Journal of Organometallic Chemistry 695 (2010) 111–119

Contents lists available at ScienceDirect

Journal of Organometallic Chemistry

journal homepage: www.elsevier.com/locate/jorganchem

A molecular-clip-based approach to cofacial zinc–porphyrin complexes

Duckhyun Kim [a], Sewon Lee [a], Guohua Gao [b], Hong Seok Kang [c], Jaejung Ko [a,*]

[a] Department of Chemistry, Korea University, Jochiwon, Chungnam 339-700, Republic of Korea
[b] Pohl Institute of Solid-State Physics, Tongji University, Shanghai 200092, PR China
[c] Department of Nano and Advanced Materials, College of Engineering, Jeonju University, Hyoja-dong, Wansan-ku, Chonju, Chonbuk 560-759, Republic of Korea

ARTICLE INFO

Article history:
Received 14 August 2009
Received in revised form 16 September 2009
Accepted 25 September 2009
Available online 3 October 2009

Keywords:
Molecular clip
Porphyrin
Rigid spacer
Self-assembly

ABSTRACT

We have synthesized molecular-clip-based cofacial zinc–porphyrin complexes. The complexes are shown to be new efficient receptors for the complexation of 1,4-diazabicyclo[2,2,2]octane, acridinium ions, 1,4,5,8-naphthalene tetracarboxylic dianhydride (NTDA) and 1,2,4,5-benzenetetracarboxylic dianhydride (BTDA). Large binding constants (K_{asso}) in the range of 2.0×10^4–1.1×10^8 M^{-1} were obtained for the 1:1 complexes of molecular tweezers (**3**) and rectangle (**8**) by inserting the hosts between the two porphyrin rings. The values of *K* and the spectroscopic results suggest that **3** and **8** serve as effective building blocks to capture the hosts. Semi-empirical calculations show that the guests position themselves within the cleft of the *bis*-porphyrins.

1. Introduction

For over two decades, intensive research focused on studying the synthesis and properties of cofacial porphyrins has generated many self-assembly [1,2]. Such porphyrin complexes have attracted considerable attention due to their light harvesting [3], catalytic [4], chirality sensing [5], and molecular recognition properties [6]. The cooperative interaction between the two porphyrins plays a crucial role in exerting these functions. Therefore, the structural modifications for the cooperative effect may be useful for the design of molecular recognition. Efficient molecular recognition of the *bis*-porphyrin host for unsaturated molecules [7] or ions [8] requires high structural and binding-site complementarity between the host and the guest. Cofacial *bis*-porphyrins have been shown to form π-complexes with acridinium ions [9] or fullerenes [10], which are inserted between the two porphyrin rings. On the other hand, metalloporphyrins can act as acceptor building blocks if the metal atom inside the porphyrin has one site available for coordination [11]. Due to their preorganized U-shaped configurations and the cooperative interaction of their two binding sites, such porphyrin units are able to coordinate with bridging donor ligands such as 1,4-diazabicyclo[2,2,2]octane (DABCO) [11]. A significant advance in this field would be the development of an efficient synthetic method for preparing cofacial porphyrin complexes that allows control over the orientation and interfacial distances of the porphyrins. One approach is to force a cofacial arrangement of the porphyrin moieties by the introduction of a rigid spacer. We recently initiated a study to explore their potential as a new generation of preorganized scaffolds [12]. The methods we have used to synthesize such porphyrins have all utilized a well-defined molecular clip [13] between the porphyrin units. We herein describe how an aromatic molecular-clip-based *bis*-zinc porphyrin is used to efficiently direct the self-assembly for a series of guests.

2. Experimental

2.1. General procedures

All reactions were carried out under an argon atmosphere. All solvents were distilled prior to use. All reagents were purchased from Sigma–Aldrich. 2,12-Diethynyl-[7-(3,5-di-*tert*-butylphenyl)-dibenzo[*c*,*h*]acridine] (**1**) [14], [5-(4-iodophenyl)-10, 15,20-tris(3, 5-di-*tert*-butylphenyl)porphinato]zinc(II) (**2**) [15], [5,15-*bis*(4-methoxy-carbonylphenyl)-10,20-dimesitylporphinato]zinc(II) (**4**) [16] and 2,12-*bis*[*trans*-Pt$(PEt_3)_2NO_3$]-[7-(3,5-di-*tert*-butylphenyl)- dibenzo[*c*,*h*]acridine] (**7**) [12] were synthesized via previously reported methods. ^1H, ^{13}C, and ^{31}P NMR spectra were recorded on a Varian Mercury 300 spectrometer operating at 300.00, 75.44, and 121.44 MHz, respectively. MALDI-MS spectra were recorded on a Voyager-DE STR MALDI-TOF mass spectrometer. Elemental analyses were performed using a Carlo Erba Instruments CHNS-O EA 1108 analyzer. Mass spectra were recorded on a JEOL JMS-SX102A mass spectrometer. Absorption spectra were recorded on a Perkin–Elmer Lambda 2S UV–Vis spectrometer.

* Corresponding author. Tel.: +82 41 860 1337; fax: +82 41 867 5396.
E-mail address: jko@korea.ac.kr (J. Ko).

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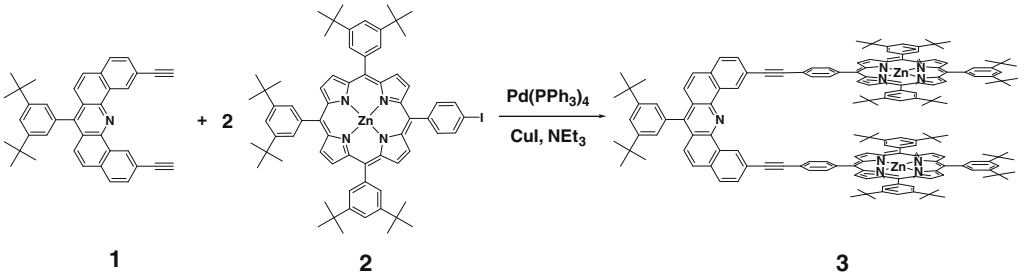
doi:10.1016/j.jorganchem.2009.09.035

