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Syntheses and CO_2 reduction activities of π -expanded/extended iron porphyrin complexes

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Abstract The construction of molecular catalysts that are active toward CO₂ reduction is of great significance for designing sustainable energy conversion systems. In this study, we aimed to develop catalysts for CO2 reduction by introducing aromatic substituents to the meso-positions of iron porphyrin complexes. Three novel iron porphyrin complexes with π -expanded substituents (5,10,15,20-tetrakis(pyren-1-yl)porphyrinato iron(III) chloride (**Fe-Py**)), π -extended substituents (5,10,15,20-tetrakis((1,1'-biphenyl)-4-yl)porphyrinato iron(III) chloride (Fe-PPh)) and π -expanded and extended substituents (5,10,15,20-tetrakis(4-(pyren-1-yl)phenyl)porphyrinato iron(III) chloride (Fe-PPy)) were successfully synthesized, and their physical properties were investigated by UV-vis absorption spectroscopy and electrochemical

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measurements under Ar in comparison with an iron complex with a basic framework, 5,10,15,20-tetrakis(phenyl) porphyrinato iron(III) chloride (**Fe-Ph**). Moreover, the catalytic activity of the complexes was studied by electrochemical measurements under CO₂, and it is found that the complex with the π -expanded substituents exhibits the highest activity among these complexes.

Keywords Iron complex \cdot Porphyrin \cdot Pyrene \cdot Electrochemistry \cdot CO₂ Reduction

Introduction

Growing global energy demands and environmental problems, such as climate change and air pollution, currently underpin the broad interest in the development of sustainable energy conversion systems. In natural photosynthetic reactions, renewable but not storable solar energy is successfully converted into storable chemical energy by reducing carbon dioxide. This reductive transformation of carbon dioxide, which results in the production of energy-rich carbon compounds, is a very attractive reaction because this technology will allow us to solve both energy and environmental problems [1, 2]. Based on such considerations, there have been numerous studies that aimed to develop molecular-based artificial catalysts for the reduction of carbon dioxide in recent years [3–20].

Iron porphyrin complexes are fascinating candidates as catalysts for carbon dioxide reduction [21-35]. One of the advantageous points of the complexes is that we can easily tune their physical properties by introducing various substituents at the *meso*-positions of the porphyrin framework. In fact, several reports revealed that the introduction of appropriate functional groups, such as acidic/basic and

electron donating/withdrawing substituents, could affect the catalytic activity [29–31]. In this context, the introduction of substituents with a large π plane is expected to be one of the ways to control the catalytic activity of the iron porphyrin catalysts because this class of substituents not only could influence the electronic structure but could also provide hydrophobicity, which is preferable for accumulating CO₂ molecules near the active center, to the molecular catalysts. However, the effect of such substituents on the catalytic activity of iron porphyrin complexes has not been explored.

In this study, we aimed to investigate the properties of iron porphyrin complexes with various types of π -conjugated substituents. We employed 5,10,15,20-tetrakis(phenyl) porphyrin (H-Ph, Fig. 1), which is known to catalyze electrochemical CO_2 reduction [32–35], as a basic framework and derivatized its structure with π -expanded substituents, π -extended substituents, and π -expanded and extended substituents to afford 5,10,15,20-tetrakis(pyren-1-yl)porphyrin (H-Py), 5,10,15,20-tetrakis((1,1'-biphenyl)-4-yl)porphyrin (H-PPh) and 5,10,15,20-tetrakis(4-(pyren-1-yl)phenyl) porphyrin (H-PPy), respectively. Described herein are the syntheses, UV-vis absorption properties, and electrochemical properties of the free-base porphyrins and iron porphyrin complexes. In addition, the catalytic activities of the iron porphyrin complexes for electrochemical CO₂ reduction are also presented.

Results and discussion

Syntheses

Syntheses of the free-base porphyrins

Four types of free-base porphyrins were prepared following the synthetic routes shown in Scheme 1. The porphyrin with a basic structure, H-Ph, was obtained in moderate yield (19%) using Adler's method [36], in which benzaldehyde and pyrrole were refluxed in propionic acid under air. The π -expanded (H-Py) and the π -extended (H-PPh) derivatives were also previously synthesized using Adler's method [37, 38]. Therefore, we initially attempted the syntheses of these compounds under the same conditions as the synthesis of **H-Ph**, and the formation of the macrocyclic porphyrin skeleton was confirmed by ¹H NMR spectroscopy. However, the isolation of the desired products (H-Py and H-PPh) from the reaction mixture using column chromatography was unsuccessful due to the generation of numerous types of side products. Therefore, we adopted Lindsey's method [39, 40], in which porphyrin derivatives were obtained by the condensation of aryl aldehydes with pyrrole and the subsequent aromatization of the porphyrinogen intermediate by



