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## Metalloporphyrins: their multitasking nature as observed in multi-metal complex systems

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Five topics pertaining to the unique chemistry of metalloporphyrins as observed in multi-metal complex systems are introduced. The topics include the following: (i) the unique chromatographic separation of cyclic porphyrins on modified silica gel; (ii) room temperature phosphorescence from the zinc porphyrin part in a zinc porphyrin/rhenium complex hetero dyad; (iii) the substituent effect, in the preparation of a readily soluble special-pair-type zinc porphyrin dimer/rhenium complex having efficient photocatalytic CO<sub>2</sub> reduction ability; (iv) assessment of the excited triplet state of a special-pair-type zinc porphyrin dimer in macrocyclic multiporphyrin rings; and (v) solvation/desolvation indicators based on exclusive transformation between the head-head type and head-tail type of supramolecular co-ordination polymers composed of bis(zinc porphyrin)s.

### Introduction

Since 1960, more than four thousand papers relating to the term “metalloporphyrin” have been published (based on the Web of Science database, up to October 2022). A third of the papers are classified as multidisciplinary in chemistry, indicating that metalloporphyrins are ubiquitous in chemistry. Why do metalloporphyrins appear in various areas of chemistry? One of the reasons is that they are multitasking molecules—they have good photo-electronic properties, rich co-ordination chemistry, rigid and hydrophobic natures, amongst others. Their multitasking nature is particularly evident when in combination with other functional molecules and materials. For more than two decades, our interest has included multiple porphyrin systems.<sup>1,2</sup> During this period, we often encountered unexpected phenomena arising from the intrinsic properties of metalloporphyrins. The latter are minor in single molecules, but they are more evident in multi-molecule systems and multi-metal complex systems. In this article, we introduce some recently discovered unique features pertaining to metalloporphyrin chemistry, derived from our unexpected observations.

### Topics

#### Unique chromatographic separation of cyclic porphyrins

Catalytic multi-electron reduction systems are important for the transformation of small molecules, such as carbon dioxide and nitrogen, to higher energy chemicals. Multi-metal com-

plexes, in which more than two metal complexes work synergistically, are expected to be suitable candidates for multi-electron reduction systems. With such a concept in mind, we designed a cyclic multiporphyrin array linked with 2,2'-bipyridyl moieties, as shown in Fig. 1.

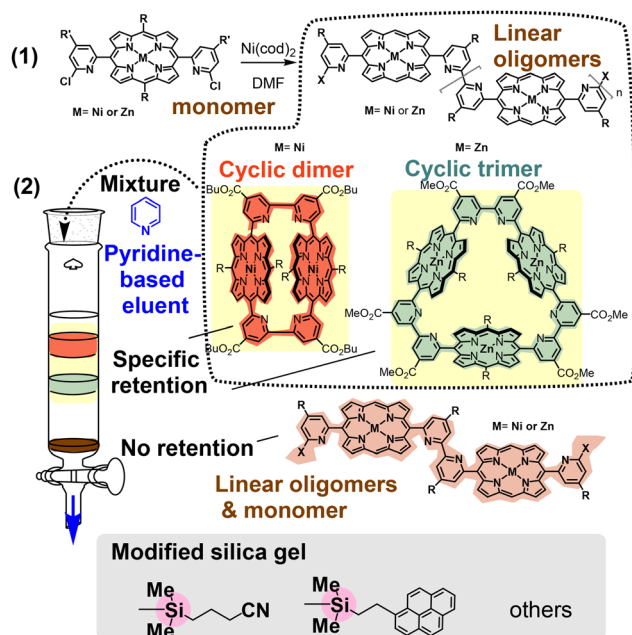
After reductive coupling of bis(chloropyridyl)porphyrinato-zinc using low-valence nickel species, mixtures of acyclic porphyrin oligomers were obtained, along with the target cyclic trimer. Efficient isolation of the cyclic trimer was difficult to achieve using conventional silica gel chromatography and gel permeation chromatography. After the elimination of by-products from the crude mixture, the isolated yields of the target compounds were found to be very low. Under this problematic situation, unexpected specific retention on modified silica gel columns was observed. When using a pyridine-based eluent, only cyclic porphyrin trimers were retained on cyanopropyl-modified silica gel, whereas other acyclic porphyrins were eluted with no retention.<sup>3,4</sup> This feature is convenient because now even small quantities of cyclic compounds could be quantitatively separated from mixtures. The limitations and principles of this type of specific retention were investigated (investigations are ongoing). We determined that the existence of more than two porphyrins, tightly linked by two appropriate spacers to make a ring, is essential. It is not only the distance between porphyrins but also the rigidity of the ring that affects their retentions.<sup>5</sup> A more detailed study that includes consideration of the mechanism and solvent effect for the unique chromatographic separation is described in our recent paper.<sup>6</sup>

