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An unprecedented porphyrin-pillar[5]arene hybrid ditopic receptor†

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A novel porphyrin-pillar[5]arene host compound ZnPor-P5 was designed and prepared for the first time. A 1 : 1 supramolecular complex (ZnPor-P5)·C4 was formed with the neutral guest 1,4-bis(imidazol-1-yl)-butane (C4) depending on the cooperative interactions between the coordination of the zinc ion locating at the center of the porphyrin moiety and the inclusion complexation of the pillar[5]arene cavity with the guest molecule according to a range of NMR, mass, electronic absorption, and fluorescence spectroscopic results in addition to ITC, demonstrating the ditopic receptor nature of this porphyrin-pillar[5]arene hybrid compound. The addition of CdI_2 into (ZnPor-P5)·C4 in chloroform induced the dissociation of the guest molecule from the zinc ion locating at the center of the porphyrin moiety due to the stronger coordination of imidazole with Cd^{2+} than with the zinc ion, yielding a new supramolecular system ZnPor-(P5)·C4·Cd with a different conformation.

Introduction

Oligo- and multitopic receptors are omnipresent in nature because multivalent binding[1] and cooperative binding[2] are two major concepts to ensure the necessary efficiency and selectivity in biological recognition events as well as the complicated cascades of processes coupled to these events. Due to different binding sites employed for the receptors to the substrate, the receptors usually exhibit different conformational changes upon binding with different guests.[3] Such kinds of conformational changes in biological systems have been well employed to control the function of proteins and enzymes during cellular metabolism.[4] As a result, a conformational change of the host upon binding with different guest and/or external stimulation has attracted increasing research interests in supramolecular chemistry in the past three decades through the development of various kinds of artificial ditopic and multitopic receptor systems based on crown ether,[5] cyclodextrin,[6] calixarene,[7] and cucurbit[*n*]uril[8] macrocyclic hosts.

Pillar[*n*]arenes, as a new class of supramolecular host system, have also received considerable attention since their first synthesis in 2008.[9] Thanks to their excellent host-guest binding ability with a number of guests, different pillar[*n*]-arenes-based supramolecular polymers,[10] functional vesicles,[11] and other supramolecular systems[12] with fascinating properties and application potentials have been developed. However, the pillarene-based ditopic receptors and in particular the pillarene-containing hetero-ditopic receptors still remain extremely rare. In 2013, Huang used pillar[5]arene and crown ether to construct a dynamic [1]catenane showing pH-responsiveness.[13] In 2014, Wen and co-workers constructed a bicyclic host molecule using pillar[5]arene and crown ether with its two cyclic subunits selectively recognizing two different guest molecules.[14] Obviously, novel pillarene-based ditopic receptors with interesting supramolecular system formation properties are highly desired for the purpose of mimicking the biological recognition events.

It is well known that porphyrins are of significant biological importance and widely used in supramolecular chemistry to mimic the porphyrin-containing active sites of proteins and enzymes.[15] In addition to the large number of metal porphyrin monotopic receptors usually with the central metal ion as the sole biding site,[16] cyclodextrins,[17] crown ethers,[18] and calix[4]-arenas[19] were also incorporated onto the porphyrin periphery as additional binding site, resulting in a number of porphyrin-containing ditopic receptors. However, pillar[*n*]arene-containing porphyrin-based ditopic receptor still remains unreported thus far, to the best of our knowledge.

In the present paper, we describe the preparation and characterization of unprecedented porphyrin-pillar[5]arene host compound ZnPor-P5. This novel hybrid compound forms a stable 1 : 1 supramolecular complex (ZnPor-P5)·C4 with neutral guest 1,4-bis(imidazol-1-yl)butane (C4) depending on the cooperative interactions between the coordination of zinc ion locating at the center of porphyrin moiety and the inclusion complexation of the pillar[5]arene cavity with the guest

