable when the transition states that were identified in PM6 calculations are taken into consideration (Table 1). In the context of the higher energy conformation of δ -HCH (Figure 5), the second process is energetically less favorable by ca. 30 kcal/mol.

Molecular Orbital Calculations

The relative reactivities of the four isomeric HCH structures can be readily rationalized based on an inspection of the angular nodal patterns of the antibonding LUMO of the HCH (Figure 6) that interacts with the $3d_{z2}$ orbital of the Fe(I) ion. The formation of transition states based on Fe-Cl bond formation is facilitated by the presence of a LUMO on the HCH which is anti-bonding with respect to several of the C-Cl bonds. The local cleavage mechanism for the C-Cl bond cleavage of HCHs through the formation of pentachlorocyclohexyl and chlorine radicals requires unhindered access of a chlorine atom to the electrochemically reduced iron porphyrin center. An example of the spin densities for this process is provided as supplementary information. The LUMO for the solitary y-HCH ring flip conformation has larger nodes on the a-type Cl atoms and smaller nodes on two of the e-type Cl atoms (Figure 6). Thus there are three major orientations and two minor ones with which an interaction with the central Fe(I) ion is likely to result

Dalton Transactions Accepted Manuscript

Journal Name

in reactivity. Statistically, this increases the possibility of a successful interaction compared to α -HCH since for α -HCH, the lower energy conformation has large LUMO nodes on only two a-type Cl atoms and smaller nodes on two e-type Cl atoms, while the higher energy conformation has large LUMO nodes on four a-type Cl atoms (**Figure 6**). This means that although there are several possibilities for a successful orientation leading to reactivity from a steric standpoint, overall an interaction with the Fe¹ ion is not as likely as it is for γ -HCH.

Although the higher energy conformation of δ -HCH has strong LUMO nodes on five CI atoms and a small LUMO node

on the remaining substituent, the 1,3-diaxial interactions make this conformation highly disfavored in energy terms as is clear from the A value of 2.15 kcal/mol (**Figure 6**), which is determined using the difference in the Gibbs free energy for aand e-type C–Cl bonds in mono-substituted cyclohexanes and a consideration of the number of both types of bond in the structures of the various structures in **Figure 6**. The lower energy conformation of δ -HCH has favorable LUMO nodes on four substituents, but the steric requirements for these three e**Figure 5** A transition state for the higher energy ring flip conformation of δ -HCH involving the abstraction of a CI atom via CI transfer to a *meso*-carbon of the porphyrin ring (**A**). Relative free energies for this example of weak Fe–C bond formation relative to the formation of a Fe–CI bond with the lower energy δ -HCH conformer (**B**).

Table 1. Relative energies (kcal/mol) of the transition states formed by the dianionic species of **1** and α -, β -, γ - and δ -HCHs that were identified during PM6 calculations. All energies are in kcal/mol

Fe–H interaction			
	HCH-1 associated	Lower energy conformer ^a	Higher energy conformer ^a
α-HCH	0.1	15.4	
β-НСН			
ү-НСН	0.0	23.8	
δ-НСН	1.1	19.4	29.2
		16.3	22.7
		31.5	
		29.2	
Fe–Cl bond formation			
α-HCH	0.1	18.0	8.2
β-НСН	0.0		-4.3
ү-НСН	-8.0	-5.4	
		4.6	
		1.5	
δ-НСН	-15.8	-4.2	
		7.8	
		-3.4	

a - The energies of the transition states were calculated relative to the free energies of the 1 and HCH isomer structures prior to their interaction.



DOI: 10.1039/C8DT02510J

Journal Name

Published on 23 July 2018. Downloaded by Nagoya Daigaku on 7/30/2018 2:42:23 PM.

Published on 23 July 2018. Downloaded by Nagoya Daigaku on 7/30/2018 2:42:23 PM.

