

# Reductive dechlorination of DDT electrocatalyzed by synthetic cobalt porphyrins in *N*,*N*'-dimethylformamide

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**ABSTRACT:** Two cobalt porphyrins, (OEP)Co<sup>II</sup> and (TPP)Co<sup>II</sup>, where OEP and TPP are the dianions of octaethylporphyrin and tetraphenylporphyrin, respectively, were examined as electrocatalysts for the reductive dechlorination of DDT (1,1-bis(4-chlorophenyl)-2,2,2-trichloroethane) in *N*,*N*'-dimethylformamide (DMF) containing 0.1 M tetra-*n*-butylammonium perchlorate (TBAP). No reaction is observed between DDT and the porphyrin in its Co(II) oxidation state but this is not the case for the reduced Co(I) forms of the porphyrins which electrocatalyze the dechlorination of DDT, giving initially DDD (1,1-bis(4-chlorophenyl)-2,2-dichloroethane), DDE (1,1-bis(4-chlorophenyl)-2, 2-dichloroethylene) and DDMU (1,1-bis(4-chlorophenyl)-2-chloroethylene) as determined by GC-MS analysis of the reaction products. A further dechlorination product, DDOH (2,2-bis(4-chlorophenyl) ethanol), is also formed on longer timescales when using (TPP)Co as the electroreduction catalyst. The effect of porphyrin structure and reaction time on the dechlorination products was examined by GC-MS, cyclic voltammetry, controlled potential electrolysis and UV-visible spectroelectrochemistry and a mechanism for the reductive dechlorination is proposed.

**KEYWORDS:** cobalt porphyrins, electrochemistry, spectroelectrochemistry, DDT, electrocatalysis, reductive dechlorination.

### INTRODUCTION

DDT (1,1-bis(4-chlorophenyl)-2,2,2-trichloroethane) was widely used for three decades as a potent pesticide for controlling malaria, typhus and other insect borne diseases but its use in agriculture has been banned in many countries since the mid-1970s because its exposure to human and wildlife can result in severe health problems [1–4]. Unfortunately, DDT is resistant to degradation in the environment and is still present in significant quantities in soil and water at numerous locations around the world. For this reason, research and development into new techniques for the degradation of DDT by various

methods of dechlorination have attracted a great deal of interest in recent years [5–15].

It has long been known that macrocycles containing transition-metal ions can be used as catalysts for the reductive dehalogenation of organohalides [16–31]. One example is vitamin  $B_{12}$  [15] which has been examined as a catalyst for the biomimetic reductive dechlorination of chlorinated pollutants such as DDT. The reduced Co(I) form of this porphyrin-like macrocycle can act as a supernucleophile which reacts with organohalides to form alkylated Co(III) complexes while also accomplishing dehalogenation [15, 25–28]. Other examples of cobalt macrocycles which have been studied as dehalogenation catalysts include phthalocyanines [19, 32] and porphyrins [16, 33].

Most cobalt(III) and cobalt(II) porphyrins can be reversibly reduced to their Co(I) forms under the application of an applied potential [34–37] and the compound in

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this oxidation state will react with alkyl halides (RX) to give the  $\sigma$ -bonded Co(III) porphyrin [31, 38] which can be further reduced to its Co(II) form as shown by Equations 1–4 where Por represents the dianion of a given porphyrin. The dechlorination step occurs in reaction 3.

$$[(Por)Co^{m}]^{+} + e \rightleftharpoons (Por)Co^{ll}$$
(1)

$$(Por)Co^{II} + e \rightleftharpoons [(Por)Co^{I}]^{-}$$
(2)

$$[(Por)Co^{I}]^{-} + RX \rightleftharpoons (Por)Co^{II}(R) + X^{-}$$
(3)

$$(Por)Co^{III}(R) + e \rightleftharpoons [(Por)Co^{II}(R)]^{-}$$
(4)

If the resulting Co(III) or Co(II)  $\sigma$ -bonded porphyrins formed in Equations 3 and 4 are unstable, a cleavage of the cobalt-carbon bond will occur to generate the monodechlorinated axial ligand in its anionic or radical forms (R<sup>-</sup> or R<sup>+</sup>) and [(Por)Co<sup>III</sup>]<sup>+</sup> or (Por)Co<sup>II</sup>, the latter of which is immediately reduced to its Co(I) form (Equation 2) under the application of an applied potential sufficient to reduce the homogeneously generated (Por)Co(R) (Equation 4). The newly formed [(Por)Co<sup>I</sup>]<sup>-</sup> can then further react with the original organohalide compound in solution or it can react with its dechlorinated product if it also contains a halogen group. This suggests that simple synthetic cobalt(II) porphyrins might be used as efficient catalysts for the electroreductive multiple dechlorination of DDT.