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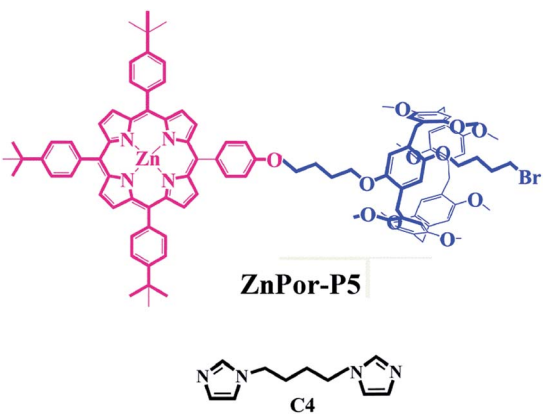
molecule according to a range of NMR, mass, electronic absorption, and fluorescence spectroscopic results in addition to ITC, demonstrating the ditopic receptor nature of this porphyrin-pillar[5]arene hybrid compound. Addition of CdI_2 into (ZnPor-P5)·C4 in chloroform induces the dissociation of the guest molecule from the zinc ion locating at the center of porphyrin moiety due to the stronger coordination of imidazole with Cd^{2+} than with zinc ion, leading to a new supramolecular system ZnPor-(P5)·C4·Cd with different conformation.

Results and discussion

Synthesis and characterization

Reaction of bromobutyl bis-substituted pillar[5]arene with the hydroxyl group of H_2(TTBP) promoted by K_2CO_3 and KI in DMF led to the formation of unprecedented porphyrin-pillar[5]arene hybrid compound H_2Por-P5, which further reacted with $Zn(OAc)_2$ in chloroform afforded the zinc complex ZnPor-P5, Scheme 1. Satisfactory elemental analysis result was obtained for this newly prepared porphyrin-functionalized pillar[5]arene derivative after repeated column chromatography. Its MALDI-TOF mass spectrum displayed intense signal at m/z = 1774.42, corresponding to the molecular ion $[M]^+$. Nevertheless, this compound was further characterized with a range of spectroscopic methods including NMR, electronic absorption, and fluorescence spectroscopy in addition to elemental analysis, Fig. S1–S4, (ESI†).

It is worth noting that during the past few years, pillar[n]-arenes have been recognized as an exceptionally versatile host for a wide variety of guests. Although the initial studies primarily focused on the cationic species,[20] the host-guest complexation of pillar[n]arene derivatives with neutral guests like bis(imidazole) derivatives in organic media has also received considerable attention in recent years.[21] As a consequence, in the present case the neutral molecule 1,4-bis(imidazol-1-yl)butane (C4) was selected as the guest to establish the binding relationship with the hybrid host compound ZnPor-P5.



Scheme 1 Schematic molecular structures of the host ZnPor-P5 and guest C4.

NMR spectroscopy

The complexation of ZnPor-P5 with the guest C4 was first studied by ^{1}H NMR spectroscopy. For comparative study, the host-guest complexation between P5 and Zn(TTBP) with C4 was also investigated.

As shown in Fig. S5 (ESI†), the ^{1}H NMR spectrum of the guest C4 in $CDCl_3$ experiences obvious change upon the addition of the host P5, indicating the effective host-guest interaction between the two species. The signals for the methylene protons of C4 exhibit substantial upfield shift in comparison with the free guest C4 due to the shielding effect of the electron-rich cavities of P5 ($\Delta\delta$ = −2.48 and −2.92 ppm for H_d and H_e, respectively, Fig. S5 (ESI†)). Meanwhile, the signals corresponding to the protons H_a and H_c of the imidazole moiety attributed to C4 also experience pronounced upfield shift, and the proton H_b takes a slight downfield shift. The above results revealed that the alkyl chain protons and partial iminazole protons of guest C4 were threaded into the cavity of P5 forming pseudorotaxane,[9e] Fig. S5 (ESI†). This is also true for host molecule Zn(TTBP). As shown in Fig. S6 (ESI†), upon adding Zn(TTBP) into the solution of C4 in $CDCl_3$, the resonances of all the protons for C4 undergo significant upfield shift due to the intense shielding effect from the porphyrin ring current, revealing the coordination between zinc ion locating at the center of porphyrin and the N atom of one of the two imidazole units in C4.

As can be expected, when adding the two active centers host compound ZnPor-P5 into the solution of guest C4 in $CDCl_3$, inclusion complexation of one of the two imidazole units with the pillar[5]arene cavity moiety, and coordination between the nitrogen atom of the remaining imidazole unit of C4 and the central zinc ion locating at the porphyrin moiety take place simultaneously, resulting in significant changes in the ^{1}H NMR spectrum of the guest C4, Fig. 1.

