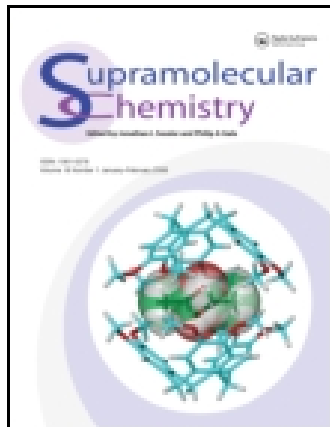


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### Novel o-Phenylenediseleno Bridged Bis ( $\beta$ -cyclodextrin)s Complexes with Platinum(IV) and Palladium(II) Ions

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# Novel *o*-Phenylenediseleno Bridged Bis( $\beta$ -cyclodextrin)s Complexes with Platinum(IV) and Palladium(II) Ions

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The novel *o*-phenylenediseleno bridged bis(cyclodextrin)s and its complexes with platinum(IV) and palladium(II) ions have been synthesized and characterized by elemental analyses, <sup>1</sup>H NMR, infrared, and thermal analysis. Fluorescence spectrophotometric titrations have been performed in aqueous buffer solution (pH 7.20) at 25.0°C to give the complex stability constants ( $K_s$ ) and Gibbs free energy change ( $-\Delta G^\circ$ ) for the 1:1 inclusion complexation of natural  $\beta$ -cyclodextrin, the *o*-phenylenediseleno bridged bis(cyclodextrin)s 1 and its platinum(IV) complex 2 with 8-Anilino-1-naphthalenesulfonic Acid Ammonium Salt (ANS ammonium). The molecular inclusion ability of ANS ammonium by the three host compounds are discussed from the viewpoints of size/shape-fit concept and the multipoint recognition mechanism.

**Keywords:** Bridged bis(cyclodextrin)s, inclusion complexation, organoselenium, ANS ammonium

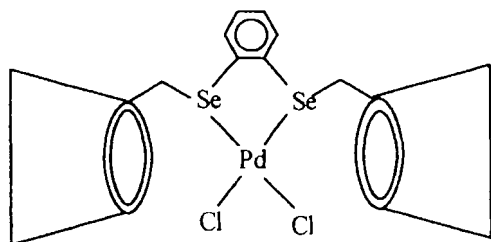
## INTRODUCTION

Recently, a great deal of effort has been devoted to the synthesis of bridged cyclodextrins and

also to the investigation of their complexes with metal ions in order to understand the nature of the noncovalent interactions. Possessing the dual hydrophobic cavities and enabling the multiple recognition, bridged cyclodextrins complexed with metal ions can act as an excellent model system mimicking more precisely the substrate-specific interaction of enzymes [1–5]. However, organoselenium bridged cyclodextrins have not been reported so far. It is well known that organo-selenium compounds are proposed as candidates for the repressor of HIV transcription and *cis*-platinum has been used as a successful anti-cancer agent [6]. These pieces of information prompted us to investigate the cyclodextrin-based supramolecular system that contains all of these components. Here we report novel supramolecular species — bridged bis( $\beta$ -cyclodextrin)s complexes containing selenium and platinum(IV) or palladium(II). It is of special interest and value to us for the good water-solubility of such a supramolecular

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structure and the low toxicity of the *o*-phenylenediseleno bridged bis(cyclodextrin)s, which are prerequisite for the use as a novel anti-cancer medicine. It is another point of interest to investigate the fluorescence properties and binding interaction of such a supramolecular species. Therefore, the complex stability constants ( $K_s$ ) and Gibbs free energy change ( $-\Delta G^\circ$ ) for the 1:1 inclusion complexation of natural  $\beta$ -cyclodextrin, the *o*-phenylenediseleno bridged bis(cyclodextrin)s **1** and its complex with platinum(IV) **2** with ANS ammonium in aqueous buffer solution (pH 7.20) at 25.0°C were determined by the method of fluorescence spectrophotometric titrations. The results obtained indicated that the stability constants of these complexes are in the order of  $2 > 1 > \text{natural } \beta\text{-CD}$ , suggesting that the multipoint recognition of host **1** and **2** plays a crucial role in inclusion complexation.



(3)

CHART 1

## EXPERIMENTAL

### General Procedure

Elemental analyses were performed on a Perkin-Elmer-240 instrument. Mass spectra were obtained on a JEOL JMS-DX-303 instrument.  $^1\text{H}$  NMR spectra were recorded at 200 MHz in  $\text{D}_2\text{O}$  on a Bruker AM200 spectrometer. FT-IR and UV spectra were obtained on a Nicolet FT-IR 5DX and Shimadzu UV-2401 spectrometer, respectively. Circular dichroism (CD) spectra were

measured on a JASCO J-720 spectropolarimeter. Fluorescence spectra were recorded on a JASCO FP-750 spectropolarimeter.