This is examined in the present paper using (OEP)Co<sup>II</sup> and (TPP)Co<sup>II</sup> as electrocatalysts, where OEP and TPP

(a) Cobalt porphyrins



(b) DDT and its dechlorinated products



**Chart 1.** Structures of (a) cobalt porphyrins and (b) DDT along with its dechlorinated products

are the dianions of octaethylporphyrin and tetraphenylporphyrin, respectively (Chart 1a). Each porphyrin was reduced to its cobalt(I) form and reacted with DDT in solutions of N,N'-dimethylformamide (DMF) containing 0.1 M tetra-*n*-butylammonium perchlorate (TBAP). The resulting dechlorination products are shown in Chart 1b and were identified by GC-MS analysis. The effect of porphyrin structure and reaction time on the dechlorination products were also examined by cyclic voltammetry, controlled potential electrolysis and UV-visible spectroelectrochemistry and a mechanism for the reductive dechlorination is proposed.

### **EXPERIMENTAL**

#### Chemicals

The cobalt porphyrins (OEP)Co and (TPP)Co and the chlorinated hydrocarbons, 1,1-bis(4-chlorophenyl)-2,2,2-trichloroethane (DDT), 1,1-bis(4-chlorophenyl)-2,2dichloroethylene (DDE) and 1,1-bis(4-chlorophenyl)-2,2dichloroethylene (DDMU) were purchased from Sigma-Aldrich and used as received. *N,N*-dimethylformamide (DMF) was purchased from Sigma-Aldrich and used as received or from Shanghai Guoyao Co. and freshly distilled before use. Tetra-*n*-butylammonium perchlorate (TBAP) was purchased from Fluka Chemical Company and used without further purification. Other solvents were of analytical grade and obtained from Shanghai Guoyao Co.

#### Instrumentation

Cyclic voltammetry was performed in a three-electrode cell using a BiStat or Chi-730C electrochemistry station. A glassy carbon disk electrode was utilized as the working electrode while a platinum wire and a saturated calomel electrode (SCE) were employed as the counter and reference electrodes, 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. The working and counter electrodes were made from platinum mesh and the reference electrode was an SCE. Both the working and reference electrodes were placed in one compartment while the counter electrode was in other compartment of the cell.

Before GC-MS measurements, a pre-treatment procedure for removing TBAP from the electrolysis solution was utilized. The solution was transferred into a 150 mL flask and evaporated to remove the DMF solvent under vacuum at 45 °C in a roto-evaporator. Cyclohexane was then added in the flask containing the residue to extract DDT and its possible dechlorinated products. After stirring and centrifuging, the TBAP supporting electrolyte was removed and the solution was subjected to the GC-MS analysis. GC-MS system Model HP6890-GC and HP5975-MSD was utilized to separate and identify the products of catalytic reductive dechlorination. The GC was equipped with an HP-5 5% phenyl methyl siloxane column (length 30 m, ID 250  $\mu$ m, film 0.25  $\mu$ m). Temperature programming was applied to the GC analysis. The initial temperature was 100 °C and increased at a rate of 15 °C/ min to 300 °C. An area-normalized method was applied for analysis of the peaks. The molar response factor of DDT was defined as 1.00 and the relative values for DDE, DDD and DDMU were measured as 1.076 ± 0.039, 0.934 ± 0.053, 1.003 ± 0.031, respectively.

UV-visible spectroelectrochemical measurements were performed with a home-made optically transparent thin-layer cell with Pt mesh as the working electrode. The potential was applied using a BiStat or Chi-730C potentiostat. Time-resolved UV-visible spectra were recorded with a HP 8453A diode array spectrophotometer. All electrochemical and spectroelectrochemical measurements were carried out under a nitrogen atmosphere.