#### Room temperature phosphorescence from the zinc porphyrin-1,10-phenanthroline rhenium dyad

Porphyrins have been used as photosensitizers in photoredox reactions due to their high visible light absorption ability. We

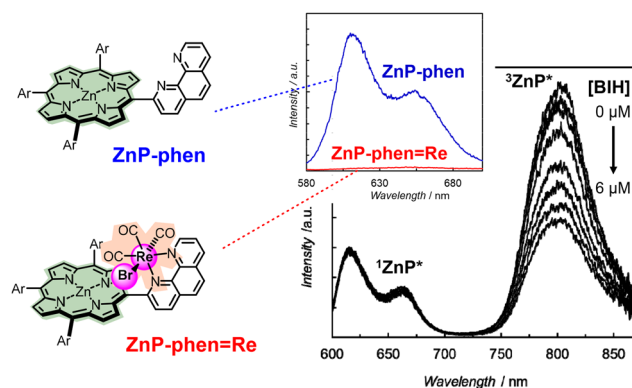
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**Fig. 1** Schematic representation of the unique chromatographic separation of cyclic porphyrins. (1) The reductive coupling reaction afforded mixtures of linear and cyclic porphyrin oligomers. (2) On a cyanopropyl-modified silica gel column, using pyridine-based eluent, only cyclic porphyrins were retained, specifically.

combined zinc porphyrin (ZnP) with a 1,10-phenanthroline (phen) rhenium diimine tricarbonyl complex (Re) as a catalyst to perform the photochemical  $\text{CO}_2$  reduction. The hetero dyad, ZnP-phen=Re, selectively affords CO as the reduction product of  $\text{CO}_2$  with high efficiency ( $\Phi_{\text{CO}} = 8\%$ , turnover number  $>1300$ ).<sup>7,8</sup> During our studies, using the hetero dyad, we found that the fluorescence of the zinc porphyrin precursor (ZnP-phen) was almost completely quenched by the introduction of the Re complex part and the zinc porphyrin part of ZnP-phen=Re showed room temperature phosphorescence (RTP) in an Ar-saturated solution (Fig. 2). In general, zinc porphyrin



**Fig. 2** Structures of ZnP-phen and ZnP-phen=Re. Emission spectra of ZnP-phen: only fluorescence, no room temperature phosphorescence (RTP). Emission spectra of ZnP-phen=Re (2  $\mu\text{M}$ ): very little fluorescence, RTP.

