

## Syntheses of Dendronized Pyridinio- $\beta$ -Diketone Metal Complexes and Their Spreading Behavior on Water

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Novel dendronized pyridinio- $\beta$ -diketone metal complexes are synthesized. These molecules form a stable monolayer on water and exhibit almost the same spreading behavior on the water surface. The limiting area ( $A_{\text{limit}}$ ) of  $\beta$ -diketone metal complex, is equivalent to the cross-sectional area of alkyl chains. The  $A_{\text{limit}}$  of **12D** was just a half of them. The experimentally obtained  $A_{\text{limit}}$  is in good agreement with the estimated value from CPK model.

Key words: pyridinium, redox active,  $\beta$ -diketone metal complex, spreading behavior, occupying area

### 1. INTRODUCTION

The air-water interface is the attractive boundary serving specific reaction field to arrange amphiphilic molecules, and numerous studies have been done about the spreading behaviors of conventional amphiphilic molecules. Recently there has been growing interest in Langmuir films composed of disc-shaped molecules which may form highly anisotropic structures at the air-water interface [1]. Therefore, if the disc-like molecule has redox active units, we believe to control the spreading behavior and the morphology of the Langmuir film by redox responsive process. In this study, the disc-like  $\beta$ -diketone metal complexes containing redox active pyridinium groups was designed. Until now the control of spreading behavior was performed by irradiating light, changing temperature, adding ionic compounds into the subphase and so on [2]. Adding reductant as dissolved substance in the subphase is easy way to do. But such an example has not been reported.

We designed redox active  $\beta$ -diketone metal complexes bearing peripheral dendron groups. To stabilize the monolayer, the introduction of amphiphilicity is favorable. Dendron is strong hydrophobic substituent, while pyridinium possesses high hydrophilicity. The strong contrast of those units is believed to enhance the stability of the monolayer at the air-water interface. The bidentate  $\beta$ -diketone ligands coordinate with divalent metal center. The coordination structure around the metal center is thought that palladium and copper metal complexes are square planar, while zinc one takes tetrahedral geometry [3].

In this paper, the synthesis and the spreading behavior of the dendronized redox active  $\beta$ -diketone

metal complexes are discussed.

### 2. EXPERIMENTAL

#### 2.1 Materials

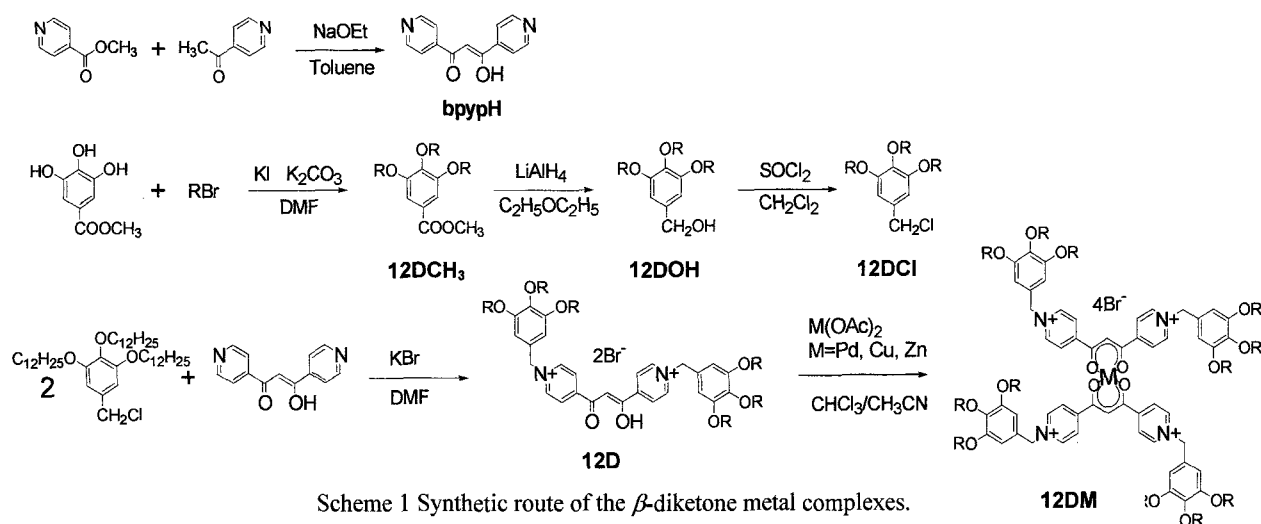
All organic reagents were purchased and used as received. These compounds are identified by <sup>1</sup>H-NMR (EX270, JEOL DATUM) and Elemental analysis (2400 CHN Elemental analyzer, PERKIN-ELMER).