Dalton Transitions

ARTICLE



Figure 6 Angular nodal patterns of the LUMOs of the lower and higher energy (LE and HE) ring flip conformations of α -, β -, γ - and δ -HCHs at the level of theory. As the number of a-type C–Cl bonds increases there is an increase in the A value (kcal/mol) and the conformation becomes increasingly disfavored in energetic terms. The number of a- and e-type C–Cl bond for each conformation is described along with the number in parentheses of e-type bonds with either none (0adj-e) or only one (1adj-e) adjacent e-type C–Cl bond.

type CI atoms to interact with the porphyrin are too high, due to their equatorial nature and the presence of further adjacent e-type Cl atoms. As such, there is effectively only one node available that can easily react with the Fe¹ ion, since the weakening of two of the C-Cl bonds is not possible due to the absence of nodal planes. For the highly energetically favored all-e-type Cl atom conformation of β -HCH (**Figure 6**), accessibility to the Fe^l ion of the porphyrin center is highly problematic for steric reasons. From the standpoint of the number of a-type C–Cl bonds alone, the β -HCH would be expected to be the most reactive in terms of the LUMO alone, since the LUMO has nodes over all of the Cl atoms (Figure 6) and a favorable transition state was identified in the PM6 calculations (Table 1). This conformation is highly energetically disfavored, however, due to the 1,3-diaxial interactions that result in an A value of 2.43 kcal/mol. Further to this, there may also be symmetry considerations that come into play, since if the C–Cl bonds are all weakened equally, no individual bond is weakened sufficiently for facile cleavage.

Conclusions

The use of molecular electrocatalysis for the dechlorination of α -, β -, γ - and δ -hexachlorocyclohexanes (HCHs) in the presence of the dianionic species of *tetrakis*-pentafluorophenyl-Fe(III)porphyrin has been analyzed through electrochemical measurements and theoretical calculations. The reactivity of the HCHs follows the order γ -HCH > α -HCH > δ -HCH > β -HCH. Steric considerations related to differing numbers of a- and e-type bonds in the possible ring flip conformations for each isomer and the ease of approach of each chlorine atom to the central Fe(I) ion, along with the effect of the magnitude of the nodes on each C–Cl bond in the LUMOs of the HCHs on relative bond strengths, can be used to

DOI: 10.1039/C8DT02510J

fully rationalize the enantioselective nature of the electrocatalysis.

Acknowledgements

Financial support was provided by the National Scientific Foundation of China (No. 21701058), NSFC of Jiangsu province of China (no. BK20160499) and the fund from the State Key Laboratory of Coordination Chemistry (SKLCC1710, SKLCC1817), the fund from Key Laboratory of Functional Inorganic Material Chemistry (Heilongjiang University) of Ministry of Education to XL and WZ, and a National Research Foundation (South Africa) CSUR grant (93627) to JM. The theoretical calculations were carried out at the Centre for High Performance Computing in Cape Town.

