

# Fluorescent properties and synthesis of porphyrin square recognized methylene crown ether

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New porphyrin square (1) was prepared by reaction of porphyrin containing pyridine and  $\text{Re}(\text{CO})_5\text{Cl}$  in THF/toluene solvent. 2-(Methylene15-crown-5)-nicotinoly ester(2) was synthesized by reaction of 2-(Hydroxymethyl-15-crown-5 and nicotinoly chloride in  $\text{CH}_2\text{Cl}_2$ . In fluorescence quenching studies luminescence was quenched by addition of the guest(2) into host(1). In the host-guest system we could obtain binding constant ( $K= 1.13 \times 10^7 \text{M}^{-1}$ ) at decreasing concentration of (2). But the luminescence was dramatically increased after  $\text{Na}^+$  was added into the host-guest system.

Key words : porphyrin square, crown ether, host-guest system.

## 1. Introduction

Macrocycles based on cis bridging ligand of transition metals represented an unusual class of compounds having tremendous promise in host-guest chemistry, inclusion chemistry, and molecular recognition chemistry<sup>1-2</sup>. The 70 or so available squares have been constructed from platinum, palladium, nickel, tungsten, and rhenium precursors and have been assembled in both homometallic and heterometallic form<sup>3-4</sup>. New materials featuring exceptional nanometer scale porosity, enormous internal surface areas and enormous molecular binding capacities could be readily fabricated from an extended family of neutral, luminescent, tetrametallic cyclophanes recently developed in our lab<sup>6</sup>. Depending on cavity size and overall charge, selected molecular squares were capable of functioning as solution phase hosts for either complex anionic guests<sup>5</sup> or neutral aromatic guests where binding was achieved, respectively, via coulombic or hydrophobic interactions. While host-guest binding was typically monitored via NMR spectroscopy, detection based on host luminescence had also been demonstrated.

Particularly versatile in the respect were molecular squares derived from  $\text{Re}(\text{CO})_5\text{Cl}$ . Here, we intended to report on the synthesis of the square and on sensing and molecular recognition applications involving higher order assemblies of the porphyrin molecular squares.

## 2. Experiment

All reaction were conducted under a dry argon atmosphere with oven-dried glassware. All solvents were purified by distillation and dried, if necessary, prior to use. All chemicals were purchased in reagent grade and used without further purification. <sup>1</sup>H-NMR and <sup>13</sup>C-NMR spectra were recorded on a Varian-300 spectrometer and referenced to residual protic solvent with chemical shifts being reported as  $\delta$  ppm from TMS. IR-spectra were recorded on a Shimadzu FT IR-470 spectrometer. Mass spectra were recorded on a high resolution mass spectrometer. The absorption and fluorescence spectra were recorded by using a UV/Vis absorption spectrophotometer (Varian, Cary3) and a spectrometer (Spex, FluoreMAX).

### 2.1. 3-Acetyl-2-heptanone 3

A mixture of 1-bromobutane(753.5g, 5.5 mole), 2,4-pentanedione(550g, 5.5 mole), potassium carbonate(912g, 6.6 mole), and dry acetone(2.5L)

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were stirred and heated at reflux for 48 hours with a 5 round bottom flask equipped with a paddle stirring device, condenser, and drying tube. During this time acetone was added as necessary to maintain solution volume. The solid were then filtered off and washed with acetone. The liquid residue was then filtered to remove precipitated solid and heated at reflux for 30 minutes with 50 mL water and 5 mL concentrated sulfuric acid. The acid was then neutralized with aqueous potassium carbonate and the aqueous layer removed.

The organic layer was dried over magnesium sulfate, filtered and distilled under reduced pressure to give the product as a liquid (420g, 49%), bp 54-60°C/3mm Hg. <sup>1</sup>H-NMR δ 0.8 (t, 3H, CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>); 1.3 (m, 4H, CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>); 1.8 (q, 2H, CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>); 2.15 (s, 6H, CH<sub>3</sub>COCH-n-butyl-COCH<sub>3</sub>); 3.6 (t, 1H, CH<sub>3</sub>COCH(n-butyl)COCH<sub>3</sub>). MS gave only fragment peaks at m/e = 113 (48%), 100 (56%), 85 (63%), and 71 (100%); no parent peak observed.

## 2.2. 4-Butyl-3,5-dimethyl-2-thoxycarbonylpyrrole 4

**Oxime:** A solution of sodium nitrite (80g, 1.15 mole) in water (215 mL) was added dropwise to a stirred solution of ethyl acetoacetate (137.5g, 1.05 mole) in acetic acid (350 mL), keeping the temperature between 0°C and 10°C with the use of an ice bath. After the addition was complete, the solution was stirred for an additional two hours at room temperature.