2.2. Synthesis of porphyrin tweezers (**3**)

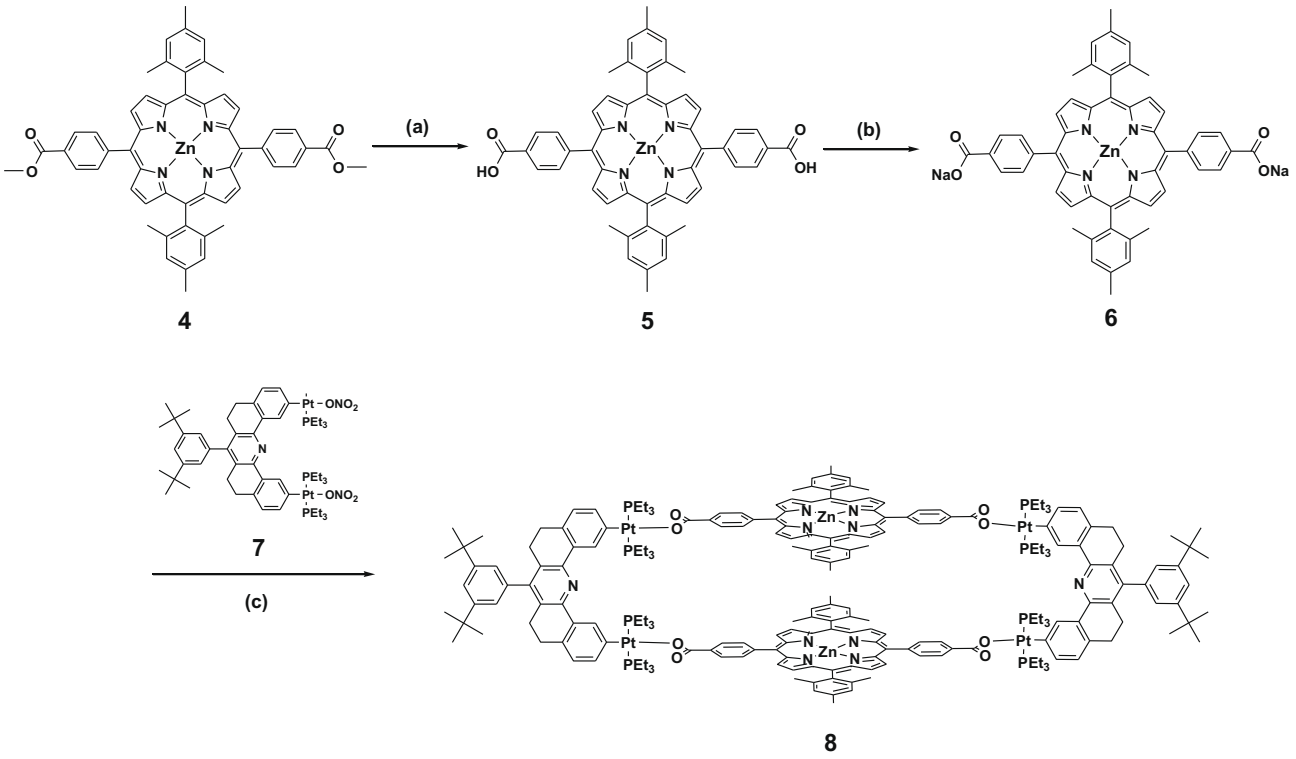
Triethylamine (30 mL) was added to a mixture of 2,12-diethynyl-[7-(3,5-di-*tert*-butylphenyl)-dibenzo[*c*,*h*]acridine] (**1**) (0.045 g, 0.087 mmol), [5-(4-iodophenyl)-10,15,20-tris(3,5-di-*tert*-butylphenyl)porphinato]zinc (**2**) (0.3 g, 0.26 mmol), tetrakis-(triphenylphosphine) palladium (0.01 g, 0.0087 mmol), and copper(I) iodide (0.001 g, 0.005 mmol). The reaction mixture was stirred under nitrogen at 80 °C for 36 h. The solvent was then removed under reduced pressure. The resulting residue was extracted with dichloromethane and then purified by chromatography on silica gel using dichloromethane/hexane (1:2, v/v) as an eluent. This afforded 0.18 g of product **3**. Yield: 81%. M.p.: >400 °C. ^{1}H NMR ($CDCl_3$): δ 10.21 (s, 2H), 8.94 (d, 4H, J = 4.8 Hz), 8.90 (d, 4H, J = 4.8 Hz), 8.88 (d, 4H, J = 4.8 Hz), 8.83 (d, 4H, J = 4.8 Hz), 8.25 (d, 4H, J = 8.1 Hz), 8.16 (d, 4H, J = 8.1 Hz), 8.13 (d, 2H, J = 9.3 Hz), 8.04 (m, 6H), 7.85 (s, 8H), 7.80 (s, 4H), 7.76 (s, 1H), 7.73 (s, 2H), 7.59 (m, 4H), 7.43 (s, 2H), 1.54 (s, 36H), 1.51 (s, 18H), 1.26 (s, 72H). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 151.2, 150.5, 150.4, 150.3, 149.8, 148.6, 148.5, 148.4, 147.8, 145.6, 143.5, 142.0, 141.8, 135.6, 134.5, 133.5, 132.6, 132.4, 132.3, 132.2, 132.1, 131.5, 130.1, 129.7, 129.5, 128.6, 128.2, 127.2, 125.5, 125.1, 124.6, 122.7, 122.6, 122.4, 122.2, 120.8, 120.6, 119.8, 91.8, 91.2, 35.3, 35.2, 34.9, 31.9, 31.7, 31.6. Anal. Calc. for $C_{175}H_{181}N_9Zn_2$: C, 81.51; H, 6.23. Found: C, 81.19; H, 6.12%.

2.3. Synthesis of [5,15-bis(4-carboxyphenyl)-10,20-dimesitylporphinato]zinc (**5**)

A mixture of THF/MeOH/water (2/1/1, 200 mL) containing [5,15-*bis*(4-methoxy-carbonylphenyl)-10,20-dimesitylporphinato]zinc(II) (**4**) (0.13 g, 0.148 mmol) and NaOH (0.9 g, 23 mmol) was refluxed for 0.5 h. After it was allowed to cool to room temperature, the reaction mixture was acidified with AcOH (5 mL) and then washed with water. The separated organic phase was dried over Na_2SO_4 and then evaporated to dryness under reduced pressure. The resulting residue was purified by recrystallization (CH_2Cl_2/hexane) to afford 0.11 g of product **5**. Yield: 87%. M.p.: 321 °C. ^{1}H NMR (DMSO-d_6): δ 13.19 (s, 2H, COOH), 8.73 (d, 4H, J = 4.2 Hz), 8.60 (d, 4H, J = 4.2 Hz), 8.34 (m, 8H), 7.32 (s, 4H), 2.56 (s, 6H), 1.77 (s, 12H). ^{13}C{^{1}H} NMR (DMSO-d_6): δ 177.1, 158.6, 158.2, 156.7, 148.5, 147.9, 146.4, 143.9, 141.4, 139.9, 139.2, 137.1,



Scheme 1. Synthesis of porphyrin tweezer **3**.



Scheme 2. Synthesis of porphyrin rectangle **8**: (a) NaOH, THF, MeOH, and H_2O (b) $NaHCO_3$, acetone, and H_2O (c) acetone and H_2O.