### Materials

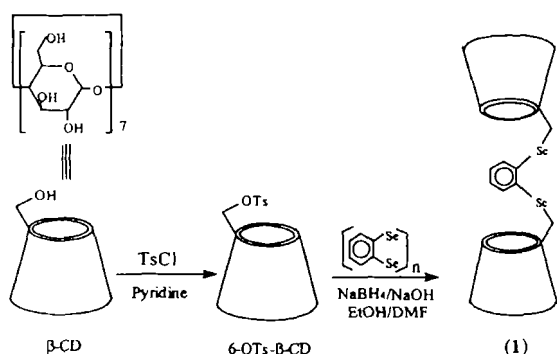
Commercially available ANS ammonium (Aldrich) was used without further purification.  $\beta$ -cyclodextrin of reagent grade (Suzhou Monosodium Glutamate Works) was recrystallized twice from water and dried in vacuo for 12 h at 100°C. *N,N*-Dimethylformamide (DMF) was dried over calcium hydride for two days and then distilled under a reduced pressure prior to use. Disodium hydrogen phosphate and sodium dihydrogen phosphate were dissolved in distilled, deionized water to make a 0.1 M phosphate buffer solution of pH 7.20 for fluorescence spectral titration.

### Synthesis

The *o*-phenylenediseleno bridged bis( $\beta$ -cyclodextrin)s (**1**) was prepared from mono-[6-*O*-(*p*-tolylsulfonyl)]- $\beta$ -cyclodextrin [7] and poly(*o*-phenylenediselenide) [8] according to the procedures as shown in Scheme 1. A solution of poly(*o*-phenylenediselenide) (0.234 g, 1 mmol), NaOH (0.12 g, 3 mmol) and  $\text{NaBH}_4$  (0.114 g, 3 mmol) in dry ethanol (50 ml) was stirred for 15 min at 85°C under nitrogen. When the color of the mixture disappeared, a solution of 6-OTs- $\beta$ -CD (2.64 g, 2 mmol) in dry DMF (75 ml) was added dropwise into the clear solution over 1 hr with magnetic stirring under  $\text{N}_2$ . The solution was stirred for 8 hr at 85°C, and then the resultant mixture was evaporated under a reduced pressure, leaving a yellow solid. The residue was dissolved in water, and then acetone was added to the solution to give a yellow precipitate. The crude product was purified by column chromatography over Sephadex G-25 with distilled, deionized water to give a pure sample (1.2 g, yield 49%). MS  $m/z$

[FAB]: 2469 ( $M + H^+$ ); IR (KBr)/ $\text{cm}^{-1}$ :  $\nu$  3379.0, 2909.5, 1630.0, 1555.3, 1535.0, 1394.5, 1380.0, 1371.2, 1305.2, 1225.4, 1146.9, 1071.0, 1020.3, 934.4, 832.3, 748.3, 697.4, 571.0.  $^1\text{H}$  NMR ( $\text{D}_2\text{O}$ , TMS):  $\delta$  3.57 ( $\text{C}^4\text{H}$ , 14H); 3.59 ( $\text{C}^2\text{H}$ , 14H); 3.80 ( $\text{C}^5\text{H}$ , 14H); 3.87 ( $\text{C}^6\text{H}$ , 24H); 3.89 ( $\text{C}^3\text{H}$ , 14H); 4.14 ( $\text{O}^6\text{H}$ , 12H); 4.44, 4.52 (subunit  $\text{C}^6\text{H}$ , 4H); 5.00 ( $\text{C}^1\text{H}$ , 14H); 5.34 ( $\text{O}^2\text{H}$ ,  $\text{O}^3\text{H}$ , 28H); 7.15, 7.37, 7.67, 7.75 (Ar-H, 4H). Anal. Calcd for  $\text{C}_{90}\text{H}_{142}\text{O}_{68}\text{Se}_2 \cdot 11\text{H}_2\text{O}$ , C: 40.51%, H: 6.20%, Se: 5.93%. Found C: 40.48%, H: 6.35%, Se: 6.00%.