#### 1,3-Bis(4-pyridyl)-1,3-propanedione (**bpypH**) [4]

Dry toluene, 12.4 g (182 mmol) of sodium ethoxide and 25 g (182 mmol) of methyl isonicotinate were added to a flask. Into the suspension stirred vigorously 22 g (182 mmol) of 4-acetylpyridine was added very slowly. During the addition, the reaction temperature was kept 50 °C. The mixture was stirred for 48 h until an off-white solid appeared. The mixture was cooled down to room temperature, and the precipitate was filtered. The solid was dissolved in water with vigorous stirring. An excess amount of acetic acid was added at 0 °C, to yield an off-white solid, which was recrystallized from hexane. (yield 40 %). <sup>1</sup>H-NMR (270 MHz, d<sub>6</sub>-DMSO)  $\delta$ =5.03 (CO-CH<sub>2</sub>-CO, 3-H of keto form, s), 7.56 (CO-CH=CO, 3-H of enol form, s), 8.08 ( $\beta$ -H, 4H, d), 8.86 ( $\alpha$ -H, 4H, d). The molecule exists in DMSO as 5.5 % of keto form, determined by <sup>1</sup>H-NMR.

#### 3,4,5-Tris(dodecan-1-yloxy) benzoate (**12DCH<sub>3</sub>**) [5]

A dry DMF solution containing 29.9 g (216 mmol) of K<sub>2</sub>CO<sub>3</sub> and 1.12 g (6.75 mmol) of KI was deaerated with N<sub>2</sub> bubbling for 1 h. A 10 g (54 mmol) of methyl 3,4,5-trihydroxybenzoate was added into the solution, and the mixture was kept 60 °C. A solution of



1-bromododecane (53.8 g, 216 mmol) was added slowly. After 48 h, the reaction mixture was poured into water and extracted with  $\text{CHCl}_3$ . The organic layer was washed with water, and concentrated with a rotary evaporator. The resulting white solid was filtered and recrystallized from hexane. (29.4 g yield 79 %), TLC (hexane: ethyl acetate, 10:1):  $R_f$  = 0.4.  $^1\text{H-NMR}$  (270 MHz,  $\text{CDCl}_3$ )  $\delta$  = 0.89 (- $\text{CH}_3$ , 9H, t,  $J$  = 6.8 Hz), 1.26-1.49 (- $\text{CH}_2$ -, 60H, broad), 1.69-1.86 (- $\text{CH}_2$ -, 6H, m), 3.89 (- $\text{OCH}_3$ , 3H, s), 3.98-4.04 (- $\text{OCH}_2$ -, 6H, t,  $J$  = 6.5 Hz), 7.25 (Ar-H, 2H, s)

#### 3,4,5-Tris(dodecan-1-yloxy)benzyl alcohol (**12DOH**) [5]

To a suspension of 1.58 g (41.6 mmol) of  $\text{LiAlH}_4$  in 50 ml of anhydrous diethyl ether, 28.7 g (41.6 mmol) of **12DCH<sub>3</sub>** was added and the mixture was stirred for 1 h at room temperature under  $\text{N}_2$  until the reactant was consumed completely. The reaction was quenched by addition of 2 ml of  $\text{H}_2\text{O}$ , 2 ml of 15 %  $\text{NaOH}$  aq, and 60 ml of  $\text{H}_2\text{O}$ . The granular salts were filtered and rinsed with diethyl ether. The diethyl ether layer was washed with  $\text{H}_2\text{O}$ , and the solvent was evaporated. Recrystallization from acetone yielded 23.0 g of a white crystal. (yield 84 %), TLC (hexane: ethyl acetate, 10:1):  $R_f$  = 0.1.  $^1\text{H-NMR}$  (270 MHz,  $\text{CDCl}_3$ )  $\delta$  = 0.88 (- $\text{CH}_3$ , 9H, t,  $J$  = 6.8 Hz), 1.26-1.46 (- $\text{CH}_2$ -, 60H, broad), 1.68-1.82 (- $\text{CH}_2$ -, 6H, m), 3.98-4.04 (- $\text{OCH}_2$ -, 6H, t,  $J$  = 6.5 Hz), 4.59 (- $\text{CH}_2\text{OH}$ , 2H, s), 6.55 (Ar-H, 2H, s)