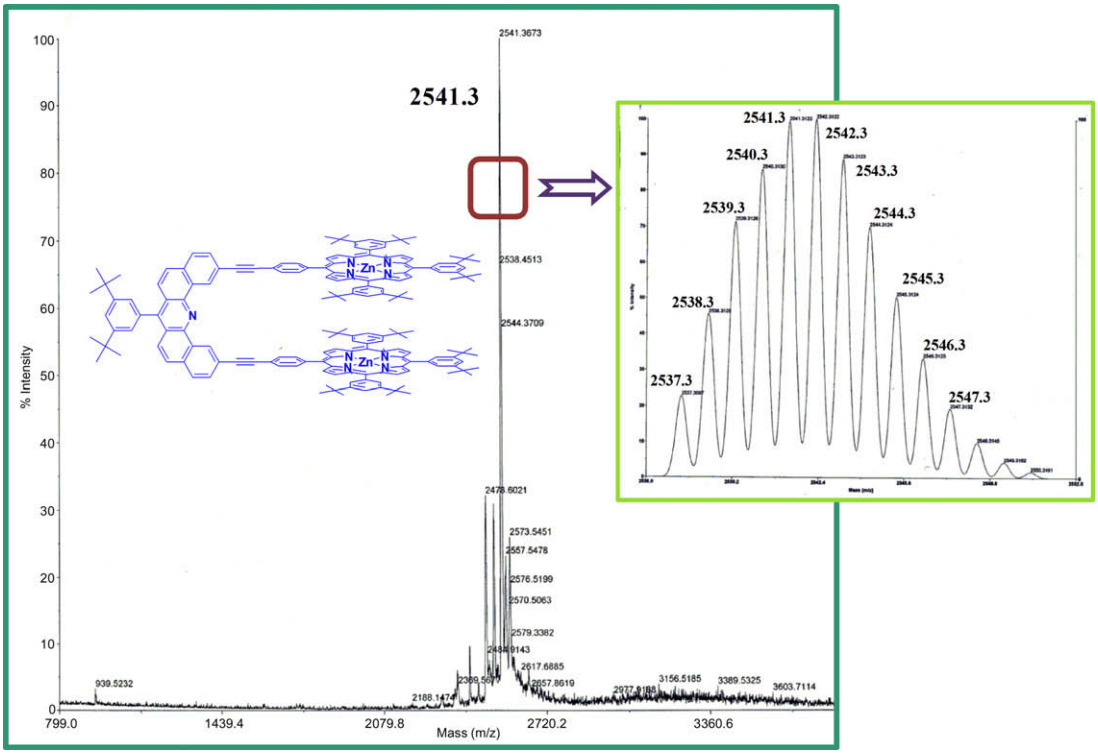


Fig. 1. MALDI-mass spectrum of compound **3** with isotopic distribution pattern.

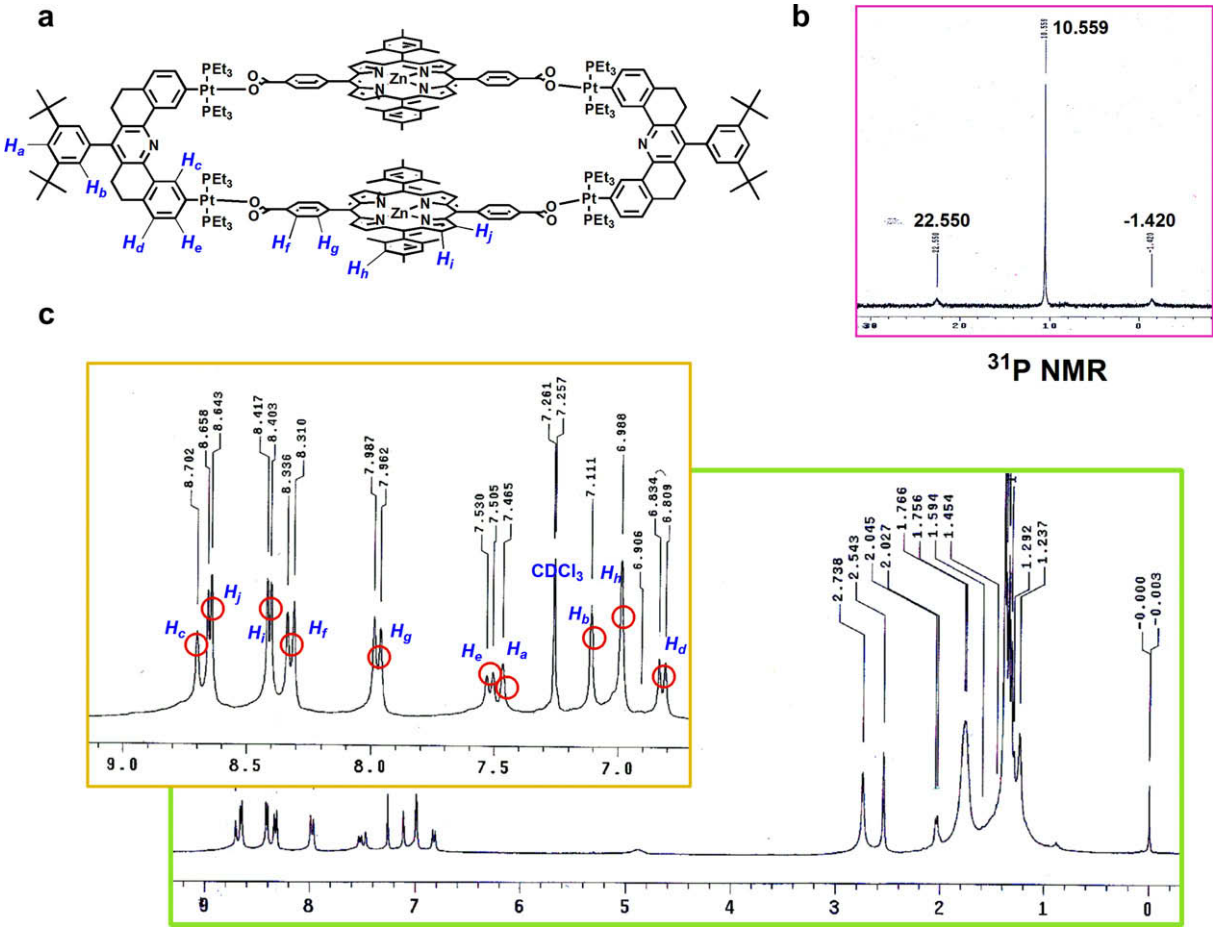


Fig. 2. NMR spectra of molecular rectangle **8** at 298 K in chloroform-d_1: (a) structure, (b) ^{31}P NMR and (c) ^{1}H NMR spectra.