**Pyrrole:** A solution of 3-acetyl-2-heptanone (159g, 1.02 mole) in acetic acid (850 mL) was heated to 65°C in a three necked 3L round bottom flask equipped with a paddle stirrer, a thermometer, a dropping funnel, and a powder funnel. The above oxime was added dropwise simultaneously with portions of a intimate mixture of zinc dust (80g) and sodium acetate (80g). The temperature was kept at 65°C by use of an ice bath. More zinc dust (40g) was added during the latter course of the reaction to maintain a finely divided suspension in the flask. After the oxime addition was complete, the contents of the flask were stirred for an additional 1.5 hours at 65 °C, then poured into a bucket of crushed ice.

The solid product was collected by filtration

and dissolved in methylene chloride. The methylene chloride was then decanted to remove zinc particles and the solvent removed on the rotary evaporator. The resulting solid residue was then recrystallized from absolute ethanol (300 mL) to give the product as soft white crystal (88g, 39%), mp 108-111°C. <sup>1</sup>H-NMR δ 0.9 (t, 3H, CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>); 1.2-1.4 (m, 7H, CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub> + CO<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>); 2.1-2.3 (s + s + t, 8H, CH<sub>3</sub> + CH<sub>3</sub> + CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>); 4.3 (q, 2H, CO<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>); 9.0 (br. s, 1H, NH). MS m/e = 223 (85%), 180 (100%), 134 (90%). HRMS. Calcd for C<sub>13</sub>H<sub>21</sub>NO<sub>2</sub>: 223.15. Found: 223.15.

## 2.3. 5-Acetoxymethyl-4-butyl-2-ethoxycarbonyl-3-methylpyrrole 5

Pyrrole (86.5g, 0.38 mole) was dissolved in glacial acetic acid (700 mL) with stirring in a 1L beaker. Lead tetraacetate (180g, 0.41 mole) was then added all at once. The resulting solution was stirred for two more hours and then poured into rapidly stirred water (1L), making sure that the acetic acid solution was thoroughly mixed with the water. The resulting viscous suspension was filtered through a buchner funnel. The collected solid was compressed with a rubber dam and then suspended in hot petroleum ether (1500 mL). Chloroform (50 mL) was added, and the clear solution was decanted into a crystallizing dish and placed in the refrigerator for 3-4 hours.

The resulting solid was filtered and dried to yield the product as fluffy white needles (94 g, 86%), mp 101-103°C. <sup>1</sup>H-NMR δ 0.9 (t, 3H, CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>); 1.25-1.45 (m, 7H, CH<sub>2</sub>CH<sub>3</sub>+CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>), 2.1 (s, 3H, CH<sub>3</sub>); 2.3 (s, 3H, CH<sub>2</sub>CO<sub>2</sub>CCH<sub>3</sub>); 2.45 (t, 2H, CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>); 4.3 (q, 2H, CO<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>); 5.05 (s, 2H, CH<sub>2</sub>CO<sub>2</sub>CCH<sub>3</sub>); 9.1 (br. s, 1H, NH). MS m/e = 281 (14%), 238 (27%), 223 (26.3%). 180 (88%), 134 (100%), HRMS. Calcd for C<sub>15</sub>H<sub>23</sub>NO<sub>4</sub>: 281.16. Found: 281.16.

## 2.4. Diethyl 3,7-Dibutyl-2,8-dimethyl-dipyryl methane-1,9-dicarboxylate 6

Acetoxymethyl pyrrole 5 (88.3g, 0.31 mole) was heated at reflux in 10% aqueous ethanol (660 mL) containing concentrated HCl (25 mL) for two hours and then in the refrigerator for four hours. The solid precipitate was filtered, washed with ethanol, and dried to give pure 6 as a white crystalline powder (60g, 89%), mp 112-113°C.

$^1\text{H-NMR}$   $\delta$  0.9 (t, 6H,  $\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$ ); 1.2-1.5 (m, 14H,  $\text{CO}_2\text{CH}_2\text{CH}_3$ ) + 2 x  $\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$ ); 2.3 (s, 6H,  $\text{CH}_3$ ); 2.4 (t, 4H,  $\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$ ); 3.9 (s, 2H,  $\text{CH}_2$ ); 4.3 (q, 4H,  $\text{CO}_2\text{CH}_2\text{CH}_3$ ); 9.15 (br. s, 1H, NH). MS  $m/e$  = 430 (26%), 221 (100%), 208 (14.3%). HRMS. Calcd for  $\text{C}_{25}\text{H}_{38}\text{N}_2\text{O}_4$ : 430.28316. Found: 430.28.