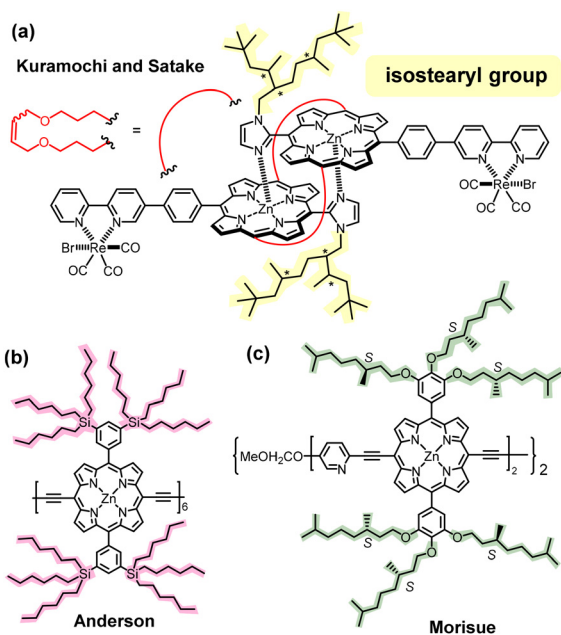
is known to undergo intersystem crossing from the excited singlet state ( $S_1$ ) to the excited triplet state ( $T_1$ ) with high efficiency, while RTP from the  $T_1$  to the ground singlet state ( $S_0$ ) of zinc porphyrin is not observed in solution. The RTP of the zinc porphyrin part of ZnP-phen=Re would be caused by spin-orbit coupling imposed by the heavy rhenium atom. The quenching experiment of RTP, by an electron donor, demonstrated that the efficient photocatalytic  $\text{CO}_2$  reduction results from the quantitative electron transfer from the electron donor (BIH: 1,3-dimethyl-2-phenyl-2,3-dihydro-1H-benzo[d]imidazole) to the long-lived  $T_1$  of the zinc porphyrin part. We are currently engaged in synthesizing several forms of the hetero dyads, in which a rhenium diimine complex is connected with zinc porphyrin through different positions of the diimine ligand, in efforts to obtain detailed mechanistic insight into the RTP and the relationship between the catalytic activity of  $\text{CO}_2$  reduction and the RTP.<sup>9</sup>

### Substituent effect in the special-pair-type porphyrin dimer and rhenium hetero dyads

Slipped-cofacial supramolecular zinc porphyrin dimers were originally synthesized by Kobuke and Miyaji as mimics of the special pair in the reaction centre of natural photosynthetic systems.<sup>10</sup> Their application was investigated by their group, and by the authors. Since the porphyrin dimers are constructed by complementary co-ordination from the imidazolyl to a zinc ion, larger structures such as macrocyclics<sup>11</sup> and wire-like assemblies<sup>12</sup> are relatively easily prepared by dynamic equilibrium, followed by covalent linking *via* a ring-closing olefin metathesis reaction using Grubbs' catalyst.<sup>13,14</sup> Another interesting feature of the zinc porphyrin dimers is observed in the case of photoinduced electron transfer. As both positive and negative charges in one-electron oxidized and reduced species are delocalized over the two porphyrins in a dimer, both the one-electron oxidized and reduced states are stabilized.<sup>15</sup> This feature accelerates the charge separation (CS) rate constant and decelerates the charge recombination (CR) rate constant.<sup>16</sup> This favourable nature could be applicable to photocatalysts. In fact, an excellent photocatalytic system was finally prepared for  $\text{CO}_2$  reduction, in which a rhenium carbonyl complex was connected to a special-pair-type zinc porphyrin dimer (Fig. 3a).<sup>17</sup> It is thought that the photocatalytic  $\text{CO}_2$  reduction reaction proceeds *via* the stabilized CS state between the porphyrin dimer and the rhenium complex. Details of catalytic reactions are not described here, but we would like to highlight the aspect of substituents on an imidazolyl group.

During the development of the dyad system, solubility problems arose. The solubility of *N*-methyl imidazolyl derivatives was too low to achieve transformation of the corresponding covalently linked dimer. In general, porphyrin derivatives tend to undergo self-aggregation by the interaction of a negatively polarized large  $\pi$ -electron system and a positively polarized peripheral hydrogen. With an increase in porphyrin and other metal complex components in a molecule, successive Coulombic interactions tend to occur, with accompanying des-





**Fig. 3** (a) Structure of the special-pair-type zinc porphyrin dimer and rhenium dyad. The asterisks in the isostearyl group indicate asymmetric carbons. (b) 3,5-Bis(trihexylsilyl)phenyl-appended porphyrin derivative. (c) 3,4,5-Tri((S)-3,7-dimethyloctyloxy)phenyl-appended porphyrin derivative.