### **RESULTS AND DISCUSSION**

### Cyclic voltammetry of $(Por)Co^{II}$ in the absence and presence of DDT

The electrochemical properties of (OEP)Co<sup>II</sup> and (TPP)Co<sup>II</sup> were previously characterized in DMF containing 0.1 M TBAP [39, 40]. Both porphyrins undergo a reversible one-electron reduction under these experimental conditions to give [(Por)Co<sup>I</sup>]<sup>-</sup> at  $E_{1/2} = -0.78$  V (Por = TPP) or -0.99 V (Por = OEP) (see Equation 2). A one-electron reduction is also seen in other non-aqueous solvents and this process may be followed by electrogeneration of a cobalt(I) porphyrin  $\pi$ -anion radical at potentials close to the negative limit of the non-aqueous solvent [36, 41–49].

The Co<sup>II</sup>/Co<sup>I</sup> reaction of (OEP)Co and (TPP)Co becomes irreversible in DMF when DDT is added to the solution as shown by the cyclic voltammograms in Figs 1 and 2. At the same time, the reduction peak current for the Co<sup>II</sup>/Co<sup>I</sup> process increases with increasing concentration of DDT while the reverse anodic peak for re-oxidation of [(Por)Co<sup>I</sup>]<sup>-</sup> disappears. This is consistent with the occurrence of a catalytic process involving DDT and the electrogenerated Co(I) porphyrin to give a  $\sigma$ -bonded Co(III) derivatives as shown in Equation 3. Similar oxidative addition reactions have been shown to occur between simple alkyl or aryl halides and the electrogenerated Co(I) form of different cobalt macrocycles [15, 25–30, 38, 46, 50].

Additional irreversible reduction peaks are observed following the Co<sup>II</sup>/Co<sup>I</sup> reduction of (Por)Co<sup>II</sup> in the DMF solutions containing DDT. These are indicated by asterisks in the cyclic voltammograms of Figs 1 and 2 and are assigned to irreversible reductions of one or more



**Fig. 1.** Cyclic voltammograms of (OEP)Co  $(1.15 \times 10^{-3} \text{ M})$  with added 0.0–1.0 eq DDT and DDT (0.02 M) in the absence of catalyst in DMF containing 0.1 M TBAP. Scan rate = 0.10 V/s. The peak with as asterisk is associated with a product of the initial reduction

σ-bonded Co(III) porphyrins which are generated from the reaction of  $[(Por)Co^{I}]^{-}$  and DDT. For example, (TPP)Co<sup>III</sup>(R) where R = CH<sub>3</sub>, C<sub>2</sub>H<sub>5</sub> or CH<sub>2</sub>Cl is reduced at  $E_{1/2} \approx -1.40$  V in CH<sub>2</sub>Cl<sub>2</sub> [46] and this potential is about 600 mV more negative than for reduction of (TPP)Co<sup>II</sup> ( $E_{1/2} = -0.78$  V) under the same solution conditions.

The increase in reduction peak current for the Co<sup>II</sup>/Co<sup>I</sup> process of (Por)Co as a function of increasing DDT concentration is shown in Fig. 3, where  $i_p$  and  $i_{p0}$  are the measured cathodic peak currents obtained from cyclic voltammograms of the porphyrin in the presence and absence of DDT, respectively. The measured  $i_p/i_{p0}$  ratio is larger for (OEP)Co than for (TPP)Co in DMF solutions containing a given DDT concentration and suggests that the rate to regenerate the corresponding catalyst is larger for [(OEP)Co<sup>I</sup>]<sup>-</sup> than [(TPP)Co<sup>I</sup>]<sup>-</sup>. This observation is not consistent with the thermodynamic ease for generating



**Fig. 2.** Cyclic voltammograms for the first reduction of (TPP) Co  $(7.49 \times 10^{-4} \text{ M})$  with added 0.0–2.0 eq DDT in DMF containing 0.1 M TBAP. Scan rate = 0.10 V/s. The peak with an asterisk is associated with a product of the initial reduction



**Fig. 3.** Plot of  $i_p/i_{p0}$  vs the ratio of [DDT]/[(Por)Co], where  $i_p$  and  $i_{p0}$  are the measured cathodic peak currents obtained from cyclic voltammograms for the first reduction of (Por)Co in the presence and absence of DDT in DMF containing 0.1 M TBAP

the Co(I) species since the first reduction of (OEP)Co is located at  $E_{1/2} = -0.99$  V while (TPP)Co is reduced to [(TPP)Co<sup>I</sup>]<sup>-</sup> at -0.78 V, implying that factors other than thermodynamic potentials dominate the catalytic process.