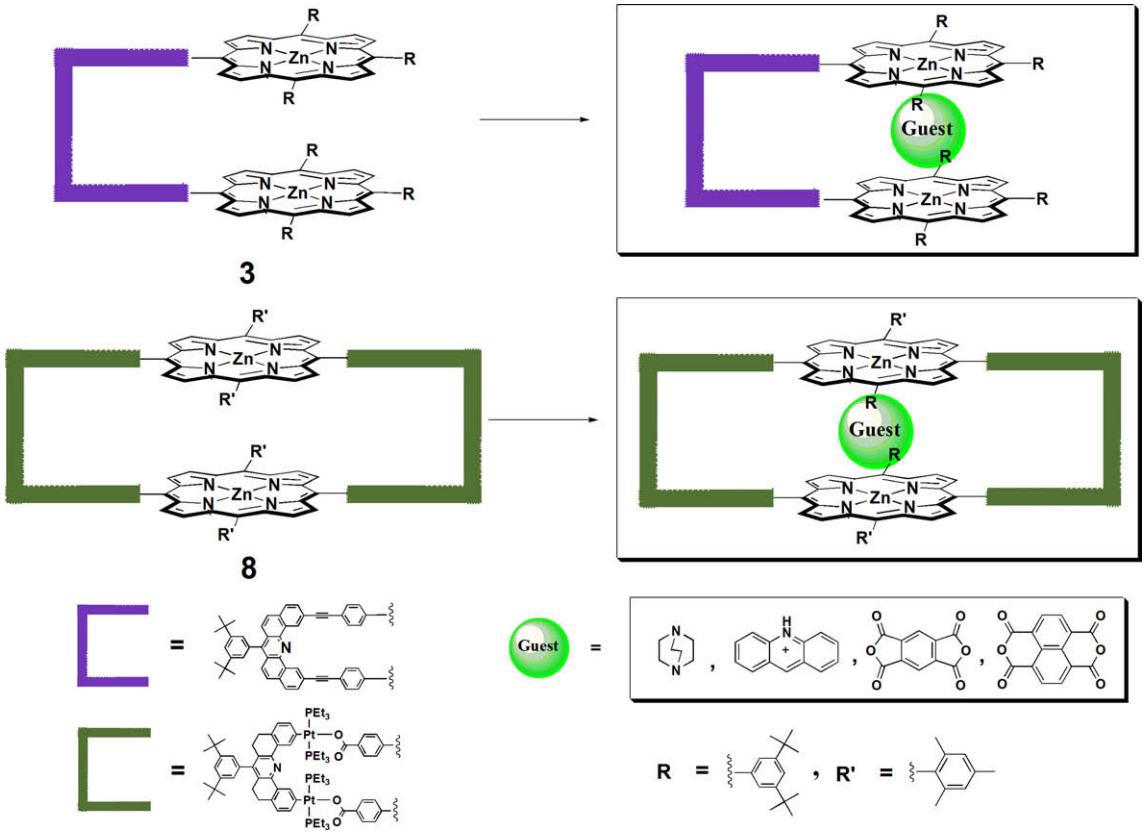
137.0, 128.1, 127.9, 30.9, 30.5. Anal. Calc. for $C_{52}H_{40}N_4O_4Zn$: C, 73.45; H, 4.74. Found: C, 73.27; H, 4.66%.

2.4. Synthesis of porphyrin rectangle (8)

A 50 mL flask was charged with [5,15-*bis*(4-carboxyphenyl)-10,20-dimesityl-porphinato]zinc(II) (**5**) (0.05 g, 0.059 mmol) and $NaHCO_3$ (0.015 g, 0.177 mmol). After adding an acetone–H_2O mixture (1:1, 8 mL) to the flask, the mixture was stirred for 1 h. This resulted in the formation of compound **6**. Compound **7** (0.085 g, 0.059 mmol) in acetone (4 mL) was then slowly added to this mixture, which was subsequently stirred overnight at 60 °C. Recrystallization from CH_2Cl_2/hexane yielded pure **8** as a dark red crystalline solid. Yield: 97%. M.p.: >400 °C. ^{1}H NMR ($CDCl_3$): δ 8.70 (s, 4H), 8.65 (d, 8H, J = 4.5 Hz), 8.41 (d, 8H, J = 4.5 Hz), 8.32 (d, 8H, J = 7.8 Hz), 7.97 (d, 8H, J = 7.8 Hz), 7.52 (d, 4H, J = 7.5 Hz), 7.46 (s, 2H), 7.11 (s, 4H), 6.98 (s, 8H), 6.82 (d, 4H, J = 7.5 Hz), 2.74 (s, 24H), 2.54 (s, 12H), 1.76 (m, 48H), 1.38 (s, 36H), 1.29 (m, 72H). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 171.7, 151.2, 150.8, 149.6, 149.4, 148.3, 144.4, 143.4, 139.1, 137.9, 137.6, 137.3, 137.1, 136.9, 134.6, 134.3, 134.0, 132.1, 131.6, 130.2, 128.4, 127.4, 127.3, 126.4, 123.4, 120.8, 119.9, 118.5, 35.1, 31.7, 30.1, 29.6, 28.1, 26.7, 14.2, 8.2. ^{31}P{^{1}H} NMR ($CDCl_3$): δ 10.5 (J_{Pt-P} = 2910 Hz). Anal. Calc. for $C_{222}H_{266}N_{10}O_8P_8Pt_4Zn_2$: C, 61.14; H, 6.15. Found: C, 61.01; H, 6.10%.

3. Results and discussion

Our strategy for the synthesis of the cofacial *bis*-zinc porphyrin utilizes a molecular clip with two parallel reactive sites facing in the same direction. The synthetic procedures for noncyclic and cyclic metalloporphyrins are outlined in Schemes 1 and 2, respectively. The synthesis of noncyclic metalloporphyrin **3** is conveniently prepared from molecular clip **1**. The palladium-catalyzed cross-coupling of 3 equiv. of [5-(4-iodophenyl)-10,15,20-tris(3,5-di-*tert*-butylphenyl)porphinato]zinc (**2**) [15] with 2,12-diethynyl-[7-(3,5-di-*tert*-butylphenyl)dibenzo[*c*,*h*]acridine] (**1**) [14] afforded **3** in 81% yield. The spectroscopic data for **3** were completely consistent with its proposed formulation. Fifteen distinct resonances in the 10.21–7.40 ppm region of the ^{1}H NMR spectrum and thirty-eight peaks in the 151.2–119.8 ppm aromatic region of the ^{13}C NMR spectrum were observed. Additional evidence for the formation of **3** was obtained from MALDI-TOF mass spectroscopy (Fig. 1). The parent ion in the mass spectrum was observed at *m*/*z* 2541. The isotopic distribution patterns matched the calculated patterns well. The cyclic platinum-based macrocycle **8** was synthesized in three steps from the rigid oxygen donor building block **4** [16] (Scheme 2). The linear dicarboxylate dianion **6** was prepared from **4** by a hydrolysis reaction, followed by a salt exchange reaction that converted **5**–**6**. The 1:1 stoichiometric combination of **7** with the linear dicarboxylate **6** produced **8** as a red solid in 97% yield. Similar Pt(II)–O bond-containing macrocycles have been reported by Stang and co-workers [17]. The NMR spectrum of **8** indicated the formation of a highly symmetrical structure. This was evidenced by the number of resonances in aromatic region of the ^{1}H NMR spectrum and the ^{13}C NMR spectrum being reduced (from 15–38, respectively, for **3**) to 10 and 28, respectively (Fig. 2). The ^{31}P NMR spectrum of **8** was also consistent with the formation of a highly symmetrical species, as indicated by the appearance of a sharp singlet with concomitant ^{195}Pt satellites (J_{p-pt} = 2910 Hz), shifted upfield by 1.70 ppm relative to that observed for **7**. The small change in the phosphorous resonance of **8** relative to that of the molecular clip is attributable to the structural similarity of the Pt–O coordinate bond.