olvation, even in a good solvent. To overcome the solubility problem, a highly branched  $C_{18}$  substituent—specifically, a unique isostearyl group—was introduced to the imidazolyl group. (The isostearyl substituent is simply derived from FINEOXOCOL 180, available from Nissan Chemical Corporation, Tokyo, Japan.) Because the isostearyl group has three chiral centres, various diastereomers would be produced, in special pair-type dimers. However, no difference among the diastereomers was observed in UV-vis spectra and from the reduction and oxidation potentials. All the diastereomers produced mixtures of complementary co-ordination dimers by random combination.

As a result, the solubility of the dimers was significantly increased by the introduction of only an isostearyl group per porphyrin derivative. Probably, it is not only the introduction of bulky substituents but also the heterogeneity of the diastereomers that contributes to the solubility. In solution chemistry, using multi-metalloporphyrin arrays, some achiral and chiral bulky substituent groups are adopted, to dissolve the porphyrin arrays, as shown in Fig. 3b and c.<sup>18,19</sup> The introduction of a highly branched isostearyl group containing diastereomers is a cost-effective method to solubilize the porphyrin-rhenium dyads.

#### Assessment of the triplet state of a special-pair-type porphyrin dimer in macrocyclic multiporphyrin ring molecule systems

Meta-phenylene-linked trisporphyrin, in which both terminal zinc porphyrins have imidazolyl groups, afforded the macrocyclic multiporphyrin ring ( $\text{FbP-ZnP}_2$ )<sub>3</sub>, where three special-

pair-type zinc porphyrin dimers and three free-base porphyrins are alternatively linked (Fig. 4).<sup>20</sup> The fluorescence spectra of ( $\text{FbP-ZnP}_2$ )<sub>3</sub> in various solvents revealed the following: in non-polar toluene, photoinduced energy transfer between the zinc porphyrin dimer and the free-base porphyrin occurs; in polar *N,N*-dimethylformamide, photoinduced electron transfer from the zinc porphyrin dimer to the free-base porphyrin occurs. As various types of metal ions can be introduced into the free-base porphyrin moieties, the cyclic porphyrin array has great potential to produce various heterometallic porphyrin arrays. In the macrocyclic structure, distances and orientations among the porphyrins are fixed. Therefore, conformational fluctuation can be eliminated. As described in the previous section, no phosphorescence from zinc porphyrin is observed generally, although the dominant excited state exists as a triplet. The special-pair-type zinc porphyrin dimer can also undergo intersystem crossing from the  $S_1$  to the  $T_1$  with high efficiency. It is then expected that the  $T_1$ , due to its long lifetime, can efficiently lead to intermolecular electron and energy transfers to donor/acceptor molecules by diffusion collision. However, in contrast to the case of the  $S_1$ , which can be monitored by steady-state fluorescence spectroscopy, observation of the  $T_1$  with conventional spectroscopy is difficult because phosphorescence from the dimer is not observed at room temperature. It has been reported that a phenylene-linked copper(II) porphyrin and zinc porphyrin dyad  $\text{ZnP-CuP}$  (Fig. 4b) shows near-IR phosphorescence from the copper porphyrin part at room temperature, which is thermally activated from the  $T_1$  of the zinc porphyrin part (energy gap  $\Delta E = 430 \text{ cm}^{-1}$ ).<sup>21</sup> The emission lifetime from the copper porphyrin part is prolonged ( $\tau_{\text{ZnP-CuP}} = 300 \text{ ns}$ ) because the  $T_1$  of the zinc porphyrin part acts as the energy reservoir.