Fig. 1 Chemical structures of the porphyrin derivatives investigated in this study

oxidation, as an alternative synthetic route. Aryl aldehydes (1-pyrenecarbaldehyde or 4-phenylbenzaldehyde) were reacted with pyrrole (1.0 eq.) in dichloromethane (DCM) at room temperature in the presence of trifluoroacetic acid (TFA). and 2,3-dichloro-5,6-dicyano-p-benzoquinone (DDQ) was added to the resultant reaction mixture as an oxidant. Under these reaction conditions, the amounts of impurities, such as polymeric pyrrole, were lower compared to the previous reaction conditions. Thus, the desired compounds were successfully isolated after their purification by silica gel column chromatography. The isolated yields were 6 and 7% for **H-Pv** and **H-PPh**, respectively. Note that the synthesis of H-PPh by a similar method has been reported previously [41]. Since the acid-catalyzed condensation reaction using Lindsey's method was effective, the synthesis of the π -expanded and extended derivative (**H-PPy**) was performed using the same method. An aryl aldehyde with a pyrenylphenyl moiety, 4-(pyren-1-yl)benzaldehyde, was prepared by a Pd-catalyzed Suzuki-Miyaura cross-coupling reaction between 1-pyrenecarbaldehyde and 4-formylphenylboronic acid, and 4-(pyren-1-yl)benzaldehyde was obtained in 77% yield. The obtained aryl aldehyde was then condensed with pyrrole, and the porphyrinogen intermediate was further oxidized by 1.2 eq. of DDQ at room temperature for 90 min. The resulting reaction mixture was quenched by triethylamine (TEA) and then purified by silica gel chromatography to afford H-PPy with a 16% yield. The obtained free-base porphyrins, H-Ph, H-Py, H-PPh, and H-PPy, were characterized by ¹H NMR spectroscopy and elemental analyses.

Scheme 1 Synthetic routes for the free-base porphyrins, H-Ph, H-Py, H-PPh, and H-PPy



In the ¹H NMR spectra of the free-base porphyrins in CDCl₃, the broad singlet signal attributed to the internal N–H moieties was observed below 0 ppm (Fig. 2) because of the ring current associated with the aromatic porphyrin. The chemical shifts of the signals were -2.80, -1.98, -2.69 and -2.51 ppm for H-Ph, H-Py, H-PPh, and H-PPy, respectively. Note that these chemical shifts were largely different depending on the substituent at the *meso*-positions. The order of chemical shifts was H-Py > H-PPy > H-PPh > H-Ph, which can be explained by considering the ring current from the aromatic substituents.

In addition to the singlet peaks of the internal N-H proton, the peaks originating from the aromatic substituents and the protons at the β -position of pyrrole rings $(\beta$ -protons) were observed in the aromatic region. The signal of the β -protons was obtained as a singlet peak for H-Ph (8.82 ppm), H-PPh (8.96 ppm) and H-PPy (9.21 ppm), whereas the β -protons of **H-Py** were observed as multiplets at 8.75-8.86 ppm and 8.39-8.42 ppm. Generally, the symmetrical tetra-substituted porphyrin structure affords a singlet peak for the β -protons, and the asymmetric porphyrins give more complicated peaks. Therefore, the multiplet signals observed for H-Pv indicate the presence of four stereoisomers formed due to the asymmetric structure and the large steric hindrance of the pyrenyl moiety. For **H-PPy**, a singlet peak for the β -protons was observed despite the asymmetric structure of the pyrenylphenyl moiety. This is because the phenylene linker allows the free rotation of the pyrenyl moiety, which results in the averaged symmetric structure in solution.

Syntheses of iron porphyrin complexes

All free-base porphyrins were converted into the iron porphyrin complexes by a reaction with iron(II) chloride tetrahydrate in DMF or N-methylpyrrolidone (NMP). The synthetic scheme employed to obtain the iron complexes is shown in Scheme 2. The reaction conditions were optimized using H-Ph as a ligand. In the procedure previously reported in the literature [42, 43], the iron salt was gradually added to the reaction mixture in several portions within a given time period, and it is a slightly cumbersome procedure. To simplify the experimental operation, we first attempted the reaction by adding the solid of the iron salt in one portion. However, the reaction yield (trace) became significantly lower than the previous report (97%) [43]. This might be because the oxidation of the iron salt to give iron(III) species is promoted upon the heating of the metal salt in the solid state, which prevents the metalation reaction. To avoid such a situation, in the modified method, a solution of iron(II) chloride was prepared beforehand and added to a solution of H-Ph dropwise