### Controlled-potential electrolysis and GC-MS analysis

In order to determine the products of DDT dechlorination, controlled-potential bulk electrolysis was carried out in DMF solutions containing  $2.0 \times 10^{-4}$  M (Por)Co<sup>II</sup>, 0.1 M TBAP and 15 eq DDT ( $3.0 \times 10^{-3}$  M). The bulk electrolysis potential was set at -1.70 V which is sufficient to generate the singly reduced species [(Por)Co<sup>I</sup>]and also to reduce the expected homogeneously generated  $\sigma$ -bonded Co(III) porphyrin products.

Because the TBAP supporting electrolyte and its decomposition components formed during the high temperature GC process will block the column and prevent determination of the DDT dechlorination products, it was necessary to first remove all TBAP from solution before it could be examined by GC analysis. The procedure adopted for solution "pre-treatment" in this present work is shown in Scheme 1. After each hour of electrolysis at a given reduction potential, 1.0 mL solution was removed from the H-cell and pretreated for GC-MS analysis. Most of the TBAP in solution was successfully removed after which the product distribution of DDT and its dechlorinated products was determined by GC-MS. Well-defined GC data from these solutions were obtained as shown by the examples in Figs 4 (OEP) and 5 (TPP). The distribution of DDT and its dechlorinated products, DDD, DDE, DDMU and DDOH were calculated from the chromatographic data and are summarized in Table 1. The distribution as a function of time is also graphically illustrated in Fig. 6.

As seen from Table 1 and Fig. 6, 15 eq DDT are completely removed from the solution within 6–8 h after starting bulk electrolysis at an applied potential of -1.70 V. Three main DDT dechlorinated products (DDD, DDE and DDMU) are detected during the first 6 h of electrolysis, when using (OEP)Co as the catalyst and an additional dechlorinated product, DDOH, is also seen in the case of (TPP)Co. These four dechlorinated products were the only ones observed after 4 h or longer of electrolysis time (see Fig. 6b).

The DDT distribution decreased as expected with increased reaction time and no DDT remained in solution after 6–8 h of bulk-electrolysis. The measured distribution of DDD was 11.1% after one hour in solutions of (OEP)Co and 8.7% in solutions of (TPP)Co. Both solutions showed a maximum amount of DDD formation (~30%) after 4 h and then this value leveled off as seen in Table 1 and Fig. 6.

The DDE distribution was 6.1% after one hour of electrolysis with the (OEP)Co catalyst, 13% with the (TPP)Co catalyst and in both cases reached a maximum of about 30% before decreasing at longer times. The



**Scheme 1.** The procedure for reductive dechlorination of DDT catalyzed by cobalt(II) porphyrins



**Fig. 4.** GC analysis of the DDT and its dechlorinated products during the controlled-potential electrolysis at -1.70 V using (OEP)Co as the catalyst

same time, the DDMU distribution increased continuously over the 8 h of electrolysis and ranged from 4.1% after one hour in the case of (OEP)Co to 44.7% after 6 h. This distribution data implies that DDE is initially formed after which DDMU is generated at longer times of electrolysis. Similar changes in the DDD and DDE distribution were obtained for the two porphyrins as a function of time but different distribution are seen for DDMU and DDOH, the latter of which is only seen for the (TPP)Co catalyst and is accompanied by a decrease in the distribution of DDMU after 8 h of electrolysis.

It summary, three main dechlorinated products are detected when DDT reacts with singly reduced (OEP)Co but four products are seen when using (TPP)Co as the catalyst. Furthermore, the type, number and the distribution of the dechlorinated products depends not only on the catalyst used but also varies with the reaction time.