However, compared to the situation for mixing the guest C4 with single active center host P5/Zn(TTBP), the chemical shifts

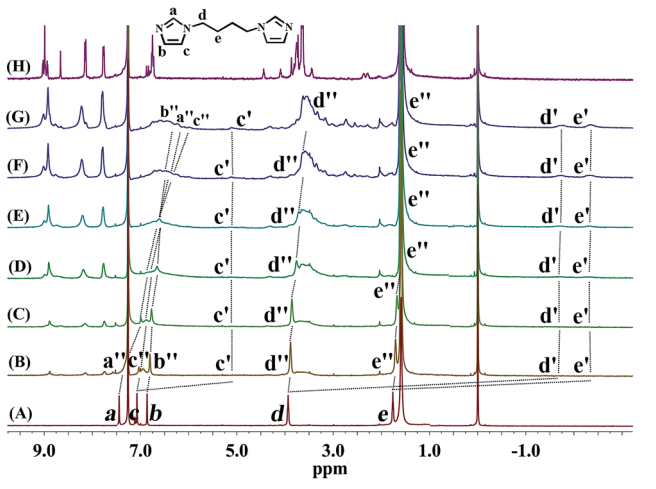


Fig. 1 ^{1}H NMR spectra of C4 in $CDCl_3$ at 25 °C upon addition of ZnPor-P5 with the molar ratio of ZnPor-P5 and C4 changing from (A) pure C4, (B) 0.1, (C) 0.2, (D) 0.4, (E) 0.6, (F) 0.8, (G) 1.0, and (H) pure ZnPor-P5.

due to the protons of ZnPor-P5 host also experience significant changes, Fig. 1, suggesting the enhanced interaction between the guest and host molecule due to the cooperative interactions between the coordination of zinc ion locating at the center of porphyrin moiety and the inclusion complexation of the pillar[5]arene cavity moiety with the guest molecule C4. The above information also demonstrates the ditopic receptor nature of this novel porphyrin-pillar[5]arene hybrid compound.

Mass spectrometry

MALDI-TOF mass spectroscopic result provides further evidence for the supramolecular complex formed between ZnPor-P5 and C4. Observation of the major signal at m/z = 1964.28, corresponding to (ZnPor-P5)·C4 (calculated 1964.60), in the MALDI-TOF MS spectrum, Fig. S8 (ESI†), directly confirms the formation of this 1 : 1 supramolecular complex.

Isothermal titration calorimetry

Isothermal titration calorimetry (ITC) measurements are able to give the quantitative information for the host-guest complex including both the binding affinity and thermodynamic origin. As a result, a solution of C4 (1.0 mM) was consecutively at 25 °C to record the exothermic binding isotherm, Fig. 2, resulting in the resolution of the binding molar ratio value of N = 1.041. This result is very much close to the expected value of 1.0, indicating the binding stoichiometry is 1 : 1 between ZnPor-P5 and C4. In addition, the association constant of K_a = (6.83 ± 0.23) × 10^4 M^{-1} was also afforded on the basis of the experimental result. Such a high binding constant suggests the relatively strong host-guest interaction between ZnPor-P5 and C4 due to the cooperative interactions between coordination and inclusion complexation as detailed above, indicating the construction of stable supramolecular system. Meanwhile, the relatively large negative enthalpy value of (ZnPor-P5)·C4 reveals that the assembly process of supramolecular complex of ZnPor-P5 with C4 is typically driven by a favorable enthalpy change, Table S1, (ESI†).