Fig. 2 ¹H NMR spectra of H-Ph, H-Py, H-PPh, and H-PPy $(400 \text{ MHz}, \text{CDCl}_3)$

before heating the solution. This modified synthetic strategy resulted in the formation of the desired complex, 5,10,15,20-tetrakis(phenyl)porphyrinato iron(III) chloride (Fe-Ph), in high yield (93%). The metalation of H-Py was also performed using the same reaction conditions, and the desired product, 5,10,15,20-tetrakis(pyren-1-yl) porphyrinato iron(III) chloride (Fe-Py), was obtained quantitatively. However, the iron complex was not formed at all when H-PPh was reacted under the same reaction conditions due to the low solubility of the ligand in DMF. Therefore, the reaction solvent was changed to NMP and the iron complex, 5,10,15,20-tetrakis((1,1'biphenyl)-4-yl)porphyrinato iron(III) chloride (Fe-PPh), was obtained with moderate yield (66%). In the case of **H-PPv**, it took almost 24 h to complete the metalation in DMF and several decomposed compounds, which formed by heating the porphyrin for a long time, were obtained. Based on this observation, we changed the reaction solvent to NMP which possesses a higher boiling point than DMF, to shorten the reaction time. As a result, the iron 5,10,15,20-tetrakis(4-(pyren-1-yl)phenyl)porcomplex, phyrinato iron(III) chloride (Fe-PPy), was successfully obtained with high yield (87%). In all cases, the progress of the iron insertion reaction and the consumption of starting material were monitored by TLC and by checking the decrease of the number of Q bands in UV-vis absorption spectra (for the assignments of absorption bands, see "UV-vis absorption properties of free-base and iron porphyrins"). All iron porphyrin complexes, Fe-Ph, Fe-Py, Fe-PPh and Fe-PPy, were characterized by UV-vis absorption spectroscopy, electrochemical measurements and elemental analyses. The characterization by ¹H NMR



Scheme 2 Synthetic routes for the iron porphyrin complexes, Fe-Ph, Fe-Py, Fe-PPh and Fe-PPy

measurement was difficult due to the paramagnetic nature of the complexes.

UV-vis absorption properties of free-base and iron porphyrins

UV-vis absorption spectra of the free-base porphyrins and the iron complexes are shown in Fig. 3, and the spectroscopic data are summarized in Table 1. All free-base porphyrins present a strong absorption band at approximately 422–436 nm and four weaker bands widely located at approximately 516–654 nm. These spectral features are caused by porphyrin macrocycle-based π – π * transitions described by Gouterman's four orbital model [44, 45]. The former band in the shorter wavelength region is assigned to the S₀ \rightarrow S₂ transition (Soret band), and the latter bands



Fig. 3 UV-vis absorption spectra of the free-base porphyrins in 1,2-dichlorobenzene a H-Ph, b H-Py, c H-PPh, d H-PPy, e Fe-Ph, f Fe-Py, g Fe-PPh and h Fe-PPy. (*Insets*) Enlarged UV-vis absorption spectra at Q-band regions

are attributed to the $S_0 \rightarrow S_1$ transition (Q bands). The Soret and Q bands of **H-Py**, **H-PPh**, and **H-PPy** are slightly red shifted compared with those of **H-Ph**, but located at a quite similar position. This result indicates that the electronic structure of the porphyrin moieties was not affected by the introduction of the aromatic substituents and is consistent with the results of the electrochemical measurements (vide infra). In addition to the typical porphyrin-based absorption **Table 1** Summary of theabsorption spectra for thefree-base porphyrins and theiron porphyrin complexes in1,2-dichlorobenzene

Compound	$\lambda_{\rm max}/{\rm nm}~(\epsilon/10^4/{\rm M/cm})$				
	Substituent's bands	Soret-band	Q-bands		
H-Ph	373 (1.30)	422 (25.52)	516 (1.08), 551 (0.48) 593 (0.30), 649 (0.24)		
H-Py	328 (6.78), 340 (7.46)	436 (19.56)	524 (1.78), 555 (1.26), 604 (0.76), 658 (3.56)		
H-PPh	311 (2.08), 377 (2.20)	427 (44.14)	520 (1.80), 557 (1.32), 596 (0.56), 653 (0.66)		
H-PPy	349 (10.54)	429 (28.12)	520 (1.82), 556 (1.34), 596 (0.72), 654 (0.84)		
Fe-Ph	378 (2.38)	420 (5.20)	510 (0.56), 575 (0.10), 691 (0.12)		
Fe-Py	346 (7.74)	431 (5.74)	513 (1.32)		
Fe-PPh	383 (2.78)	426 (6.30)	513 (0.74), 695 (0.18)		
Fc-PPy	351 (11.22)	427 (11.66)	512 (1.48), 694 (0.34)		

bands, several absorption bands were observed at shorter wavelength (<384 nm) in the case of **H-Py** and **H-PPy**, and assigned to the π - π * transitions of the aromatic substituents [46–49].

All iron porphyrin complexes show a strong absorption band at approximately 420–431 nm (Soret band) and weaker bands located in a wider region between 510 and 695 nm (Q bands). The decrease in the number of Q bands is due to the degeneration of the HOMO and the HOMO–1 for each porphyrin, thus indicating the generation of more symmetric structures via metalation [50]. There is no significant change in the absorption maxima of the Soret bands upon metalation, which was characteristic of iron porphyrin complexes [43].

