Supporting Information

Unprecedented Porphyrin-pillar[5]arene Hybrid Ditopic Receptor

Nana Sun,^a Xin Xiao,^{*a,b} Chenxi Liu,^a Chao Chen,^a and Jianzhuang Jiang^{*a}

^a Beijing Key Laboratory for Science and Application of Functional Molecular and Crystalline Materials, Department of Chemistry, University of Science and Technology Beijing, Beijing 100083, China

^b Key Laboratory of Macrocyclic and Supramolecular Chemistry of Guizhou Province, Department of Chemistry, Guizhou University, Guiyang 550025, China

Caption of Content

Scheme S1 Synthesis of ZnPor-P5.

Fig. S1 ¹H NMR and ¹³C NMR spectra of ZnPor-P5 recorded in CDCl₃ at 25 °C.

Fig. S2 ¹H-¹H COSY NMR spectrum of ZnPor-P5 recorded in CDCl₃ at 25 °C.

Fig. S3 The MALDI-TOF mass spectrum of ZnPor-P5.

Fig. S4 Electronic absorption spectra (top) and fluorescence spectra (bottom) of ZnPor-P5 at a fixed concentration of 2×10^{-6} mol/L in CHCl₃ at 25°C.

Fig. S5 ¹H NMR spectra of C4 in CDCl₃ at 25°C upon addition of P5.

Fig. S6 ¹H NMR spectra of C4 in CDCl₃ at 25°C upon addition of Zn(TTBP).

Fig. S7 Partial ROESY NMR spectra (400 MHz, $CDCl_3$, 25°C) of (ZnPor-P5)·C4 with the molar ratio of C4 and Zn(Por-P5) 1:1.

Fig. S8 The MALDI-TOF mass spectrum of (ZnPor-P5)·C4.

Fig. S9 Electronic absorption spectra titration of Zn(TTBP) (2×10^{-6} mol/L) upon addition of C4 in CHCl₃ at 25°C.

Fig. S10 Fluorescence spectra of ZnPor-P5 (2 \times 10⁻⁶ mol/L) upon addition of C4 in CHCl₃ at 25°C.

Fig. S11 Fluorescence spectra titration of Zn(TTBP) (2×10^{-6} mol/L) upon addition of C4 in CHCl₃ at 25°C.

Fig. S12 Electronic absorption spectra of $Zn(TTBP) \cdot C4$ upon addition of Cd^{2+} in CHCl₃ at 25°C.

Fig. S13 Fluorescence spectra of $(ZnPor-P5) \cdot C4$ upon addition of Cd^{2+} in $CHCl_3$ at 25°C.

Fig. S14 Fluorescence spectra of $Zn(TTBP) \cdot C4$ upon addition of Cd^{2+} in $CHCl_3$ at 25°C.

Table S1 Complex stability constant (K_a), enthalpy (ΔH°), and entropy changes ($T\Delta S^\circ$) for (ZnPor-P5)·C4.



Scheme S1 Synthesis of ZnPor-P5.



Fig. S1 ¹H NMR and ¹³C NMR spectra of ZnPor-P5 recorded in CDCl₃ at 25 °C.



Fig. S2 ¹H-¹H COSY NMR spectrum of ZnPor-P5 recorded in CDCl₃ at 25 °C.



Fig. S3 The MALDI-TOF mass spectrum of ZnPor-P5.



Fig. S4 Electronic absorption spectra (top) and fluorescence spectra (bottom) of ZnPor-P5 at a fixed concentration of 2×10^{-6} mol/L in CHCl₃ at 25 °C.



Fig. S5 1 H NMR spectra of C4 in CDCl3 at 25 °C upon addition of P5 with the molarratio of P5 and C4 changing from (A) pure C4, (B) 0.2, (C) 0.6, (D) 0.8, (E) 1.0, and(F)pureP5.



Fig. S6 ¹H NMR spectra of C4 in CDCl₃ at 25 °C upon addition of Zn(TTBP) with the molar ratio of Zn(TTBP) 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 Zn(TTBP).



Fig. S7 Partial ROESY NMR spectra (400 MHz, CDCl₃, 25 °C) of (ZnPor-P5)·C4 with the molar ratio of C4 and Zn(Por-P5) 1:1. The ROESY spectrum of (ZnPor-P5) C4 in CDCl₃ shows obvious cross-signals between the alkyl chain methylene protons H_e of the guest C4 and the porphyrin β protons as well as the phenol protons of pillar[5]arene moiety, further indicating that simultaneous inclusion complexation of one of the two imidazole units by the pillar[5]arene cavity and coordination between the nitrogen atom of the remaining imidazole unit of C4 and the central zinc ion locating at the porphyrin moiety of the host take place.