### Spectroelectrochemical monitoring of the reduction products and proposed mechanism for dechlorination of DDT

The fate of [(Por)Co<sup>I</sup>]<sup>-</sup> electrogenerated from (Por)Co in the presence of DDT was spectroelectrochemically monitored to provide a better understanding of the DDT reduc-

tive dechlorination mechanism. The UV-visible spectra of  $[(Por)Co]^{n+}$  where n = 3, 2 or 1 are known for Por = OEP and TPP as are the spectra for (TPP)Co(R) where R is a simple alkyl or aryl group. Thus the progress of the catalytic reaction could be monitored by measuring



**Fig. 5.** GC analysis of the DDT and its dechlorinated products during the controlled-potential electrolysis at -1.70 V using (TPP)Co as the catalyst

Compound	Rxn time, h	Distribution, % <sup>a</sup>				
		DDT	DDD	DDE	DDMU	DDOH
(OEP)Co	0.0	100.0	0.0	0.0	0.0	0.0
	1.0	78.8	11.1	6.1	4.1	0.0
	2.0	58.1	19.7	12.3	9.9	0.0
	3.0	30.1	27.5	25.6	16.8	0.0
	4.0	15.5	30.2	28.7	25.6	0.0
	5.0	3.9	29.9	30.6	35.6	0.0
	6.0	0.0	30.2	25.1	44.7	0.0
(TPP)Co	0.0	100.0	0.0	0.0	0.0	0.0
	1.0	72.0	8.7	13.0	6.2	0.0
	2.0	55.4	16.8	16.9	10.9	0.0
	3.0	32.2	24.4	23.2	20.2	0.0
	4.0	15.2	27.7	27.8	26.3	3.0
	5.0	4.1	29.0	29.6	33.5	3.7
	8.0	0.0	30.6	13.4	28.9	27.2

Table 1. Analysis data of DDT and its dechlorinated products obtained at different reaction time during the controlled-potential electrolysis at -1.70 V

<sup>a</sup> Distribution (%) = [(moles of a specific compound)/(moles of all compounds)]  $\times 100\%$ .



**Fig. 6.** Distribution of DDT and its dechlorinated products obtained in DMF at different electrolysis time during controlled-potential reduction of (a) (OEP)Co and (b) (TPP)Co at -1.70 V

the UV-visible spectra as a function of time during the electroreduction.

Neutral (OEP)Co in DMF has a Soret band at 393 nm and two visible bands at 525 and 547 nm while (TPP)Co is characterized by a Soret band at 414 nm and a broad visible band at 520 nm. The two cobalt(I) porphyrins both display a split Soret band and these spectra are observed during the Co<sup>II</sup>/Co<sup>I</sup> process in the absence of DDT as shown in Fig. 7 where  $\lambda_{max} = 354$  and 414 nm for [(OEP)Co<sup>I</sup>]<sup>-</sup> and at 365 and 432 nm for [(TPP)Co<sup>I</sup>]<sup>-</sup>. Similar spectral transformations have been reported in

the literature for reduction of related cobalt(II) porphyrins in other non-aqueous solvents [44, 47].

No spectral changes are seen when DDT is added to solutions containing unreduced (OEP)Co<sup>II</sup> or (TPP)Co<sup>II</sup>, indicating the lack of a reaction with the neutral cobalt porphyrins. However, the spectra of the electroreduced compounds change significantly in solutions containing DDT. As seen from Fig. 7, the Soret band of (OEP)Co (393 nm) and (TPP)Co (414 nm) both decrease in intensity during controlled potential reduction, but the split Soret band characteristic of Co(I) formation is not observed in



**Fig. 7.** Thin-layer UV-visible spectral changes obtained during the first reduction of (a) (OEP)Co<sup>II</sup> and (b) (TPP)Co<sup>II</sup> without or with DDT in DMF containing 0.1 M TBAP



Scheme 2. Proposed mechanism of DDT dechlorination catalyzed by cobalt porphyrins

the solutions containing DDT. Instead the final spectrum obtained from the reduction of (OEP)Co or (TPP)Co displays a Soret band at 390 or 410 nm, respectively, and this spectrum is assigned to the transient formation of a (Por)Co<sup>III</sup>(R) species. A similar spectrum has been reported for (TPP)Co<sup>III</sup>( $C_2H_5$ ) which has a Soret band at 407 nm [46].