#### 3,4,5-Tris(dodecan-1-yloxy)benzyl chloride (**12DCl**) [5]

To a solution of 18 g (27.3 mmol) of **12DOH** in 210 ml of dry  $\text{CH}_2\text{Cl}_2$ , a catalytic amount (4 ml) of DMF, followed by 5.4 g (45.4 mmol) of  $\text{SOCl}_2$  was added dropwise with stirring. Approximately 30 min after the addition of  $\text{SOCl}_2$ , the reaction was completed. The solvent were distilled under vacuum. Diethyl ether dissolving the resulting white solid was washed three times with  $\text{H}_2\text{O}$ , dried over  $\text{MgSO}_4$ , and filtered, and the solvent was evaporated. Then recrystallization of

the resulting solid from acetone yields 23.0 g of a white powder. (yield 85 %), TLC (hexane: ethyl acetate, 10:1):  $R_f$  = 0.7.  $^1\text{H-NMR}$  (270 MHz,  $\text{CDCl}_3$ )  $\delta$  = 0.88 (- $\text{CH}_3$ , 9H, t,  $J$  = 6.5 Hz), 1.26-1.49 (- $\text{CH}_2$ -, 60H, broad), 1.68-1.84 (- $\text{CH}_2$ -, 6H, m), 3.91-3.99 (- $\text{OCH}_2$ -, 6H, t,  $J$  = 6.8 Hz), 4.51 (- $\text{CH}_2\text{Cl}$ , 2H, s), 6.56 (Ar-H, 2H, s)

#### $\text{N,N}'$ -Di-(3,4,5-Tris(dodecan-1-yloxy) benzyl)-1,3-(4-pyridyl)-1,3-propanedione (**12D**)

A mixture of 300mg (1.32mmol) of **bppyH**, 3.84g (5.28mmol) of **12DCl**, 6.3g (52.8mmol) of  $\text{KBr}$  in 25 ml of dry DMF was heated to 70  $^\circ\text{C}$  for 48 hours. The reaction mixture was cooled and the brown precipitate was collected and then washed with water. Recrystallization with ethanol gave 1.5g of brown powder. (yield 45 %),  $^1\text{H-NMR}$  (270 MHz,  $\text{CDCl}_3$ )  $\delta$  = 0.87 (- $\text{CH}_3$ , 18H, t,  $J$  = 6.8 Hz), 1.22-1.47 (- $\text{CH}_2$ -, 120H, m), 1.68-1.81 (- $\text{CH}_2$ -, 12H, m), 3.93-4.00 (- $\text{OCH}_2$ -, 12H, m), 6.05 (- $\text{CH}_2\text{-N}^+$ , 4H, s), 6.81 (Ar-H, 4H, s), 8.02 (- $\text{CH}_2$ -, 1H, s), 9.21 (pyridinium  $\beta$ -H, 4H, d,  $J$  = 5.9 Hz), 9.39 (pyridinium  $\alpha$ -H, 4H, d,  $J$  = 5.9 Hz) Anal Calcd for  $\text{C}_{99}\text{H}_{168}\text{Br}_2\text{N}_2\text{O}_8$ : C, 71.02; H, 10.11; N, 1.67 %. Found: C, 71.32; H, 9.69; N, 1.59 %.