Electrochemical properties

The cyclic voltammograms (CVs) of the free-base porphyrins (H-Ph, H-Py, H-PPh, and H-PPy) and the iron porphyrin complexes (Fe-Ph, Fe-Py, Fe-PPh, and Fe-PPy) are shown in Fig. 4 and the redox potentials of these compounds are summarized in Table 2. The CVs were measured with 0.1 M tetrabutylammonium perchlorate (TBAP) in 1,2-dichlorobenzene. The concentrations of the free-base porphyrins and iron porphyrin complexes were 1.0 mM except for H-PPh. The CV of H-PPh was measured using a saturated solution due to its low solubility in the electrolyte solution. All free-base porphyrins displayed two reversible waves, which are assigned to the two-step one electron reduction of the porphyrin ring [25]. The half wave potentials $(E_{1/2} (1)/V \text{ vs. ferrocene/ferrocenium (Fc/Fc^+)})$ for the first reduction were -2.01 (H-Ph), -1.99 (H-Py), -1.97 (H-PPh) and -1.99 V (H-PPy), and those for the second reduction ($E_{1/2}$ (2)) were -2.32 (**H-Ph**), -2.38 (**H-**Py), -2.27 (H-PPh) and -2.28 V (H-PPy), respectively. The redox potentials of the free-base porphyrins are quite similar to each other, indicating almost no electronic interaction between the porphyrin framework and the substituent. In the cases of the iron porphyrin complexes, three reversible reduction peaks, which are possibly assigned to be Fe(III)/Fe(II), Fe(II)/Fe(I) and Fe(I)/Fe(0) redox couples



Fig. 4 Cyclic voltammograms of the free-base porphyrins (H-Ph, H-Py, and H-PPy, 1.0 mM) and the iron porphyrin complexes (Fe-Ph, Fe-Py, Fe-PPy and Fe-PPy, 1.0 mM) in a 0.1 M TBAP/1,2dichlorobenzene solution under an Ar atmosphere (WE: GC; CE: Pt wire; RE: Ag⁺/Ag; scan rate: 20 mV s⁻¹). Note that the measurement of H-PPh was performed using a saturated solution due to its low solubility in the electrolyte solution. Potential sweeps were started from the open circuit potential -0.93 V (H-Ph), -0.62 V (H-Py), -1.00 V (H-PPh), -0.79 V (H-PPy), -0.75 V (Fe-Ph), -0.59 V (Fe-Py), -0.72 V (Fe-PPh) and -0.62 V (Fe-PPy). Arrows in the voltammograms indicate the direction of potential sweep

according to the previous report [33], were observed [51, 52].¹ Similar to the results of the CVs of the free-base por-

¹ In the iron porphyrin complexes, there are several possible resonant forms to describe the electronic structure of the reduced species, and all resonant forms presumably contribute to the electronic structure of the complexes. In the case of **Fe-Ph**, previous reports suggested that the three electron reduced species should be best formulated as a Fe(0) complex, based on the results of UV–vis and resonance Raman spectroscopy and the studies on electrocatalytic reactions (Ref. [33, 51, 52]). Given that redox potentials of the newly synthesized complexes (**Fe-Py, Fe-Pph** and **Fe-Ppy**) are quite similar to the reported complex, **Fe-Ph**, the nature of the redox processes and the electronic structure of the reduced species are probably similar. Therefore, we have assigned the redox processes of the newly synthesized complexes to be Fe(III)/Fe(II), Fe(II)/Fe(I) and Fe(I)/Fe(0) according to the previous reports.

Table 2 Redox potentials of the prepared free-base porphyrins and the iron porphyrin complexes $(E_{1/2}/V \text{ vs. Fc/Fc}^+)$ in 1,2-dichlorobenzene under an Ar atmosphere

Compound	$E_{1/2}(1)/V$	$E_{1/2}(2)/V$	E _{1/2} (3)/V	
H-Ph	-2.01	-2.32	_	
H-Py	-1.99	-2.38	-	
H-PPh	-1.97	-2.27	-	
H-PPy	-1.99	-2.28	_	
Fe-Ph	-1.14	-1.88	-2.49	
Fe-Py	-1.18	-1.89	-2.52	
Fe-PPh	-1.12	-1.86	-2.45	
Fe-PPy	-1.19	-1.93	-2.52	

phyrins, the redox potentials of the iron complexes are located at almost identical positions, reflecting the similar electronic structure of the ligands.

Catalytic activity

Iron porphyrin complexes are known to catalyze the CO_2 reduction reaction to generate CO under electrochemical conditions [29–35]. In the cyclic voltammograms of the complexes under a CO_2 atmosphere, an increase of the irreversible current coupled with the third reduction wave was observed. This irreversible current is called the catalytic current and indicates the occurrence of the electrocatalytic reduction of CO_2 . It is also known that the intensity of the catalytic current basically is correlated to the rate of the catalytic reaction [30, 53, 54]. Therefore, the electrochemical measurements of the newly synthesized complexes were also conducted under a CO_2 atmosphere to investigate the catalytic activity.