Scheme 3.

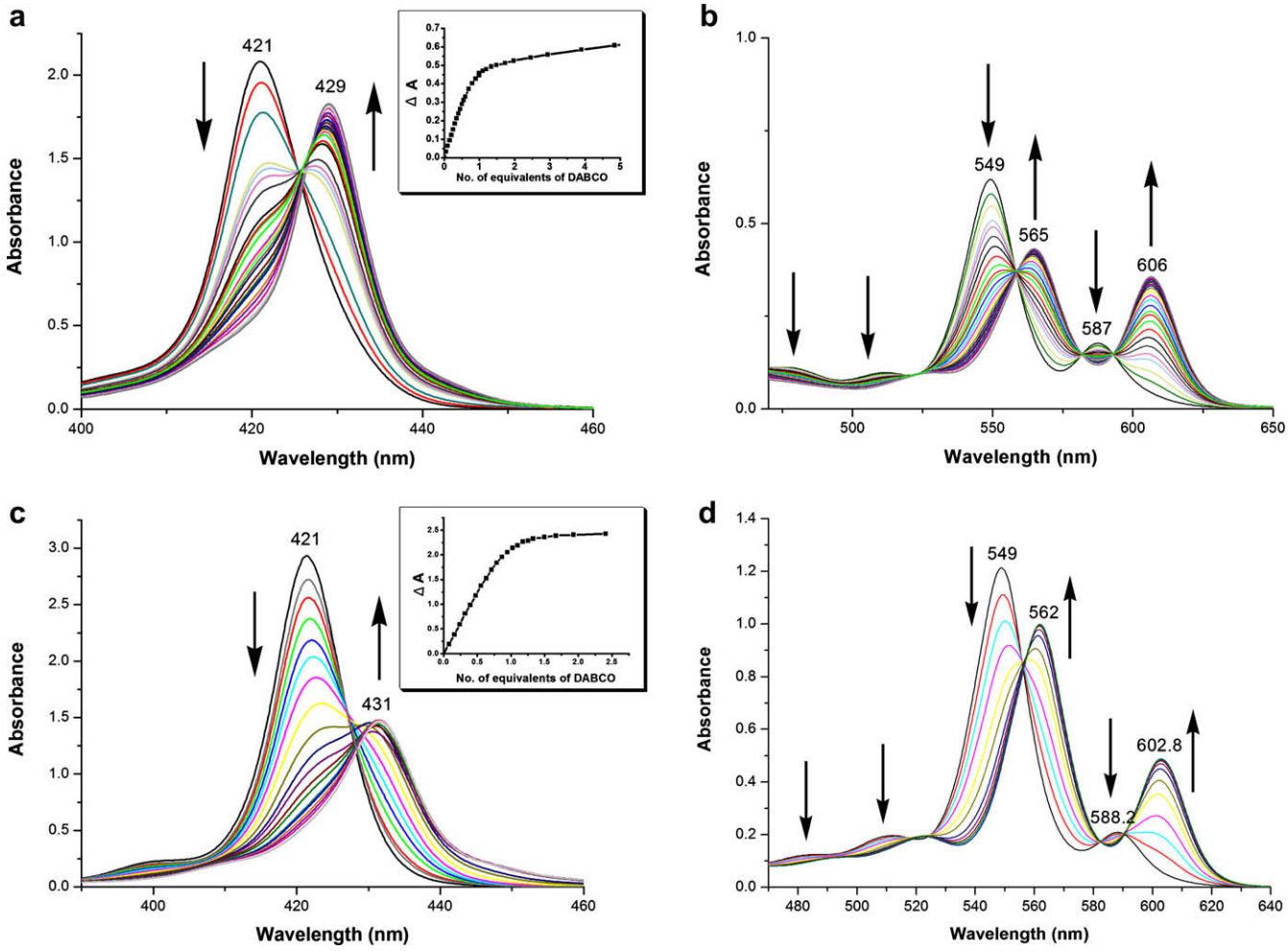


Fig. 3. Spectral changes of the Soret band of (a) **3** (4.7×10^{-7} M), (c) **8** (4.7×10^{-6} M) and the Q-band of (b) **3** (5.9×10^{-7} M), (d) **8** (4.7×10^{-6} M) upon the addition of DABCO. The concentrations of DABCO were: (a) 0–2.9×10^{-6} M, (b) 0–1.4×10^{-6} M, (c) 0–1.4×10^{-5} M and (d) 0–8.6×10^{-6} M in $CHCl_3$. Inset: the plot of absorbance change at 421 nm versus **3** and **8**.

Table 1
Association constants (K_a (M^{-1})) and Gibbs enthalpies ($\Delta G°$ (kcal/mol)) for the formation of host–guest complexes in $CHCl_3$ at the Soret band.

Substrate	Tweezers (**3**)			Rectangle (**8**)		
	λ (nm)	K_{asso} (M^{-1})	$\Delta G°$ (Kcal/mol)	λ (nm)	K_{asso} (M^{-1})	$\Delta G°$ (Kcal/mol)
DABCO	421.2	1.1×10^8	−10.85 ± 0.2	421.4	4.5×10^6	−8.98 ± 0.2
Acridinium	420	1.6×10^7	−9.72 ± 0.1	421.3	3.1×10^7	−10.11 ± 0.1
NTDA	420.8	6.5×10^4	−6.50 ± 0.1	417.5	1.3×10^5	−6.90 ± 0.1
BTDA	421.4	4.0×10^4	−6.21 ± 0.1	417.4	4.0×10^4	−6.21 ± 0.1