We used this methodology to observe the  $T_1$  of the special-pair-type porphyrin dimer in ( $\text{CuP-ZnP}_2$ )<sub>3</sub>. The emission lifetime from the copper porphyrin in the cyclic array was 500 times longer ( $\tau_{\text{ZnP}_2\text{-CuP}} = 15 \mu\text{s}$ ) than that of a copper porphyrin monomer (e.g.,  $\text{Cu(II)TPP}$ ; TPP = *meso*-tetraphenylporphyrin;  $\tau_{\text{CuP}} = 30 \text{ ns}$ ), supporting the energy transfer from the long-lived  $T_1$  of the dimer.<sup>22</sup> The RTP in the cyclic array was dramatically quenched by oxygen, which hardly quenched the RTP of  $\text{Cu(II)TPP}$ , indicating that the quenching event mainly occurs at the  $T_1$  of the zinc porphyrin dimer. The quenching event at the non-emissive  $T_1$  state of the special-pair-type porphyrin dimer was determined through the emission from the neighbouring copper porphyrin. The emission lifetime of ( $\text{CuP-ZnP}_2$ )<sub>3</sub> is 50 times longer than that of  $\text{ZnP-CuP}$ , resulting from the larger energy gap  $\Delta E = 1030 \text{ cm}^{-1}$  between the  $T_1$  of the zinc porphyrin dimer and the  $T_1$  of the copper porphyrin because the axial ligand of the imidazolyl group lowers the  $T_1$  of the zinc porphyrin part.

#### Porphyrin-based solvation/desolvation indicators

Solvation and desolvation significantly affect the dynamic phenomena of molecular systems in solution. However, it is difficult to directly observe the solvating solvent in solution. This is because the solvating solvent frequently exchanges with



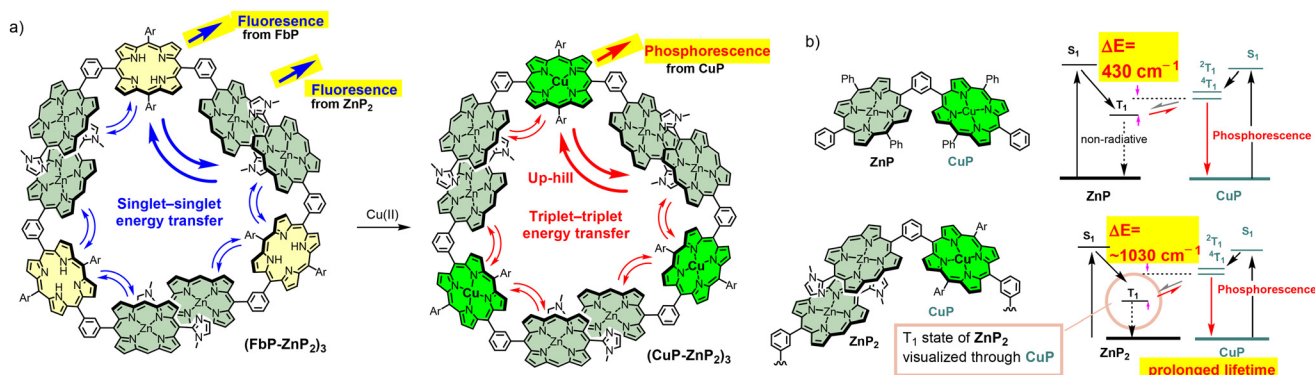


Fig. 4 Structures of cyclic porphyrin arrays based on special-pair-type porphyrin dimers, and the conceptual diagram of intramolecular energy transfer and copper porphyrin emission in toluene.