In summary, the electrochemistry, spectroelectrochemistry and GC analysis of the dechlorinated products suggest the proposed catalytic cycle for reductive dechlorination of DDT which is illustrated in Scheme 2. The neutral (OEP)Co<sup>II</sup> and (TPP)Co<sup>II</sup> initially undergo a oneelectron reduction to yield the corresponding cobalt(I) complex,  $[(Por)Co^{I}]^{-}$  which then reacts with DDT to generate the organometallic intermediate with a Co-C  $\sigma$  bond, (Por)Co<sup>III</sup>(R). This intermediate can undergo a photoinduced cleavage of the Co-C bond leading to DDD or DDE and the unreduced Co<sup>II</sup> or Co<sup>III</sup> porphyrins which would then be immediately reduced under the application of an applied reducing potential. The  $\sigma$ -bonded Co(III) porphyrin can also be reduced by one-electron to form a  $[(Por)Co^{II}(R)]^{-}$  species at the applied potential of -1.70 V after which the electrogenerated  $\sigma$ -bonded Co(II) compound will undergo a cleavage of the Co-C bond leading to formation of DDD as shown in the last reaction step of Scheme 2.

### CONCLUSION

Cyclic voltammetry, controlled potential bulk electrolysis and thin-layer UV-visible spectroelectrochemistry of (OEP)Co<sup>II</sup> and (TPP)Co<sup>II</sup> in the presence of DDT show that the two singly reduced porphyrins, represented as [(Por)Co<sup>I</sup>]<sup>-</sup>, will catalyze the dechlorination of DDT to generate DDD, DDE, DDMU as well as some less chlorinated products on longer electrolysis timescales. The Co(I) forms of the reduced porphyrins will also react with DDT leading to the formation of intermediates having a Co-C  $\sigma$  bond, but a cleavage of the bond will occur with formation of the DDT dechlorination products.

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### REFERENCES

- 1. Beard J. Sci. Total Environ. 2006; 355: 78-89.
- 2. Rogan W and Chen A. Lancet 2005; 366: 763–773.
- 3. Sharma VP. Curr. Sci. 2003; 85: 1532–1537.
- Turusov V, Rakitsky V and Tomatis L. *Environ. Health Perspect.* 2002; **110**: 125–128.
- Quensen III JF, Mueller SA, Jain MK and Tiedje JM. Science 1998; 280: 722–724.

- Gautam SK and Sumathi S. *Environ. Technol.* 2006; 27: 387–394.
- Wang YS, Chiu TC and Yen J. Organohalogen Compd. 2004; 66: 2232–2236.
- Huang HJ, Liu SM and Kuo CE. J. Environ. Sci. Health., Part B 2001; B36: 273–288.
- Kitamura S, Yoshida M, Sugihara K and Ohta S. J. Health Sci. 1999; 45: 217–221.
- Sayles GD, You G, Wang MX and Kupferle MJ. Environ. Sci. Technol. 1997; 31: 3448–3454.
- Purnomo AS, Koyama F, Mori T and Kondo R. Chemosphere 2010; 80: 619–624.
- Gfrerer M and Lankmayr E. J. Chromatogr. A 2005; 1072: 117–125.
- Gach PC, Mubarak MS, Karty JA and Peters DG. J. Electrochem. Soc. 2007; 154: F1–F6.
- 14. Mubarak MS, Gach PC and Peters DG. *Electroanalysis* 2006; **18**: 417–422.
- Hisaeda Y and Shimakoshi H. In *Handbook of Porphyrin Science*, Vol. 10, Kadish KM, Smith KM and Guilard R. (Eds.) World Scientific: New Jersey, 2010; Chapter 48, pp 313–370.
- Alonso F, Beletskaya IP and Yus M. Chem. Rev. 2002; 102: 4009–4091.
- Argüello JE, Costentin C, Griveau S and Savéant J-M. J. Am. Chem. Soc. 2005; 124: 5049–5055.
- Davies TJ, Garner AC, Davies SG and Compton RG. J. Electroanal. Chem. 2004; 570: 171–185.
- Zhou DL, Gao J and Rusling JF. J. Am. Chem. Soc. 1995; 117: 1127–1134.
- Ukrainczyk L, Chibwe M, Pinnavaia TJ and Boyd SA. *Environ. Sci. Technol.* 1995; 29: 439–445.
- Maldotti A, Amadelli R, Bartocci C, Carassiti V, Polo E and Varani G. *Coord. Chem. Rev.* 1993; 125: 143–154.
- Krone UE, Thauer RK, Hogenkamp HPC and Steinbach K. *Biochemistry* 1991; 30: 2713–2719.
- 23. Gantzer CJ and Wackett LP. *Environ. Sci. Technol.* 1991; **25**: 715–722.
- 24. Rusling JF, Miaw CL and Couture EC. *Inorg. Chem.* 1990; **29**: 2025–2027.
- 25. Jabbar A, Shimakoshi H and Hisaeda Y. Chem. Commun. 2007; 1653–1655.
- 26. Shimakoshi H, Tokunaga M, Baba T and Hisaeda Y. *Chem. Commun.* 2004; 1806–1807.
- Shimakoshi H, Tokunaga M and Hisaeda Y. Dalton Trans. 2004; 878–882.
- Pratt DA and Van der Donk WA. *Chem. Commun.* 2006; 558–560.
- 29. Shimakoshi H, Tokunaga M, Kuroiwa K, Kimizuka N and Hisaeda Y. *Chem. Commun.* 2004; 50–51.
- Shimakoshi H, Nakazato A, Tokunaga M, Katagiri K, Ariga K, Kikuchi J-I and Hisaeda Y. *Dalton Trans.* 2003; 2308–2312.
- Kadish KM, Franzen MM, Han BC, Araullo-McAdams C and Sazou D. *Inorg. Chem.* 1992; 31: 4399–4403.