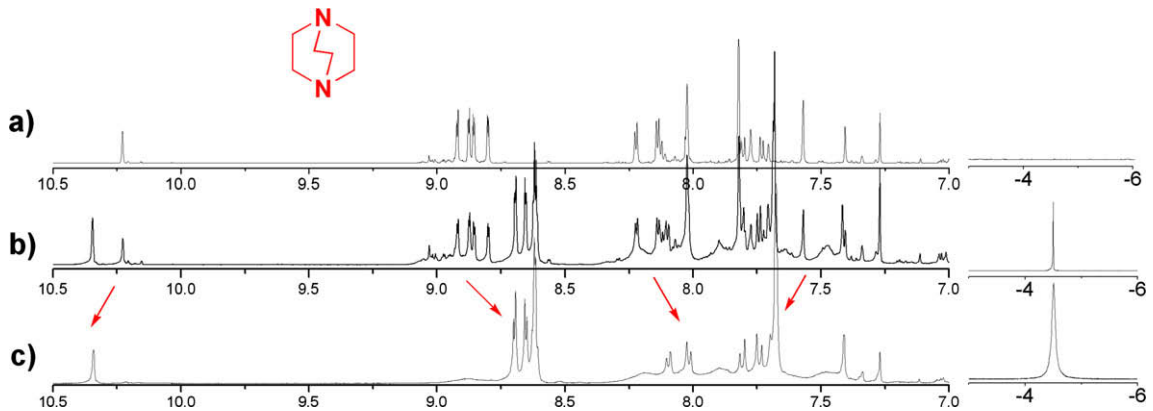


Fig. 4. ^1H NMR spectra of **3** (3.9×10^{-2} mol L^{-1}) in the presence of DABCO in $CDCl_3$ at 298 K. The concentrations of DABCO were: (a) 0.0, (b) 2.4×10^{-2}, and (c) 3.9×10^{-2} mol L^{-1}.

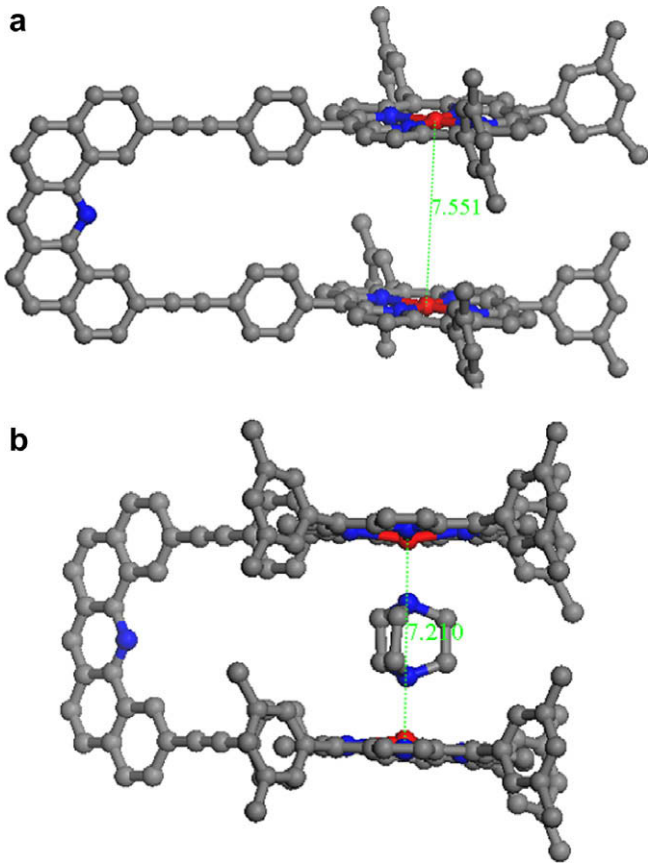


Fig. 5. Molecular modeling of the *bis*-porphyrin tweezer **3**: (a) in the absence of a guest and (b) with DABCO, thereby forming a 1:1 complex formation. The 3,5-di-*tert*-butylphenyl in the molecular clip was omitted in order to simplify the calculation.

The coordination of DABCO to **3** was probed by UV–Vis spectroscopy in chloroform (Scheme 3). The addition of incremental amounts of DABCO to the solution of receptor **3** gave a series of UV-vis spectra with one isosbestic point. The Soret band of **3** was significantly shifted from 421.2 to 429.4 nm with a half bandwidth of 12.1 nm. The Q-bands were also significantly red-shifted with isosbestic points. This red-shift and the isosbestic point of the Soret and Q-bands absorption are characteristic of a DABCO-porphyrin sandwich complex [2,18,19]. Fig. 3a shows the data for the titrations up to 25 equiv. of DABCO. Analysis of the binding isotherm for **3** with a 1:1 binding model [20] gave an association constant K_{asso} of $1.1 \times 10^8\ M^{-1}$. This is comparable with previously reported values for other zinc porphyrins and DABCO [2,19]. The UV–Vis spectrum of rectangular macrocycle **8** in $CHCl_3$ at 25 °C changed as the DABCO was added. The Soret band and Q-bands underwent a significant hypochromic and bathochromic shift in the same manner as the host **3**. The titration curve for **8**, shown in the inset of Fig. 3c, is essentially a straight line with an abrupt endpoint after the addition of 1 equiv. of DABCO to **8**. Analysis of this binding isotherm yields an association constant K_{asso} of $4.5 \times 10^6\ M^{-1}$ (Table 1). The relatively small constant for **8** compared with that for **3** may result from the rigidity of macrocycle **8**, which causes the shrinkage of bond distance between the two porphyrins. The 1:1 complex formation is further confirmed by the ^{1}H NMR spectra shown in Fig. 4. When 0.6 equiv. of DABCO were added to **3**, a new signal appeared at −4.5 ppm. This signal is indicative of the formation of the binary complex and can be assigned to the methylene protons of a DABCO molecule situated between two zinc–porphyrin complexes. The unusual upfield shift of the signal is attributable to the influence of the porphyrin ring current, which is diagnostic of a sandwich complex. When a 1:1 concentration ratio of **3** and DABCO was added, a new set of resonances corresponding to the 1:1 complex formation were observed and the resonances due to **3** completely disappeared. The ^{1}H NMR resonances of the 1:1 complex exhibited upfield shifts of around 0.2–0.5 ppm upon complexation relative to the porphyrin signals for free **3**. This was due to the proximity of the two porphyrin π-sys-