#### $\beta$ -Diketone metal complex (**12DM**: M = Pd, Cu, Zn)

A 1 ml  $\text{CH}_3\text{CN}$  solution of a 10% excess of metal acetate was added to a solution of **12D** (50mg, 0.030mmol) in 10 ml of chloroform. The solution was stirred for 1 hour at room temperature. After evaporating the reaction mixture, the resulting brown solid was washed with  $\text{CH}_3\text{CN}$ . Recrystallization with ethanol gave brown powder. (yield: for Pd complex 87%, for Cu 100%, for Zn 98%),  $^1\text{H-NMR}$  (270 MHz,  $\text{CDCl}_3$ )  $\delta$  = 0.87 (- $\text{CH}_3$ , 36H, broad), 1.25-1.45 (- $\text{CH}_2$ -, 240H, m), 1.68-1.77 (- $\text{CH}_2$ -, 24H, m), 3.95 (- $\text{OCH}_2$ -, 24H, m), 5.77 (- $\text{CH}_2\text{-N}^+$ , 8H, s), 6.73 (Ar-H, 8H, s), 8.87 (pyridinium  $\beta$ -H, 8H, broad), 9.08 (pyridinium  $\alpha$ -H, 8H, broad) Anal Calcd for  $\text{C}_{198}\text{H}_{334}\text{Br}_4\text{N}_4\text{O}_{16}\text{Pd}$ : C, 68.87; H, 9.75; N, 1.62 %. Found: C, 68.78; H, 9.55; N, 1.58 %. Anal Calcd for  $\text{C}_{198}\text{H}_{334}\text{Br}_4\text{N}_4\text{O}_{16}\text{Cu}$ : C, 69.74; H, 9.87; N, 1.64 %. Found: C, 69.54; H, 9.67; N,

1.51 %. Anal Calcd for  $C_{198}H_{334}Br_4N_4O_{16}Zn$ : C, 69.70; H, 9.87; N, 1.64 %. Found: C, 68.49; H, 9.57; N, 1.52 %.

## 2.2 Spreading Behavior on water

The spreading behavior of the dendronized molecules was evaluated on pure water (Milli-Q grade,  $18M\Omega\text{ cm}^{-1}$ ,  $\text{pH} = 5.8$ ) using a Lauda FW1 film balance. The temperature of subphase was maintained  $20 \pm 0.5\text{ }^\circ\text{C}$  by water circulation. The  $\beta$ -diketone metal complexes and ligand (**12D**, **12DPd**, **12DCu**, **12DZn**) were spread from a chloroform solution ( $1.0 \times 10^{-4}\text{ mol dm}^{-3}$ ). After evaporation of chloroform, the molecule on water was compressed at a speed of  $30\text{ cm}^2\text{ min}^{-1}$ . The surface pressure was recorded *versus* the molecular area. Brewster angle microscope (BAM) images were taken with an NLE-EMM633 (Nippon Laser Electronics). The surface topography of the **12DCu** film on water was visualized and recorded during the compression. The BAM images were analyzed at different surface pressures.

## 3. RESULTS AND DISCUSSION

### 3.1 Synthesis and Identification

Novel  $\beta$ -diketone metal complexes were successfully synthesized, as scheme 1 shows. Starting from the product of the nucleophilic substitution of methyl 3,4,5-trihydroxybenzoate with 1-bromododecane, **12DCH<sub>3</sub>**, was reduced with  $\text{LiAlH}_4$  to give the benzyl alcohol, **12DOH**, in 84 %. Its quantitative chlorination with  $\text{SOCl}_2$  and a catalytic amount of DMF produced the benzylchloride, **12DCI**, in 85 % yield. The **bpypH** was synthesized by Claisen condensation, and then quaternarized with **12DCI** to give **12D** in 45 % yield. Metal complexes were obtained from complexation of **12D** with the corresponding metal acetates in over 87 % yield. The high coordinating ability of  $\beta$ -diketone moiety enables one to obtain metal complexes efficiently.