Initially, the measurements were performed using 0.1 M TBAP/1,2-dichlorobenzene solution. The results of the measurements are shown in Fig. 5. Under a CO_2 atmosphere, an increase of the irreversible currents was observed at a potential close to the third redox wave for all compounds, suggesting the electrocatalytic reduction of CO_2 [29–35]. However, the intensities of these catalytic currents were very small. In the CO_2 reduction catalyzed by iron porphyrin complexes, the existence of proton source is essential to promote the reaction [30]. It is also reported that water contained in the solvent is known to serve as a proton source [28, 35]. However, the concentration of water is low in 1,2-dichlorobenzene due to its hydrophobicity, which may result in the small catalytic current.² Therefore,

we measured the CVs of the iron complexes using a more hydrophilic solvent, DMF. The results of the measurements and a summary of the electrochemical data are shown in Fig. 6 and Table 3, respectively. It should be noted the CV measurement of Fe-PPh was unsuccessful due to the low solubility of the complex in DMF. Fe-Ph and Fe-Py exhibited three reversible redox waves (-0.63, -1.51, and-2.15 V for **Fe-Ph**, and -0.63, -1.47, -2.08 V for **Fe-Pv**) under an Ar atmosphere, which is in good agreement with the CVs measured in 1,2-dichlorobenzene. For Fe-PPy, in addition to the three reversible redox waves (-0.62, -1.50, -1.50)and -2.11 V), one new reversible redox peak appeared at -2.43 V. This additional peak was assigned to the reduction of the 1-phenylpyrene substituents by comparing the CVs of related compounds (Figure S1 in the Electronic Supplementary Material). Under a CO₂ atmosphere, Fe-Ph exhibited large irreversible cathodic currents attributed to the catalytic reduction of CO₂ to CO at a potential close to the third redox couple $(-2.1 \text{ V vs. Fc/Fc}^+)$, and the result is consistent with the previous report [35]. Similarly, an irreversible current in a similar potential region was observed in the CV of Fe-Py under CO₂. To confirm the origin of the irreversible current, controlled potential electrolysis of Fe-Pv and Fe-Ph was performed. Solutions containing 1.0 mM of the complexes were electrolyzed at -2.2 V (vs. Fc/Fc⁺) for 1 h. After the electrolysis, both the gas and the liquid phases were analyzed and CO as a major product and small amount of dihydrogen (H₂) as a minor product were detected. The formation of formic acid was not detected. The faradaic efficiencies for the conversion of CO₂ to CO were determined to be 87 (Fe-Py) and 93 (Fe-Ph) % (for experimental details, see the ESM). These results clearly indicate the irreversible current is attributed to the electrocatalytic CO₂ reduction by the complexes. In the case of Fe-PPy, an increase of the irreversible current was observed both at the Fe(I)/Fe(0) redox couple (-2.11 V) and the reduction of the substituent (-2.43 V). Among the three complexes, Fe-Py exhibited the largest catalytic current under our experimental conditions, which suggests that the introduction of π -expanded substituents can improve the catalytic activity. Additionally, the controlled potential electrolysis revealed that the amounts of CO evolved during the electrolysis were 2978 and 1999 µL for Fe-Py and Fe-Ph, respectively (Table S4). We also calculated the turnover frequency (TOF) and turnover number (TON) of the reaction for each complex based on the result of CPE experiments. TOF values were 120 (Fe-Py) and 60 (Fe-Ph) s^{-1} and TON values were 4.3×10^5 (Fe-Py) and 2.2×10^5 (**Fe-Ph**) s^{-1} for 1 h (for details of the calculation of TOF) and TON values, see the ESM). These results clearly indicate that the reaction rate of **Fe-Py** is approximately 2.0 times higher than that of Fe-Ph. Based on these observations, we can conclude that the introduction of π -expanded

² It should be noted that the concentration of CO₂ in solution can be an important factor to affect the reaction rate. In our experiments, CO₂-saturated solutions were employed in all the electrochemical measurements under a CO₂ atmosphere although the exact concentration of CO₂ in the 1,2-diclorobenzene solutions was unknown.