### 2.5. 3,7-Dibutyl-2,8-dimethyl-1,9-dipyrylmethane 7

Ester 6 (71.6g, 0.17 mole) was suspended in ethylene glycol (500 mL) in a 1L round bottom flask. Sodium hydroxide (29g, 0.72 mole) and the solution heated at reflux for 1 h under nitrogen. The solution first turned red and then to a yellow brown color. The solution was then poured into ice-water and filtered. The resulting solid was dissolved in hot ethanol (200 mL), filtered through celite, and concentrated in vacuo to give crude 1.09 (46g, 0.16 mole)

Recrystallization from ethanol gave colorless prisms, mp 96-97 °C.  $^1\text{H-NMR}$  (300 MHz,  $\text{CDCl}_3$ )  $\delta$  0.8(t, 6H,  $\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$ ), 1.4 (m, 8H,  $\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$ ), 2.05 (s, 6H,  $\text{CH}_3$ ), 2.45 (t, 4H, 2 x  $\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$ ), 3.7 (s, 2H,  $\text{CH}_2$ ), 6.25 (br. s, 2H, pyrrole CH), 7.1 (br. s, 2H, pyrrole NH);  $^{13}\text{C-NMR}$  (300 MHz,  $\text{CDCl}_3$ )  $\delta$  10.4, 14.0, 22.7, 24.0, 33.7, 113.7, 118.1, 119.7, 124.9 MS  $m/z$  = 286 (M+, 62%), 229 (30%), 149 (100%). HRMS: Calcd for  $\text{C}_{19}\text{H}_{30}\text{N}_2$ : 286.24. Found: 286.24.

### 2.6. 2,8,12,18,-Tetrabutyl-3,7,13,17,-tetramethyl-5,15,-bis(4pyridyl) porphyrin 8

7 (2g, 6.98 mmol) and freshly distilled 4-pyridine carboxaldehyde (0.748g, 6.98 mmol) were dissolved in methanol (700 mL) and the solution was deaired by bubbling with argon for 10 min while stirring. Trifluoroacetic acid (0.55 mL 6.98 mmol) was added and the solution was stirred overnight at room temperature under argon. At this time DDQ (2.37g, 10.5 mmol) dissolved in THF (100mL) was added and the resulting solution was stirred for an additional 4 h. The solvent was removed in vacuo. This residue was redissolved in dichloromethane, washed with saturated sodium bicarbonate solution, water, dried over anhydrous sodium sulfate, and concentrated in vacuo. The resulting solid was eluted through a silica column (1%

$\text{MeOH}/\text{CH}_2\text{Cl}_2$ ) and the second band was collected, concentrated to 80 mL, and crystallized by addition of methanol (200 mL).

The dark red-purple crystals were filtered and dried in vacuo to yield (1.08g, 1.45 mmol) 41.5%: mp > 300°C Uv-vis ( $\text{CH}_2\text{Cl}_2$ )  $\lambda_{\text{max}}$  406 ( $\epsilon$ 181 000), 506 (15 300) 538 (5 820), 574 (6 380) 624 (1 820)  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ )  $\delta$  -2.42 (br s, 2H, NH) 1.10 (t, 12H,  $\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$ ), 2.50 (s, 12H,  $\text{CH}_3$ ), 3.97 (t, 8H,  $\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$ ), 8.04 (d, 4H,  $\beta$ -pyridine H), 9.01 (d, 4H,  $\alpha$ -pyridine H), 10.26 (s, 2H, 10, 20 meso H). MS  $m/z$  (%) 744 (M+,7), 668 (100), 624 (25). HRMS: calcd. for  $\text{C}_{50}\text{H}_{60}\text{N}_6$  744.4879, found 744.4851. Anal calcd. for  $\text{C}_{50}\text{H}_{60}\text{N}_6 \cdot \text{H}_2\text{O}$  78.70, H 8.19, N 11.01; found C 78.68, H 7.99, N 10.97. On the basis of  $^1\text{H-NMR}$  and Mass spectral data the leading band was determined to be 2,8,12,18,-Tetrabutyl-3,7,13,17-tetramethyl-5-(4'-pyridyl)porphyrin mp, 202  $^1\text{H-NMR}$  (300 MHz,  $\text{CDCl}_3$ )  $\delta$ -2.25 (br s, 2H, NH), 0.89 (t, 12H  $\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$ ), 1.08 (m, 8H,  $\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$ ), 2.03 (m, 4H,  $\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$ ) 3.72 (t, 4H,  $\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$ ), 3.81 (t, 4H,  $\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$ ), 7.87 (d, 2H,  $\beta$ -pyridine H), 8.92 (d, 2H,  $\alpha$ -pyridine H), 9.56 (s, 1 H, 15 meso H), 9.59 (s, 2H, 10, 20 meso H). MS  $m/z$  (relative intensity %) 6 67 (M+, 100), 624 (13), 334 (10)