### 3.2 Spreading Behavior on water

Figure 1 shows  $\pi$ -A isotherms of metal complexes (**12DM**: M = Pd, Cu and Zn) and ligand (**12D**) at the air-water interface. All the compounds gave stable monolayers with high collapse pressure on water. The limiting area,  $A_{\text{limit}}$ , of  $2.40 - 2.50\text{ nm}^2$  were independent of the kinds of metal center, and these

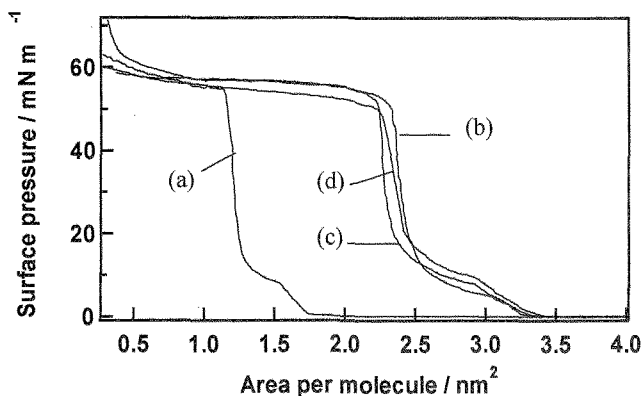
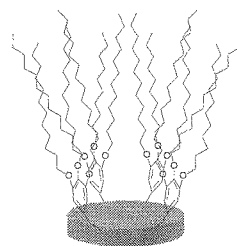


Figure 1  $\pi$ -A isotherms of **12D** (a), **12DPd** (b), **12DCu** (c) and **12DZn** (d) at  $20\text{ }^\circ\text{C}$ .

values were showed twice the limiting area of the ligand **12D** ( $1.25\text{ nm}^2$ ). Besides, the molecular cross sectional areas derived from the CPK models were in good agreement with the areas of  $\pi$ -A curves, at which the surface pressure increased steeply. Crystallographical studies showed copper and palladium complexes of acetylacetonone ligand take planar disk structures and zinc complex has tetrahedral coordination [3]. The coordination structure around metal center less influenced the spreading behavior at the air-water interface.

The metal complexes looked to be compressed with dendrons directing to the gaseous phase because of their high hydrophobicity [1]. Around  $2.5\text{ nm}^2$  in the  $\pi$ -A isotherm curve, the alkyl chains are tightly stacked, as is drawn below.



The  $A_{\text{limit}}$  is equivalent to the total cross-sectional area of alkyl chains ( $2.4\text{ nm}^2$ ). The morphologies of the monolayer on water during the compression process were observed by BAM, as is shown in Figure 2a. At a

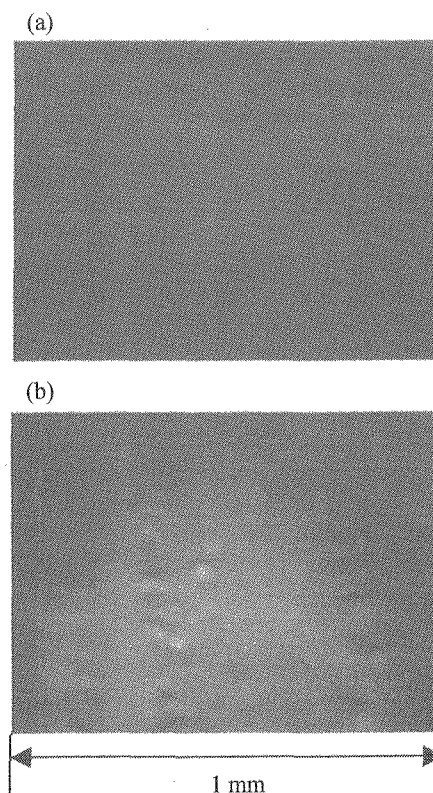


Figure 2 BAM images of **12DCu** on water at  $20\text{ }^\circ\text{C}$ . Surface pressure is  $10\text{ mN m}^{-1}$  (a),  $55\text{ mN m}^{-1}$  (b).

large area of  $3.0 \text{ nm}^2$  ( $10 \text{ mN m}^{-1}$ ), the BAM images of these three metal complexes did not exhibit optical heterogeneity. This indicates the monolayers were ultra thin and homogeneous. By compression monolayers caused collapse and non-uniform thick film was visualized as several bright parts in the image, as Figure 2b shows.

#### 4. CONCLUSION

Novel dendronized  $\beta$ -diketone metal complexes bearing redox active pyridinium groups were successfully synthesized. These metal complexes and the ligand form stable monolayer on water with high collapse pressure.

#### 5. ACKNOWLEDGEMENT

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