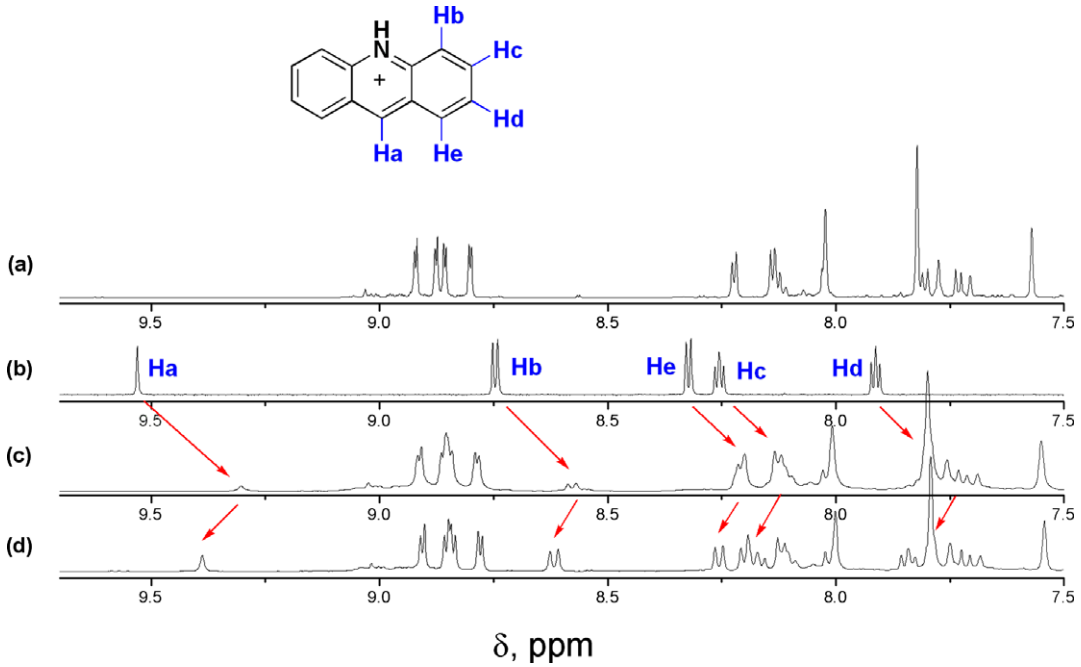


Fig. 6. ^{1}H NMR spectra of **3** (3.9×10^{-2} mol L^{-1}) in the presence of acridinium ions (b) in $CDCl_3$ at 298 K. The acridinium ion concentrations were (a) 0.0, (c) 1.9×10^{-2}, and (d) 3.9×10^{-2} mol L^{-1}.

tem in the complex, which caused the protons to experience a large ring-current-induced shift. On the other hand, the proton resonances of the molecular clip framework exhibited a slightly downfield shift or remained unchanged.

As crystals of suitable quality for X-ray crystallographic analysis could not be obtained, calculations were required to visualize the size and shape of the molecule. We carried out *ab initio* calculations to obtain reliable structural information. The geometry of **3** was optimized by Hartree–Fock (HF) calculations using a suite of GAUSSIAN 98 programs. Stereoplots of the optimized structures of **3** and DABCO•**3** are shown in Fig. 5. The optimized structures show that the *bis*-porphyrin tweezer **3** has a cofacial arrangement of porphyrins with a centre-to-centre distance of 7.551 Å. Therefore, the molecular modeling indicates that the *bis*-porphyrin tweezer having such a distance is a suitable as a host for molecular recognition. Based on these sizes, the guest, DABCO was chosen as a suitable one because the *N–N* distance in these bidentate ligands is 2.7 Å and the Zn in the porphyrin to nitrogen bond distance is 2.2 Å. As expected, these guests form 1:1 host–guest complexes with **3**. The optimized model reveals a porphyrin centre-to-centre distance of 7.210 Å, showing that the host shrinks slightly to accommodate the guest. This configuration is a very reasonable one in view of the total summation of the three bond distances (7.1 Å). Since the distance between the two porphyrins of the two hosts is 7.551 Å, the acridinium ion is suitably positioned for stacking interactions within the cleft of the *bis*-porphyrins. An electronic interaction between **3** and the acridinium ion was evidenced by the UV–Vis titration experiment. The gradual addition of acridinium ions to a chloroform solution of **3** slightly decreased the absorbance of the Soret band at 420 nm. Fitting the data to a 1:1 binding mode gave rise to an association constant K_{asso} of $1 \times 10^7\ M^{-1}$ (Table 1). Similar results were also obtained for the rectangular macrocycle **8**. Upon the addition of the acridinium ions to the solution of the receptor **8** in $CHCl_3$, the Soret band of **8** in the UV–Vis spectrum significantly shifted from 421.3 to 427.1 nm and we calculated the K_{asso} of the 1:1 complex to be $3.1 \times 10^7\ M^{-1}$. The K_{asso} values of the acridinium ions for **3** and **8** are much larger than those of other cofacial *bis*-porphyrins. This demonstrates that the two hosts **3** and **8** form strong π-complexes with acridinium ions via π–π interactions due to the rigid molecular clip spacer. The presence of a 1:1 complex is also evidenced by the ^1H NMR spectra shown in Fig. 6. The titration of **3** with 0.5 equiv. of acridinium ions caused upfield shifts in the proton signals of both the acridinium and **3**. Of particular note is the largest upfield shift of the acridinium ion relative to that of **3**. In particular, the signals of the H_a and H_b protons of the acridinium ion underwent an apparent upfield shift of 0.26–0.28 ppm. This is thought to be due to the ring-current effect of the porphyrin rings. When a 1:1 concentration ratio of **3** and acridinium ion was combined, the proton resonances of the acridinium ions slightly downfield shift relative to 1:0.5 titration. The proton signals of the porphyrin unit in the 1:1 complex showed no detectable shift, indicating that the guest only weakly interacts with the two porphyrins. Similar behavior was observed when **8** was titrated with acridinium ions. All of these observations indicate that hosts **3** and **8** each experience some interaction with the acridinium ion and that the ion is located between the two porphyrin rings of each host.

Molecular clips and rectangular macrocycles such as **3** and **8**, which have two porphyrins connected by a spacer, may be suitable hosts for a variety of aromatic guests since they can retain the guest between the two porphyrin units via π–π stacking interactions. When simple aromatics, such as naphthalene and anthracene, are added to host **3**, they show no propensity for binding. This was deduced from the fact that the absorption spectra did not show any characteristic Soret and Q-band changes. On the other hand, π-electron-deficient species, such as 1,4,5,8-naphthalene tetracarboxylic dianhydride (NTDA) and 1,2,4,5-benzenetetracarboxylic dianhydride (BTDA), are complexed in solution. The binding behavior between BTDA and host **3** was investigated in chloroform (Fig. 7). Upon adding BTDA, the position of the Soret band of **3** showed a characteristic change from 421.4 to 426.3 nm with decreasing of intensity. A new, broad charge transfer band was observed at 426.3 nm, indicating that the guest is inserted in the cleft of **3**. The UV–Vis titration experiments and the fitting of the data yielded an association constant K_{asso} of $4.0 \times 10^4\ M^{-1}$. Similar behavior was observed when **3** was titrated with NTDA. Following the above procedure, it was determined that **3** and NTDA form a 1:1 complex with an association constant of $6.5 \times 10^4\ M^{-1}$. This relatively large constant indicates that **3** experiences appreciable interactions with the NTDA through π–π interactions and charge-induced interactions. The ^1H NMR experiment also revealed that **3** could bind BTDA within the cleft of the *bis*-porphyrins to form a 1:1 complex. The stepwise addition of BTDA (0.1, 0.5, and 1.0 equiv.) to **3** caused upfield shifts of all of the signals of the porphyrin in **3** and those of BTDA (Fig. 8). Of particular note is the resonance at 1.26 ppm, which is assigned to the H_α of the BTDA located between the two porphyrins. The unusual upfield shift (7.40 ppm) of the H_α signal is caused by the ring-current effect of the porphyrin rings. This shift supports the 1:1 complexation (see Supplementary material). Such an unusual upfield shift