Fig. 5 Cyclic voltammograms of the iron porphyrin complexes (a Fe-Ph, b Fe-Py, c Fe-PPy and d Fe-PPy, 1.0 mM) in a 0.1 M TBAP/1,2-dichlorobenzene solution under Ar (*solid lines*) and CO₂ (*dotted lines*) atmospheres. (WE: GC; CE: Pt wire; RE: Ag⁺/Ag; scan rate: 20 mV s⁻¹). The solutions were saturated with Ar or CO₂ prior to the experiments. Potential sweeps were started from the open circuit potential -0.75 V (Fe-Ph), -0.59 V (Fe-Py), -0.72 V (Fe-PPh) and -0.62 V (Fe-PPy). Arrows in the voltammograms indicate the direction of potential sweep

substituents can improve the catalytic activity. Given that the redox potentials attributed to the iron porphyrin complexes are quite similar in these complexes (Table 3), the substituents rarely affected the electronic structure of the iron centers. It should be also noted that the adsorption of **Fe-Py** on the GC electrode rarely occur under the experimental conditions employed in this study (Figures S2–S4 and S6). One possible explanation for the difference in the catalytic activity is that the hydrophobic space created by the substituents could promote the accumulation of the substrate, CO_2 , and the faster supply of the substrate during catalysis resulted in a larger reaction rate.

Conclusions

This study describes the syntheses and the spectroscopic and electrochemical properties of iron porphyrin complexes with π -conjugated substituents at the *meso* position. Three novel iron complexes, Fe-Py, Fe-PPh, and Fe-PPy, were synthesized by the reaction of the corresponding freebase porphyrins (H-Py, H-PPh, and H-PPy) with iron(II) chloride tetrahydrate in DMF or NMP and characterized by elemental analyses and UV-vis absorption spectroscopy. The electrochemical analyses of the complexes under an Ar atmosphere indicated that the introduction of the π -conjugated substituents rarely affects the electronic structures of the iron porphyrin complexes. However, the catalytic activity of Fe-Pv was found to be much higher than that of Fe-Ph. These results indicate that the introduction of large π -conjugated substituents directly to the *meso*positions of a porphyrin moiety could provide a hydrophobic space suitable for the accumulation of CO₂ molecules.

Experimental

Materials and methods

Pyrrole was purchased from Sigma-Aldrich Co., LLC. 1,2-dichlorobenzene, ferrocene (Fc), 4-formylphenylboronic acid, iron(II) chloride tetrahydrate, 1-methylpyrrolidin-2-one (NMP), 1-pyrenecarbaldehyde, triethylamine (TEA), trifluoroacetic acid (TFA), bis(triphenylphosphine)



Fig. 6 Cyclic voltammograms of a Fe-Ph, b Fe-Pv and c Fe-PPy (1.0 mM) in a 0.1 M TBAP/DMF solution under Ar (solid lines) and CO₂ (dotted lines) atmospheres. (WE: GC; CE: Pt wire; RE: Ag⁺/Ag; scan rate: 20 mV s^{-1}) The solutions were saturated with Ar or CO₂ prior to the experiments. The concentration of CO2 in a 0.1 M TBAP/DMF solution is approximately 0.23 M [55]. Potential sweeps were started from the open circuit potential -0.40 V (Fe-Ph), -0.28 V (Fe-Py) and -0.41 V (Fe-PPy). Arrows in the voltammograms indicate the direction of potential sweep





Table 3 Redox potential for the prepared iron porphyrin complexes $(E_{1/2}/V \text{ vs. Fc/Fc}^+)$ in a 0.1 M TBAP/DMF solution under Ar atmosphere

Compound	$E_{1/2}(1)/V$	$E_{1/2}(2)/V$	$E_{1/2}(3)/V$
Fe-Ph	-0.63	-1.51	-2.15
Fe-Py	-0.63	-1.47	-2.08
Fc-PPy	-0.62	-1.5	-2.11

palladium(II) dichloride and tripotassium phosphate were purchased from Wako Pure Chemical Industries, Ltd. Hexane (Hex) and *N*,*N*-dimethylformamide (DMF) were purchased from Kanto Chemical Co., Inc. Tetra(*n*butyl)ammonium perchlorate (TBAP), 1-bromopyrene, 2,3-dichloro-5,6-dicyano-1,4-benzoquinone and 4-phenylbenzaldehyde were purchased from Tokyo Chemical Industry Co., Ltd. CDCl₃ was obtained from Cambridge Isotopes, Inc. All reagents were used without further purification. TBAP was recrystallized from absolute ethanol and dried in vacuo. Dichloromethane (DCM) and tetrahydrofuran (THF) were degassed and purified under an N₂ atmosphere using a GlassContour solvent system (Nikko Hansen Co., Ltd.).

¹H NMR spectra were recorded on a JEOL 400 MHz instrument. All ¹H NMR spectra were referenced against residual proton signals of CDCl₃. Elemental analyses were measured on a MICRO CORDER JM10. Electrochemical experiments were performed under argon and CO₂ atmospheres using a BAS ALS Model 650DKMP electrochemical analyzer. Cyclic voltammograms were recorded in 1,2-dichlorobenzene ([complex] = 1.0 mM; 0.1 M TBAP) using a glassy carbon disk, a platinum wire and an Ag⁺/Ag electrode (Ag/0.01 M AgNO₃) that were used as the working, auxiliary, and reference electrodes, respectively. The redox potentials of the samples were calibrated against the redox signal for the ferrocene/ferrocenium (Fc/Fc⁺) couple. UV–vis absorption measurements were performed on a Shimadzu UV-1800 spectrometer at room temperature.