Fig. S9 Top: Electronic absorption spectra titration of Zn(TTBP) (2 × 10⁻⁶ mol/L) upon addition of C4 in CHCl₃ at 25°C with the [C4]/[Zn(TTBP)] molar ratio changing from 0 to 25. Arrows indicate the absorbance change along with increasing the guest concentrations (Inset: the isosbestic point appears at 427 nm, indicating the binding stoichiometry is 1:1 between Zn(TTBP) and C4.) (A). Bottom: According to the plot of ΔA vs. [C4]/[Zn(TTBP)] at 422 nm, the non-linear fitting curve gives the association constant $K_a = (7.44 \pm 0.50) \times 10^3$ M⁻¹, the correlation coefficient of R² = 0.99959, where R² was used to judge the fit to the data (B). As shown in Figure S9, the association constant K_a of Zn(TTBP)·C4 system is lower than that of (ZnPor-P5)·C4 system, further indicating that the cooperative interactions benefit the formation of the complex (ZnPor-P5)·C4, namely, the coordination of zinc ion locating at the center of porphyrin moiety and the inclusion complexation of the pillar[5]arene cavity with/to the guest molecule C4.



Fig. S10 Fluorescence spectra of ZnPor-P5 (2×10^{-6} mol/L) upon addition of C4 in CHCl₃ at 25°C with the [C4]/[ZnPor-P5] molar ratio changing from 0 to 25.



Fig. S11 Fluorescence spectra titration of Zn(TTBP) (2 × 10⁻⁶ mol/L) upon addition of C4 in CHCl₃ at 25°C with [C4]/[Zn(TTBP)] molar ratio changing from 0 to 25. As shown in Figure S11, upon gradual addition of guest C4 into the solution of Zn(TTBP), the emission intensity decreases slightly, accompanied by slight bathochromic shift due to the porphyrin Q band, also indicating the interaction between C4 and Zn(TTBP) is weaker than that in (ZnPor-P5)·C4 system, Figure S10 (Supporting Information).



Fig. S12 Electronic absorption spectra of $Zn(TTBP) \cdot C4$ recorded in CHCl₃ at 25°C at a fixed concentration for Zn(TTBP) of 2×10^{-6} mol/L with the [C4]/[Zn(TTBP)] molar ratio of 25 upon addition of Cd²⁺ with the [Cd²⁺]/[C4] molar ratio changing from 0 to 0.5, 0.6, 0.7, 1.0. As shown in Figure S12, upon addition of CdI₂ into the Zn(TTBP) ·C4 system, the electronic absorption spectra fully recovered to the state of the Zn(TTBP), confirming the dissociation of coordination between zinc ion locating at the center of porphyrin and imidazole unit of guest C4 in $Zn(TTBP) \cdot C4$ system.



Fig. S13 Fluorescence spectra of $(ZnPor-P5) \cdot C4$ recorded in CHCl₃ at 25°C at a fixed concentration for ZnPor-P5 of 2 × 10⁻⁶ mol/L with the [C4]/[ZnPor-P5] molar ratio of 25 upon addition of Cd²⁺ with the [Cd²⁺]/[C4] molar ratio changing from 0 to 0.5, 0.6, 0.7, 1.0.



Fig. S14 Fluorescence spectra of $Zn(TTBP) \cdot C4$ recorded in CHCl₃ at 25°C at a fixed concentration for Zn(TTBP) of 2×10^{-6} mol/L with the [C4]/[Zn(TTBP)] molar ratio of 25 upon addition of Cd²⁺ with the [Cd²⁺]/[C4] molar ratio changing from 0 to 0.5, 0.6, 0.7, 1.0. As shown in Figure S14, upon addition of CdI₂ into the Zn(TTBP)·C4 system, the fluorescence spectra completely recovered to the state of the Zn(TTBP), further confirming the dissociation of coordination between zinc ion locating at the center of porphyrin and imidazole unit of guest C4 in Zn(TTBP)·C4 system.

Table S1 Complex stability constant (K_a), enthalpy (ΔH°), and entropy changes ($T\Delta S^\circ$) for (ZnPor-P5)·C4.

Complex	$K_{\rm a}({ m M}^{-1})$	ΔH° (kJ mol ⁻¹)	$T\Delta S^{\circ}$ (kJ mol ⁻¹)
(ZnPor-P5)·C4	$(6.83 \pm 0.23) \times 10^4$	-28.60	-3.82