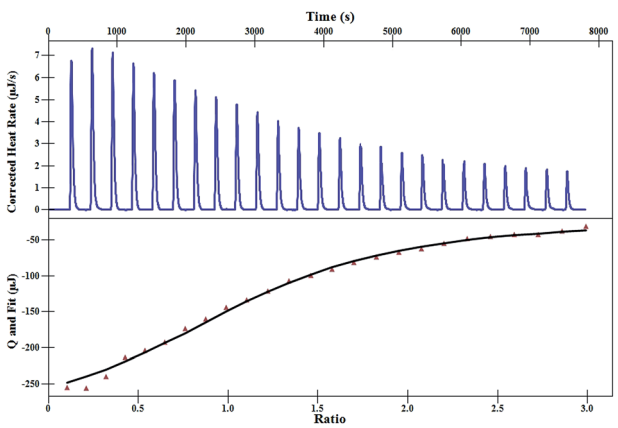


Fig. 2 ITC data for the binding of ZnPor-P5 with C4 in $CHCl_3$ at 25 °C.

Electronic absorption and fluorescence spectroscopy

Both the electronic absorption and fluorescence emission spectroscopy were utilized to collect additional information about the host-guest interaction between ZnPor-P5 and C4. According to the electronic absorption spectroscopic results, Fig. 3, upon gradual addition of guest C4 into ZnPor-P5 at a fixed concentration of 2.0 × 10^{-6} M in $CHCl_3$, the porphyrin Soret absorption underwent bathochromic shift from 422 to 433 nm due to the formation of supramolecular complex (ZnPor-P5)·C4. A sharp isosbestic point appears at 427 nm, which verifies the 1 : 1 stoichiometry of host with guest and allows the determination of the association constants (K_a) by applying a non-linear curve-fitting method. The association constant K_a, (5.02 ± 0.50) × 10^4 M^{-1}, thus deduced is consistent with that deduced from the ITC analysis as detailed above, Fig. 2. Further support for this point comes from the fluorescence spectroscopic result with the observation of decrease in the emission intensity, accompanied by a 13 nm bathochromic shift due to the porphyrin Q band, after gradually adding guest C4 into the solution of ZnPor-P5, Fig. S10, (ESI†).

Supramolecular complex mediated by Cd^{2+}

Due to the stronger coordination ability of imidazole with Cd^{2+} than with the zinc ion,[22] as shown in Fig. 4, upon addition of

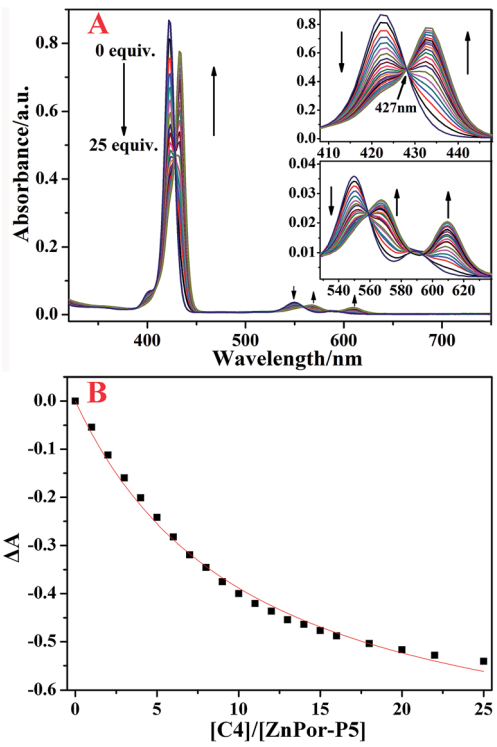


Fig. 3 Electronic absorption spectra of ZnPor-P5 (2 × 10^{-6} M) upon addition of C4 in $CHCl_3$ at 25 °C with the C4/ZnPor-P5 molar ratio changing from 0 to 25. Arrows indicate the absorbance change along with increasing the guest concentration (Inset: the isosbestic point appears at 427 nm) (A). According to the plot of ΔA *vs.* C4/ZnPor-P5 at 422 nm, the non-linear fitting curve gives the association constant K_a = (5.02 ± 0.50) × 10^4 M^{-1} and the correlation coefficient of R^2 = 0.99518, where R^2 was used to judge the fit to the date (B).