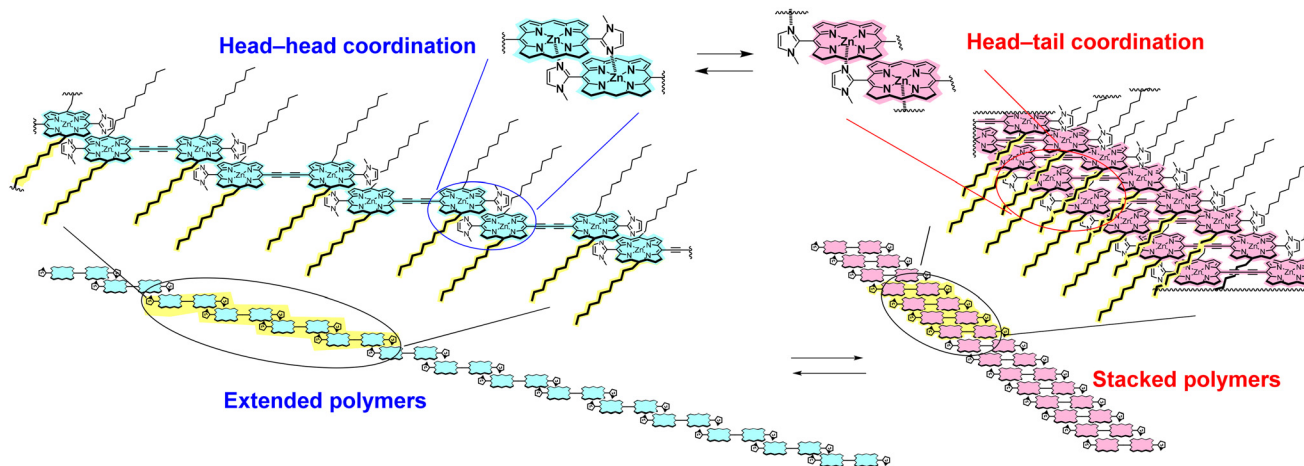


Fig. 5 Schematic representation of extended and stacked polymers composed of bis(imidazolylporphyrinatozinc) linked through the 1,3-butadiyne group. Extended and stacked polymers are formed by head-head and head-tail co-ordinations, respectively. Transformation between extended and stacked polymers is controlled by substituent groups and solvents.

large amounts of free solvent. Solubility parameters are often used as an index of solvent parameters.<sup>23</sup> However, as described in the previous section, large porphyrin derivatives and arrays tend to aggregate with one another significantly, even in solvents considered to be good solvents. Therefore, other index systems to estimate the solvation and desolvation of porphyrin derivatives are useful. During our studies on molecular wires using porphyrin derivatives,<sup>12</sup> we noticed that two types of co-ordination dimers and polymers exist in different solvent systems.<sup>24,25</sup> In the case of bis(imidazolylporphyrinatozinc) linked through a 1,3-butadiyne group, an extended co-ordination polymer is formed in a head-head co-ordination manner in mainly chlorinated solvents, such as chloroform, whereas a stacked co-ordination polymer is formed in a head-tail co-ordination manner in various other solvents (e.g., propan-2-ol, acetonitrile, acetone) (Fig. 5). Because only one co-ordination mode must be adopted within one co-ordination porphyrin wire, an extended or stacked polymer is formed exclusively. This nature is beneficial in the

assessment of the solvation/desolvation abilities (SA) of various solvent systems.<sup>26–28</sup> After using the systems, we recently reported the SA values of various solvents.<sup>29</sup> The equilibrium between the head-head and head-tail co-ordination manners is interesting and would be controlled by changing substituent groups on porphyrins and the environment, such as solvents and fluid matrices. Such dynamic natures will be applicable to smart materials in various fields.

## Conclusions and outlook

Metalloporphyrins, especially zinc porphyrins, are multitalented. Their large molar extinction coefficients in the visible region are beneficial to detect and treat them, even under highly diluted conditions. The large values generate exciton coupling among porphyrins, which can be useful to estimate their aggregation states. The aggregation states are perturbed by concentrations and solvents, but they can be controlled by



metal–ligand co-ordination and adjustment of van der Waals interactions of the porphyrin skeleton and peripheral substituents. Porphyrins have good photoelectronic properties. In the case of zinc porphyrin derivatives, both the excited singlet and triplet states can be useful for photocatalysis. The excited triplet state has rarely been detected, but it clearly appears in combination with other metal complexes. Multi-metal complexes of porphyrins in combination with other metal complexes should continue to yield interesting new findings.

## Author contributions

YK and AS wrote the manuscript. AS prepared the final one.

## Conflicts of interest

There are no conflicts to declare.

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