- 32. Shao JG, Thomas A, Han BC and Hansen CA. *J. Porphyrins Phthalocyanines* 2010; **14**: 133–141.
- 33. Imaoka T, Takatsuka T and Yamamoto K. *J. Porphyrins Phthalocyanines* 2006; **10**: 1066–1070.
- Zhu WH, Sintic M, Ou ZP, Sintic PJ, McDonald JA, Brotherhood PR, Crossley MJ and Kadish KM. *Inorg. Chem.* 2010; 49: 1027–1038.
- Kadish KM, Shao JG, Ou ZP, Comte C, Gros CP and Guilard R. J. Porphyrins Phthalocyanines 2000; 4: 639–648.
- Sazou D, Araullo-McAdams C, Han BC, Franzen MM and Kadish KM. *J. Am. Chem. Soc.* 1990; **112**: 7879–7886.
- Kadish KM, Van Caemelbecke E and Royal G. In *The Porphyrin Handbook*, Vol. 8, Kadish KM, Smith KM and Guilard G. (Eds.) Academic Press: New York, 2000; Chapter 55, pp 1–114.
- Maiya GB, Han BC and Kadish KM. *Langmuir* 1989; 5: 645–650.
- Zhu WH, Zhao XF, Ou Z, Zhou F, Wang XH and Kadish KM. J. Porphyrins Phthalocyanines 2009; 13: 1233–1242.
- 40. Dobson DJ and Saini S. Anal. Chem. 1997; 69: 3532–3538.

- 41. Truxillo LA and Davis DG. *Anal. Chem.* 1975; **47**: 2260–2267.
- 42. Walker FA, Beroiz D and Kadish KM. *J. Am. Chem. Soc.* 1976; **98**: 3484–3489.
- 43. Kadish KM, Bottomley LA and Beroiz D. *Inorg. Chem.* 1978; **17**: 1124–1129.
- 44. Mu XH, Lin XQ and Kadish KM. *Electroanalysis* 1989; **1**: 113–116.
- 45. Araullo-McAdams C and Kadish KM. *Inorg. Chem.* 1990; **29**: 2749–2757.
- 46. Kadish KM, Han BC and Endo A. *Inorg. Chem.* 1991; **30**: 4502–4506.
- D'Souza F, Villard A, Van Caemelbecke E, Franzen M, Boschi T, Tagliatesta P and Kadish KM. *Inorg. Chem.* 1993; **32**: 4042–4048.
- Kadish KM, Guo N, Van Caemelbecke E, Paolesse R, Monti D and Tagliatesta P. J. Porphyrins Phthalocyanines 1998; 2: 439–450.
- 49. Kadish KM, Ou ZP, Tan XY, Boschi T, Monti D, Fares V and Tagliatesta P. J. Chem. Soc., Dalton Trans. 1999; 1595–1601.
- 50. Guilard R and Kadish KM. *Chem. Rev.* 1988; **88**: 1121–1146.