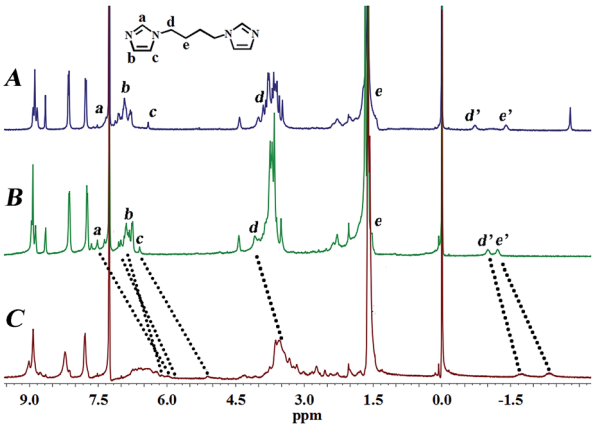


Fig. 4 ^{1}H NMR spectra of (H_2Por-P5)·C4 (A), upon addition of 1.0 equiv. Cd^{2+} to the solution of (ZnPor-P5)·C4 (B), and (ZnPor-P5)·C4 (C) recorded in $CDCl_3$ at 25 °C.

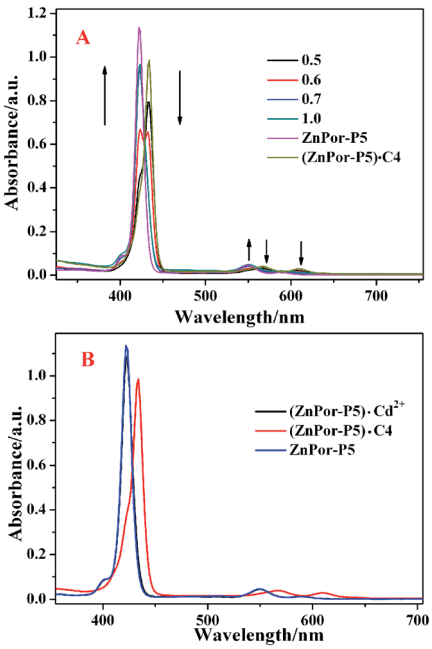


Fig. 5 Electronic absorption spectra of (ZnPor-P5)·C4 with the C4/ZnPor-P5 molar ratio of 25 recorded in $CHCl_3$ at 25 °C, upon addition of Cd^{2+} with the Cd^{2+}/C4 molar ratio changing from 0 to 0.5, 0.6, 0.7, 1.0.

CdI_2 into the (ZnPor-P5)·C4 supramolecular complex in $CDCl_3$, the protons H_d and H_e of methylene moieties in the supramolecular complex take downfield shift from −1.73 and −2.36 ppm to −1.01 and −1.27 ppm, respectively, indicating the dissociation of coordination between zinc ion locating at the center of porphyrin moiety and one of the two imidazole units of guest C4 in (ZnPor-P5)·C4 system, accompanied by the formation of a new supramolecular system ZnPor-(P5)·C4·Cd with the guest C4 only bound into the pillar[5]arene cavity of the ditopic receptor ZnPor-P5. Further support for this point comes from the electronic absorption and fluorescence spectroscopic results. Upon addition of CdI_2 into the above-mentioned (ZnPor-P5)·C4 system, the electronic absorption and fluorescence spectra completely recovered to the state of the ZnPor-P5 system, confirming the dissociation of coordination between zinc ion locating at the center of porphyrin moiety and one imidazole unit of guest C4 in (ZnPor-P5)·C4 system, Fig. 5 and S13, (ESI†).

Binding mode of ZnPor-P5 with C4

Briefly summarizing above, according to the above-described NMR, mass, electronic absorption, and fluorescence spectra as well as ITC results, ZnPor-P5 provides two binding sites, namely the pillar[5]arene cavity moiety and zinc site locating at the center of porphyrin moiety, to efficiently bind with the neutral guest C4 molecule and form inclusion complex. However, the alkyl chain that links pillar[5]arene moiety and porphyrin moiety in the host (ZnPor-P5) molecule has to be bent to some degree to simultaneously accommodate the ditopic binding of (ZnPor-P5) with C4 molecule using both binding sites due to the shorter length of the guest molecule, Fig. 6. Nevertheless, adding Cd^{2+} into the supramolecular system in $CHCl_3$ results in the dissociation of the guest C4 molecule from the zinc site, accompanied by the cavity of pillar[5]arence site still bound with the guest molecule, leading to the alkyl chain that links the pillar[5]arene moiety and porphyrin moiety in the host molecule stretching back to the original conformation of ZnPor-P5 before forming the supramolecular complex with C4, Fig. 6.