Notes and references

Published on 23 July 2018. Downloaded by Nagoya Daigaku on 7/30/2018 2:42:23 PM

- 1 a) G. Famiglini, P. Palma, E. Pierini, H. Trufelli and A. Cappiello, *Anal. Chem.*, 2008, **80**, 3445; b) N. Durán, E. Esposito. *App. Catal. B: Environ.*, 2000, **28**, 83.
- 2 a) A. Solano, C. Araújo, J. Melo, J. Peralta-Hernandez, D. Silva, C. Martínez-Huitle. *App. Catal. B: Environ.*, 2013, 7, 112;
 b) F. Moreira, R. Boaventura, E. Brillas, V. Vilar. *App. Catal. B: Environ.*, 2017, 202, 217.
- 3 a) E. Brillas, C. Martínez-Huitle. App. Catal. B: Environ., 2015, 166–167, 603; b) J. Nelson, J. Jiang, S. Zinder, Environ. Sci. Technol., 2014, 48, 3776.
- 4 a) S. Pavlostathis, M. Prytula, Environ. Sci. Technol., 2000, 34 4001; b) X. Fan, L. Zang, M. Zhang, H. Qiu, Z. Wang, J. Yin, H. Jia, S. Pan, C. Wang, Chem. Mater., 2014, 26, 3169; c) M. Humayun, Y. Qu, F. Raziq, R. Yan, Z. Li, X. Zhang, L. Jing, *Environ. Sci. Technol.*, 2016, 50, 13600.
- 5 a) E. Patterson, C. Cramer, D. Truhlar, J. Am. Chem. Soc., 2001, 123, 2025; C. Baumanis, J. Bloh, R. Dillert, D. Bahnemann, J. Phys. Chem. C, 2011, 51, 25442; b) H. Choi, S. Al-Abed, S. Agarwal, Environ. Sci. Technol., 2009, 43, 4137; c) N. Lombard, U. Ghosh, B. Kjellerup, K. Sowers, Environ. Sci. Technol., 2014, 48, 4353.
- a) K. McCauley, D. Pratt, S. Wilson, J. Shey, T. Burkey, van der Donk, J. Am. Chem. Soc., 2005, 127, 1126; b) X. Mao, A. Ciblak, M. Amiri, A. Alshawabkeh, Environ. Sci. Technol., 2011, 45 6517; c) A. Matsunaga, A. Yasuhara, Environ. Sci. Technol., 2003, 37, 3435.
- 7 a) J. Fritsch, K. McNeill, *Inorg. Chem.*, 2005, 44, 4852; b) W.
 Zhu, T. Huang, M. Qin, M. Li, J. Mack, X. Liang, *J. Electroanal. Chem.*, 2016, 774, 58; c) K. Jeon, N. Lee, S. Bae, W. Goddard III, H. Kim, W. Lee, *J. Phys. Chem.* A, 2015, 119, 5714.
- 8 a) A. Krzemińska, P. Paneth, *Environ. Sci. Technol.*, 2016, **50**, 6293; b) J. Wen, B. Yu, T. Huang, J. Mack, M. Wildervanck, T. Nyokong, M. Li, W. Zhu, X. Liang, *J. Electroanal. Chem.*, 2017, **803**, 111.
- 9 a) J. Shao, A. Thomas, B. Han, C. Hansen, J. Porphyrins Phthalocyanines, 2010, 14, 133; b) M. Li, L. Liang, C. Ni, X. Liang, W. Zhu, J. Electroanal. Chem., 2016, 766, 135.
- 10 a) L. Ukrainczyk, M. Chibwe, T. Pinnavaia, S. Boyd, *Environ. Sci. Technol.*, 1995, **29**, 439; b) P. Afanasiev, A. Sorokin, *Acc. Chem. Res.*; 2016, **49**, 583; c) C. Gantzer, L. Wackett, *Environ. Sci. Technol.*, 1991, **25**, 715–722.
- 11 W. Zhu, T. Huang, M. Li, L. Zheng, S. Bao, X. Liang, ChemistrySelect, 2017, 2, 645.
- 12 X. Liang, T. Huang, M. Li, J. Mack, M. Wildervanck, T. Nyokong, W. Zhu, Appl. Cat. A, 2017, 545, 44.

- 13 J. Moisey, A. Fisk, K. Hobson, R. Norstrom, *Environ. Sci. Technol.*, 2001, **35**, 1920.
- 14 M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, M. J. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, Ö. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski and D. J. Fox, Gaussian 09, Revision D.01, Gaussian, Inc., Wallingford, CT, 2009.
- 15 R. Peverati, D.G. Truhlar, Phys. Chem. Chem. Phys., 2012, 14., 13171.
- 16 a) A. D. Becke, Phys. Rev. A, 1988, 38, 3098; b) J. Perdew, Phys. Rev. B, 1986, 33, 8822.
- 17 J. J. P. Stewart, J. Mol. Model., 2007, 13, 1173.
- 18 a) K. Kadish, E. Caemelbecke, F. D'Souza, C. Medforth, K. Smith, A. Tabard, R. Guilard, *Inorg. Chem.*, 1995, 34, 2984; b)
 K. Araki, H. Toma, *J. Electroanal. Chem.*, 1991, 297, 301; c) K. Araki, H. Toma, *Electrochim. Acta*, 1999, 44, 1577.