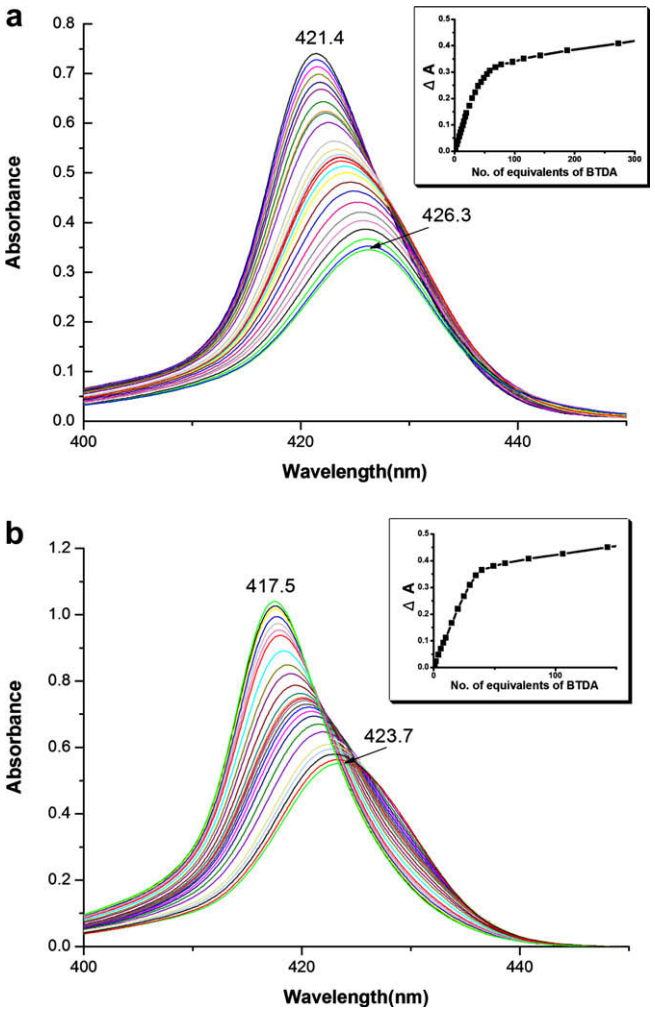


Fig. 7. UV-visible titration data showing the Soret band shift for (a) **3** and (b) **8** upon adding BTDA. The concentrations of BTDA were: (a) $0–1.4 \times 10^{-4}$ M in $CHCl_3$ and (b) $0–7.1 \times 10^{-5}$ M in $CHCl_3$. Inset: the plot of absorbance change at 421.4 nm and 417.5 nm versus **3** and **8**, respectively.

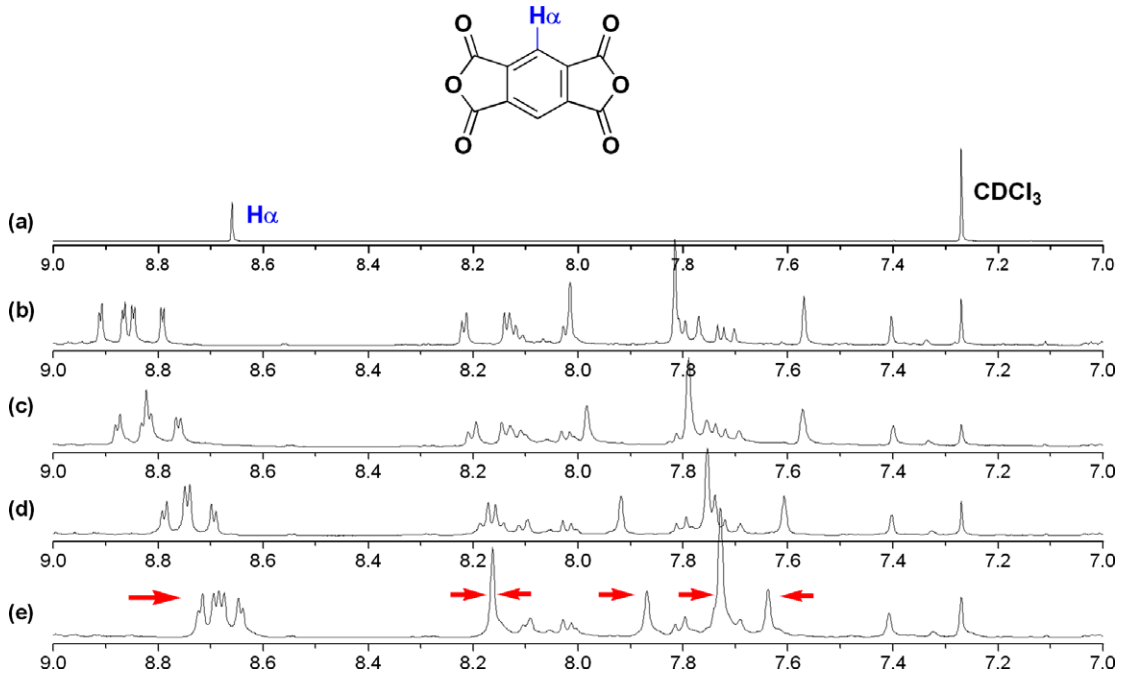


Fig. 8. ^{1}H NMR spectra of **3** (3.9×10^{-2} mol L^{-1}) in the presence of BTDA (a) in $CDCl_3$ at 298 K. The BTDA concentrations were: (b) 0.0, (c) 3.9×10^{-3}, (d) 1.9×10^{-2}, and (e) 3.9×10^{-2} mol L^{-1}.

of the BTDA has been previously observed for a similar *bis*-porphyrin [21].

4. Conclusions

In conclusion, we have described a molecular-clip-based approach to synthesizing cofacial zinc–porphyrin complexes. The new preorganized zinc–porphyrin complexes represent new efficient receptors for the complexation of 1,4-diazabicyclo[2,2,2]octane (DABCO), acridinium ions, 1,2,4,5-benzenetetracarboxylic dianhydride (BTDA), and 1,4,5,8-naphthalene tetracarboxylic dianhydride (NTDA). Their preorganized configuration and the 7.551 Å centre-to-centre distance between their cofacial *bis*-porphyrins mean that guests can readily position themselves within the new receptors. The association constants and spectroscopic results obtained for these new complexes show that the *bis*-porphyrin receptors are suitable hosts for molecular recognition. The results demonstrate the great potential of molecular-clip-based cofacial porphyrin complexes as building blocks for developing novel receptors.

Acknowledgements

This work was supported by the Korea Science and Engineering Foundation (KOSEF) through BK21 (2006) program, and World Class University (WCU) program (No. R31-2008-000-10035-0).

Appendix A. Supplementary material

^{1}H NMR spectra (1.8–1.0 ppm) of **3** in the presence of BTDA. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2009.09.035.

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