### 2.7. 2-(Methylene15-crown-5)-nicotinoyl ester 2

2-(Hyroxymethyl)-15-crown-5 250mg(1 mmol) was refluxed in  $\text{CH}_2\text{Cl}_2$  with nicotinoyl chloride 178mg(1 mmol) and triethylamine for 12h. The mixture was filtered after cooling, and the filter cake was washed with ethylacetate. Following removal of the solvent in vacuo, the residue was crystallized from ethylacetate and hexane (10 : 1) to yield 159mg (45%) of the compound 2 as white solid.  $^1\text{H-NMR}$ ( $\text{CDCl}_3$ , $\delta$ ): 3.4~3.6(m, 16H,  $\text{OCH}_2\text{CH}_2\text{O}$ ), 3.6~3.7(m, 2H,  $\text{OCHCH}_2\text{O}$ ), 3.8~3.9(m, 1H,  $\text{OCHCH}_2\text{O}$ ), 4.1~4.4(m, 2H,  $\text{OCHCH}_2\text{O}$ ) 7.2~7.3(m, 1H, pyridine H), 8.1~8.2(d, 1H, pyridine H), 8.6~8.7(d, 1H, pyridine H), 9.0~9.1(s, 1H, pyridine H), MS(EI):  $m/e$  372 .

Compound 1 was obtained as a maroon microcrystalline in high yield by combining

Compound **8** 169mg with 82mg(0.227 mmol) of  $\text{Re}(\text{CO})_5\text{Cl}$  dissolved in 100 mL of freshly distilled 4:1 tetrahydrofuran-toluene as a solvent and heated to reflux for 48 hours. Following cooling, 100mL of hexanes was added to get product precipitation, The product was isolated at 86% yield by filtration, washed with hexanes, and dried in vacuo. NMR indicated complete coordination of available pyridyl fragments. The analogous tetra-zincmetallated square was obtained in nearly quantitative yield by first dissolving **1** in a minimum volume of  $\text{CH}_2\text{Cl}_2$ , adding a 5 mL volume of saturated  $\text{Zn} \text{II}$  acetate in methanol, and stirring for 4h. Compound **1** was precipitated by adding a large volume of methanol-water mixture. The product was isolated by filtration, washed with water and then ether, and dried in vacuo.

### 3. Results and Discussion

A new class tetraporphyrin square has been synthesized which introduces octahedral transition metal centers of square frameworks. The  $\text{fac-Re}(\text{CO})_3(\text{u-imine})_2\text{Cl}$  corners were capable of forming luminescent excited states(MLCT excited states) following visible ligands were employed as edges, however, the luminescence observed was that of the porphyrin. The tetraporphyrin square were highly soluble in  $\text{CHCl}_3$ , tetrahydrofuran, and  $\text{CH}_2\text{Cl}_2$  but insoluble in water. This square also was enormously chromophoric, especially in the porphyrin Soret region(400 nm ~).

The square formation induced a bathochromic shift of 6 nm in the Soret region, consistent with net removal of electron density from the porphyrin  $\pi$  system upon rhenium-pyridine bond formation. Near-UV fluorescence excitation studies(MLCT region) established that rhenium corners served only a structural, rather than a direct photophysical, role within the square frame work. Luminescence measurements show that square was unresponsive to millimolar additions of pyridine, however, lead to significant red shift in the fluorescence the porphyrine square. From the known fluorescence response of monomeric  $\text{Zn} \text{II}$  porphyrin species and the lack of response by porphyrine square was clearly associated with axial ligation of porphyrine bound zine by pyridine.

As indicated emission from tetra-zinc metallated

square was decreased by added the crown ether binding to the square host cavity. From additional measurements at lower host concentrations, the host-guest association constant was  $1.13 \times 10^7 \text{M}^{-1}$ . Further insight into the porphyrin square binding was provided by electronic absorption measurements. At micromolar concentrations, 1:1 mixtures exhibit an essentially complete loss of host Q band features at 542 and 576 nm. The absorption studies were consistent, therefore, with a binding geometry which entails pyridine ligation of all available Zn sites. Emission was enhanced again by adding NaSCN because the metal ion was bound by crown ether cavity in host-guest system. From addition of Na ion, binding constant was dramatically increased and the binding constant at that time was  $4.35 \times 10^7 \text{M}^{-1}$ .

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