Syntheses

Synthesis of 5, 10, 15, 20-tetrakis(phenyl)porphyrin (H-Ph)

H-Ph was synthesized according to the published method (yield 19%) [36]. ¹H NMR (400 MHz, CDCl₃) δ 8.82 (s, 8H), 8.19–8.21 (m, 8H), 7.71–7.78 (m, 12H), -2.80 (s, 2H) ppm. Anal. Calcd for C₄₄H₃₀N₄: C, 85.97; H, 4.92; N, 9.11. Found: C, 85.90; H, 5.02; N, 9.04%.

Synthesis of 5,10,15,20-tetrakis(pyren-1-yl)porphyrin (*H-Py*)

To a solution of 1-pyrenecarbaldehyde (0.93 g, 4.05 mmol) in dry DCM (600 mL) was added pyrrole (0.28 mL, 4.05 mmol) in one portion at rt. After stirring for 5 min, to the reaction mixture was added TFA (0.93 mL, 12.2 mmol) at rt. The mixture was stirred for 21 h at rt and then DDQ (1.1 g, 4.9 mmol) was added. After 90 min, the reaction was quenched by TEA (1.7 mL, 12.2 mmol). The resulting mixture was passed through a silica short column to give a black solution. The resulting residue was purified by column chromatography (DCM/Hex) to afford a dark purple solution. The desired product was recrystallized from a tiny amount of THF and diethyl ether to give a purple solid, and the product was washed with several portions of methanol and diethyl ether (73 mg, yield 6%). ¹H NMR (400 MHz, CDCl₃) δ 8.75–8.86 (m, 4H), 8.46 (d, J = 7.9 Hz, 4H), 8.39–8.42 (m, 8H), 8.33 (d, J = 9.2 Hz, 4H), 8.24–8.29 (m, 8H), 8.08 (d, J = 6.4 Hz, 4H), 7.98-8.04 (m, 4H), 7.70-7.76 (m, 4H),7.59-7.64 (m, 1H), 7.56 (dd, J = 9.2, 5.8 Hz, 2H), 7.47-7.51

(m, 1H), -1.98 (s, 2H) ppm. Anal. Calcd for $C_{84}H_{46}N_4 \cdot H_2O$: C, 89.34; H, 4.28; N, 4.96. Found: C, 89.61; H, 4.70; N, 4.95%.

Synthesis of 5,10,15,20-tetrakis((1,1'-biphenyl)-4-yl) porphyrin (**H-PPh**)

To a solution of 4-phenylbenzaldehyde (1.2 g, 6.6 mmol) in dry DCM (300 mL) was added pyrrole (0.46 mL, 6.6 mmol) in one portion at rt. After stirring for 5 min, to the reaction mixture was added TFA (1.5 mL, 20 mmol) at rt. The mixture was stirred for 1 h at rt and then DDO (1.8 g, 8.0 mmol) was added. After 90 min, the reaction was quenched by TEA (2.8 mL, 20 mmol). The resulting mixture was purified by column chromatography (DCM/Hex) to afford a dark purple solution. The desired product was recrystallized from a tiny amount of THF and diethyl ether to give a purple solid (0.108 mg, yield 7%). ¹H NMR (400 MHz, CDCl₃) δ 8.96 (s, 8H), 8.31 (d, J = 8.2 Hz, 8H), 8.00 (d, J = 8.2 Hz, 8H), 7.93 (d, J = 7.0 Hz, 8H), 7.60 (t, J = 7.6 Hz, 8H), 7.47 (t, J = 7.5 Hz, 4H), -2.69 (s, 2H) ppm. Anal. Calcd for C₆₈H₄₆N₄·H₂O: C, 87.15; H, 5.16; N, 5.98. Found: C, 87.45; H, 5.62; N, 5.71%.

Synthesis of 4-(pyren-1-yl)benzaldehyde

To the mixture of 1-bromopyrene (4.5 g, 16 mmol), 4-formylphenylboronic acid (2.5 g, 17 mmol), tripotassium phosphate (10 g, 48 mmol) and bis(triphenylphosphine)palladium(II) dichloride (0.56 g, 0.80 mmol) was added dry THF (160 mL) and water (21 mL). The mixture was refluxed with stirring for 19 h. After evaporation of THF, the precipitate was washed by water and methanol. The mixture was purified by column chromatography (DCM: Hex = 1:1) to afford the desired product (4.3 g, yield 88%). ¹H NMR (400 MHz, CDCl₃) δ 10.15 (s, 1H), 8.17–8.24 (m, 3H), 8.01–8.13 (m, 7H), 7.96 (d, J = 7.9 Hz, 1H), 7.80 (dt, J = 8.0, 1.6 Hz, 2H) ppm.