At the end of this section, it is worth noting that despite numerous attempts, all the efforts thus far paid failed to grow X-ray quality single crystals of the supramolecular complex. As a result, molecular modeling was employed to provide the supramolecular architecture information by density functional theory (DFT) calculations at the B3LYP/6-31G (D, P) level, Fig. 6.

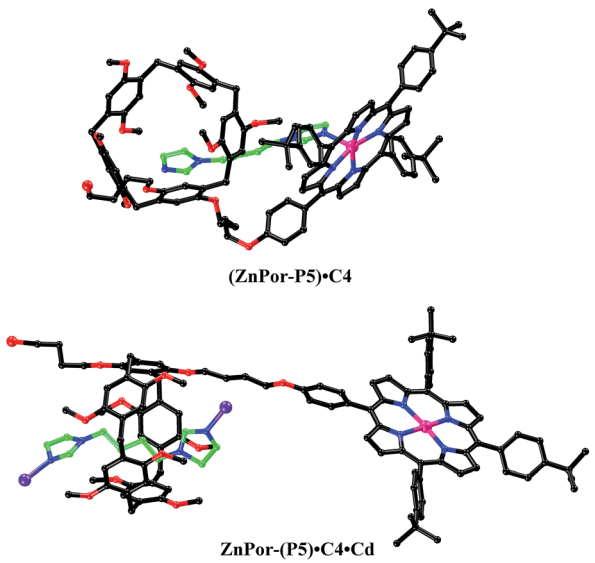


Fig. 6 The low-energy molecular conformations of (ZnPor-P5)·C4 and ZnPor-(P5)·C4·Cd obtained by density functional theory (DFT) calculations at the B3LYP/6-31G (D, P) level with all the hydrogen atoms omitted for clarity.

Conclusions

In conclusion, novel hybrid ditopic receptor with pillar[5]arene and porphyrin covalently linked with alkyl chain was designed and prepared for the first time, which forms a stable supramolecular complex with neutral guest C4 depending on the cooperative interactions between the coordination of zinc ion locating at the center of porphyrin moiety and the inclusion complexation of the pillar[5]arene cavity with the guest C4 molecule. Addition of Cd^{2+} into the supramolecular complex leads to the dissociation of the guest molecule from the zinc site locating at the center of porphyrin moiety, yielding a new supramolecular system with different conformation.

Experimental section

General remarks

All reagents were obtained from commercial sources without further purification. The compounds of metal free 5-(*p*-hydroxylphenyl)-10,15,20-tris(4-*tert*-butylphenyl)porphyrin H_2(TTBP), its zinc complex Zn(TTBP), and bromobutyl bis-substituted pillar[5]arene (P5) were prepared according to the published procedures.[12d,23]

Measurements

^{1}H NMR spectra were recorded on a Bruker DPX 400 spectrometer in $CDCl_3$ and DMSO-d_6. Electronic absorption spectra were recorded on a Hitachi U-4100 spectrophotometer. Steady-state fluorescence spectroscopic studies were performed on an F4500 (Hitachi). MALDI-TOF mass spectra were taken on a Bruker BIFLEX III ultra-high resolution Fourier transform ion cyclotron resonance (FT-ICR) mass spectrometer with α-cyano-4-hydroxycinnamic acid as matrix. Elemental analysis was performed on an Elementar Vavio El III. Titration experiments were carried out on a ITC200 from Microcal Inc. at 25 °C.

Synthetic procedures

Preparation of 1,4-bis(4-bromobutoxy)benzene. In a 500 mL three round-bottom flask, a mixture of anhydrous potassium carbonate (30.0 g, 0.22 mol), 1,4-dibromobutane (216.0 g, 1.0 mol), KI (1.0 g, 6.0 mmol) were added into dry DMF (250 mL), and then hydroquinone (11.0 g, 0.1 mol) was added dropwise into the solution under nitrogen atmosphere at 65 °C. The reaction mixture was stirred for 72 h. After the solid was filtered off, the solvent was removed. The residue was precipitated by the mixed solvent CH_3OH and H_2O (3/2, v/v) to afford 1,4-bis(4-bromobutoxy)benzene as a white solid with the yield of 24.7 g, 65.0%. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): $\delta = 6.76$ (d, $J =$ 20 Hz, 4H), 3.92 (t, $J = 12$ Hz, 4H), 3.46 (t, $J = 16$ Hz, 4H), 2.02 (m, 4H), 1.86 (m, 4H). Anal. calcd. for $C_{14}H_{20}O_2Br_2$: C, 44.24; H, 5.30; found C, 43.98; H, 5.41.

Preparation of P5. A mixture of 1,4-dimethoxybenzene (1.3 g, 9.6 mmol), 1,4-bis(4-bromobutoxy)benzene (0.9 g, 2.4 mmol), paraformaldehyde (0.51 g, 17.0 mmol) in 1,2-dichloromethane was stirred about 15 min under nitrogen atmosphere at room temperature. To which was added the boron trifluoride diethyl etherate (1.5 mL) under nitrogen atmosphere at room temperature. The solution was then stirred for 4 h. The solution was precipitated by adding CH_3OH. After the solid was filtered off, the residue was purified by flash column chromatography on silica gel with CH_2Cl_2/CH_3OH (300/1, v/v) as eluent to afford P5 as a white solid with the yield of 300.0 mg, 12.6%. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): $\delta = 6.78$ (m, 10H), 3.77 (m, 14H), 3.66 (s, 24H), 3.21 (t, 4H), 1.81 (m, 8H). MS calcd. for $C_{51}H_{60}O_{10}Br_2$: 992.83; found: *m*/*z* 993.34. Anal. calcd. for $C_{51}H_{60}O_{10}Br_2$: C, 61.70; H, 6.09; found C, 61.71; H,5.98.

Preparation of H_2(TTBP). 4-*Tert*-butylbenzaldehyde (1.6 g, 9.9 mmol), 4-hydroxybenzaldehyde (0.40 g, 3.3 mmol), and pyrrole (0.89 g, 0.91 mL, 13.2 mmol) were dissolved in propionic acid (300 mL) and purged with nitrogen whilst stirring for 30 min. The mixture was stirring for 1 h under nitrogen atmosphere at 150 °C. The solvent was removed under reduced pressure and the crude product was subjected to silica gel column chromatography using CH_2Cl_2. After removing the solvent with rotary evaporator, a purple solid was obtained with 264.0 mg, 10%. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): $\delta = -2.75$ (s, 2H, NH), 1.61 (s, 27H, CH_3),7.20 (d, $J = 8.0$ Hz, 2H, Ar), 7.75 (d, $J = 8.0$ Hz, 6H, Ar), 8.07 (d, $J = 8.0$ Hz, 2H, Ar), 8.14 (d, $J = 8.0$ Hz, 6H, Ar), 8.87 (m, 8H, pyrrole)ppm. MS calcd. for $C_{56}H_{54}N_4O$: 799.05; found: *m*/*z* 799.62. Anal. calcd. for $C_{56}H_{54}N_4O$: C, 84.17; H, 6.81; N,7.01; found C, 84.09; H, 6.92; N, 7.13. UV/vis [in $CHCl_3$, λ_{max}/nm (log ε)]: 421 (5.64), 518 (4.19), 554 (3.96), 593 (3.66), 649 (3.65).

Preparation of Zn(TTBP). $Zn(OAc)_2 \cdot 2H_2O$ (1.7 g, 8.0 mmol) was added into a solution of 3 (0.32 g, 0.40 mmol) in $CHCl_3/CH_3OH$ (2/1, v/v, 100 mL), and the mixture was stirred at room temperature for 24 h (along with a gradual color change from dark purple to pink-purple). The metalation progress was monitored by UV-vis spectroscopy. The solution was diluted with $CHCl_3$ and washed with saturated $NaHCO_3$ and water. The organic layer was dried with $MgSO_4$, and the solvent was removed. The residue was purified by flash column chromatography on silica gel using CH_2Cl_2 as eluent to afford Zn(TTBP) as a pink solid with the yield of 335.0 mg, 97%. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): $\delta = 1.62$ (s, 27H, CH_3), 7.20 (d, $J = 8.0$ Hz, 2H, Ar), 7.75 (d, $J = 8.0$ Hz, 6H, Ar), 8.08 (d, $J = 8.0$ Hz, 2H, Ar), 8.14 (d, $J = 8.0$ Hz, 6H, Ar), 8.97 (m, 8H, pyrrole) ppm. MS Calcd. for $C_{56}H_{52}N_4OZn$: 862.45; found: *m*/*z* 862.46. Anal. calcd. for $C_{56}H_{52}N_4OZn$: C, 77.99; H, 6.08; N, 6.50; found C, 77.91; H, 6.14; N, 6.62. UV/vis [in $CHCl_3$, λ_{max}/nm (log ε)]: 422 (5.80), 550 (4.38), 587 (3.77).