Synthesis of 5,10,15,20-tetrakis(4-(pyren-1-yl)phenyl) porphyrin (**H-PPy**)

To a solution of 4-(pyren-1-yl)benzaldehyde (2.03 g, 6.6 mmol) in dry DCM (300 mL) was added pyrrole (0.46 mL, 6.6 mmol) in one portion at rt. After stirring for 5 min, to the reaction mixture was added TFA (1.5 mL, 20 mmol) at rt. The mixture was stirred for 1 h at rt and then DDQ (1.8 g, 8.0 mmol) was added. After 90 min, the reaction was quenched by TEA (2.8 mL, 20 mmol). The resulting mixture was purified by column chromatography (DCM) to afford a dark purple solution. The desired product was recrystallized from a tiny amount of THF and diethyl ether to give a purple solid

(0.38 mg, yield 16%). ¹H NMR (400 MHz, CDCl₃) δ 9.21 (s, 8H), 8.66 (d, J = 9.2 Hz, 4H), 8.52 (d, J = 7.9 Hz, 8H), 8.40 (dd, J = 13.0, 7.8 Hz, 8H), 8.17–8.28 (m, 20H), 8.06–8.11 (m, 12H), -2.51 (s, 2H) ppm. Anal. Calcd for C₁₀₈H₆₂N₄·2.5H₂O: C, 88.80; H, 4.62; N, 3.84. Found: C, 88.87; H, 4.57; N, 3.71%.

Synthesis of 5,10,15,20-tetrakis(phenyl)porphyrinato iron(III) chloride (**Fe-Ph**)

Fe-Ph was prepared by the modification of a previous report [43]. To a solution of **H-Ph** (0.50 g, 0.81 mmol) in DMF (60 mL), a DMF (21 mL) solution of FeCl₂·4H₂O (0.97 g, 4.9 mmol) was added dropwise at room temperature. The mixture was refluxed for 30 min and then cooled to room temperature. After evaporating all the solvent, the resulting mixture was extracted with DCM. The extract was dried over anhydrous Na₂SO₄, and concentrated under reduced pressure. The desired product was precipitated from DCM and Hex to give a purple solid that was collected by filtration (0.53 g, yield 93%). Anal. Calcd for C₄₄H₂₈ClFeN₄: C, 75.06; H, 4.01; N, 7.96. Found: C, 75.19; H, 4.31; N, 7.82%.

Synthesis of 5,10,15,20-tetrakis(pyren-1-yl)porphyrinato iron(III) chloride (**Fe-Py**)

To a solution of **H-Py** (0.63 g, 0.56 mmol) in DMF (41 mL), a DMF (15 mL) solution of FeCl₂·4H₂O (0.67 g, 3.4 mmol) was added dropwise at room temperature. The mixture was refluxed for 3 h and then cooled to room temperature. After evaporating all the solvent, the resulting mixture was extracted with DCM. The extract was dried over anhydrous Na₂SO₄, and concentrated under reduced pressure. The desired product was precipitated from DCM and Hex to give a dark brown solid (0.68 g, yield quant.). Anal. Calcd for C₈₄H₄₄CIFeN₄·2.5H₂O: C, 81.00; H, 3.97; N, 4.50. Found: C, 81.33; H, 4.06; N, 4.19%.

Synthesis of 5,10,15,20-tetrakis((1,1'-biphenyl)-4-yl) porphyrinato iron(III) chloride (**Fe-PPh**)

To the mixture of **H-PPh** (41 mg, 0.045 mmol) and FeCl₂·4H₂O (89 mg, 0.45 mmol) was added NMP (9 mL). The mixture was refluxed for 1 h and then cooled to room temperature. After evaporating all the solvent, the resulting mixture was extracted with DCM. The extract was dried over anhydrous Na₂SO₄, and concentrated under reduced pressure. The desired product was recrystallized from a tiny amount of THF and diethyl ether to give a dark purple solid (30 mg, yield 66%). Anal. Calcd for C₆₈H₄₄ClFeN₄·1.75H₂O: C, 78.54; H, 4.60; N, 5.39. Found: C, 78.53; H, 4.80; N, 5.38%.

Synthesis of 5,10,15,20-tetrakis(4-(pyren-1-yl)phenyl) porphyrinato iron(III) chloride (**Fe-PPy**)

To the mixture of **H-PPy** (0.10 g, 0.071 mmol) and $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ (0.14 g, 0.71 mmol) was added NMP (14 mL). The mixture was refluxed for 1 h and then cooled to room temperature. After evaporating all the solvent, the resulting mixture was extracted with DCM. The extract was dried over anhydrous Na₂SO₄, and concentrated under reduced pressure. The desired product was recrystallized from a tiny amount of THF and diethyl ether to give a dark purple solid (92 mg, yield 87%). Anal. Calcd for C₁₀₈H₆₀ClFeN₄·2.25H₂O: C, 83.93; H, 4.21; N, 3.63. Found: C, 83.80; H, 4.31; N, 3.86%.

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