Preparation of H_2Por-P5. In a 500 mL three round-bottom flask, a mixture of anhydrous potassium carbonate (304.1 mg, 2.2 mmol), 3 (120 mg, 0.15 mmol), KI (30.0 mg, 0.18 mmol) are added into the dry mixed solvent 1,4-dioxane and DMF (3/1, v/v), and then 2 (49.6 mg, 0.05 mmol) was added into the solution under nitrogen atmosphere at 65 °C. The reaction mixture was stirred for 72 h. After the solid was filtered off, the solvent was removed. The residue was purified by flash column chromatography on silica gel and gelatum gel to afford H_2Por-P5 as a black red solid with the yield of 15.0 mg, 17.5%. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): $\delta = -2.76$ (s, 2H), 1.62 (m, 29H), 2.27 (m, 6H), 3.64 (m, 2H), 3.88 (m, 36H), 4.09 (m, 2H), 4.44 (m, 2H),

6.82 (m, 10H), 7.26 (d, $J = 8.0$ Hz, 2H, Ar), 7.76 (d, $J = 4.0$ Hz, 6H, Ar), 8.14 (d, $J = 16.0$ Hz, 8H, Ar), 8.93 (m, 8H, pyrrole) ppm. MS calcd. for $C_{107}H_{113}N_4O_{11}Br$: 1710.97; found: *m*/*z* 1710.81. Anal. calcd. for $C_{107}H_{113}N_4O_{11}Br$: C, 75.11; H, 6.66; N, 3.27; found C, 75.22; H, 6.58; N, 3.18. UV/vis [in $CHCl_3$, λ_{max}/nm (log ε)]: 422 (5.68), 518 (4.25), 554 (4.04), 593 (3.78), 649 (3.73).

Preparation of ZnPor-P5. $Zn(OAc)_2 \cdot 2H_2O$ (88.0 mg, 0.4 mmol) was added to a solution of H_2Por-P5 (34.2 mg, 0.02 mmol) in $CHCl_3/CH_3OH$ (2/1, v/v, 100 mL), and the mixture was stirred at room temperature for 24 h (along with gradual color change from dark purple to pink-purple). The metalation progress was monitored by UV-vis spectroscopy. The solution was diluted with $CHCl_3$ and washed with saturated $NaHCO_3$ and water. The organic layer was dried with $MgSO_4$, and the solvent was removed. The residue was purified by flash column chromatography on silica gel using CH_2Cl_2 to afford ZnPor-P5 as a pink solid with the yield of 34.4 mg, 97%. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 1.62 (m, 29H), 2.03 (m, 6H), 3.02 (t, 2H), 3.60 (m, 36H), 4.10 (m, 2H), 4.30 (m, 2H), 6.67 (m, 10H), 7.26 (2H, Ar), 7.75 (d, $J = 8.0$ Hz, 6H, Ar), 8.14 (d, $J = 8.0$ Hz, 8H, Ar), 8.97 (m, 8H, pyrrole) ppm. MS calcd. for $C_{107}H_{111}N_4O_{11}BrZn$: 1774.36; found: *m*/*z* 1774.42. Anal. calcd. for $C_{107}H_{111}N_4O_{11}BrZn$: C, 72.43; H, 6.31; N, 3.16; found C, 72.35; H, 6.41; N, 3.18. UV/vis [in $CHCl_3$, λ_{max}/nm (log ε)]: 423 (5.73), 550(4.34), 589 (3.80).

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