1654.9, 1457.4, 1432.3, 1408.1, 1363.7, 1341.2, 1329.0, 1293.0, 1250.4, 1148.4, 1071.7, 1016.8, 933.3, 846.0, 745.6, 694.6, 669.0, 573.2.  $^1\text{H}$  NMR ( $\text{D}_2\text{O}$ , TMS):  $\delta$  3.57 ( $\text{C}^4\text{H}$ , 14H); 3.59 ( $\text{C}^2\text{H}$ , 14H); 3.81 ( $\text{C}^5\text{H}$ , 14H); 3.87 ( $\text{C}^6\text{H}$ , 24H); 3.89 ( $\text{C}^3\text{H}$ , 14H); 4.15 ( $\text{O}^6\text{H}$ , 12H); 4.44, 4.52 (subunit  $\text{C}^6\text{H}$ , 4H); 5.00 ( $\text{C}^1\text{H}$ , 14H); 5.34 ( $\text{O}^2\text{H}$ ,  $\text{O}^3\text{H}$ , 28H); 7.62, 7.86 (Ar-H, 4H). Anal. Calcd for  $\text{C}_{90}\text{H}_{142}\text{O}_{68}\text{Se}_2 \cdot \text{PdCl}_2 \cdot 11\text{H}_2\text{O}$ , C: 37.99%, H: 5.81%. Found C: 38.07%, H: 6.16%.



SCHEME 1

The platinum and palladium complexes (2) and (3) were synthesized by the reaction of *o*-phenylenediseleno bridged bis( $\beta$ -cyclodextrin)s with  $\text{K}_2\text{PtCl}_6$  and  $\text{PdCl}_2$  in aqueous solution, respectively. The complexes obtained were purified by column chromatography over Sephadex G-25 with distilled, deionized water to give a pure sample in isolated yields of 70% and 65%, respectively. The palladium complexes (3) was shown in Chart 1. Complex (2): IR (KBr)/ $\text{cm}^{-1}$ :  $\nu$  3324.5, 2905.5, 1655.0, 1640.0, 1633.2, 1458.9, 1438.2, 1404.7, 1356.9, 1330.9, 1294.2, 1250.5, 1146.6, 1068.8, 1017.4, 933.0, 842.3, 785.5, 749.3, 701.4, 575.8.  $^1\text{H}$  NMR ( $\text{D}_2\text{O}$ , TMS):  $\delta$  3.58 ( $\text{C}^4\text{H}$ , 14H); 3.59 ( $\text{C}^2\text{H}$ , 14H); 3.81 ( $\text{C}^5\text{H}$ , 14H); 3.87 ( $\text{C}^6\text{H}$ , 24H); 3.90 ( $\text{C}^3\text{H}$ , 14H); 4.14 ( $\text{O}^6\text{H}$ , 12H); 4.45, 4.52 (subunit  $\text{C}^6\text{H}$ , 4H); 5.01 ( $\text{C}^1\text{H}$ , 14H); 5.35 ( $\text{O}^2\text{H}$ ,  $\text{O}^3\text{H}$ , 28H); 7.60, 7.87 (Ar-H, 4H). Anal. Calcd for  $\text{C}_{90}\text{H}_{142}\text{O}_{68}\text{Se}_2 \cdot \text{K}_2\text{PtCl}_6 \cdot 10\text{H}_2\text{O}$ , C: 34.47%, H: 5.21%. Found C: 34.65%, H: 5.55%. Complex (3): IR (KBr)/ $\text{cm}^{-1}$ :  $\nu$  3297.0, 2901.5,

## RESULTS AND DISCUSSION

### Synthesis and Characterization

The novel *o*-phenylenediseleno bridged bis( $\beta$ -cyclodextrin)s and its complexes with platinum(IV) and palladium(II) ions have been synthesized in satisfactory yields. The toxicity assessment with rat is 10 g/kg feeding and no death has been observed for seven days, indicating that compound 1 possesses very low toxicity. The complexes were characterized by elemental analyses,  $^1\text{H}$ -NMR, infrared, and thermal analysis. The results of elemental analyses give 1:1 stoichiometry of the two complexes. By measuring the conductivity of the mixed solution of bis( $\beta$ -cyclodextrin)s 1 with  $\text{K}_2\text{PtCl}_6$  and  $\text{PdCl}_2$  at various molar ratios, ranging from 10:1 to 1:10, conductometric titrations also indicated the 1:1 stoichiometry for the complexation of 1 with Pt(IV) and Pd(II).

The IR spectral changes also support the complex formation, since the coupled poly O—H antisymmetric vibration of the complexes shifted to smaller wave numbers accompanying the peak broadening, and the peaks were broadened obviously with decreasing wavelength in the range from 1200 ~ 1400  $\text{cm}^{-1}$ .

Figure 1 shows  $^1\text{H}$ -NMR spectra of the compound 1 and the two complexes in  $\text{D}_2\text{O}$ . The evidence for complexation rests on the fact that the aromatic protons of 1 ( $\delta$  7.15–7.75) move downfield upon complexation with Pt ( $\delta$  7.60–7.87) and

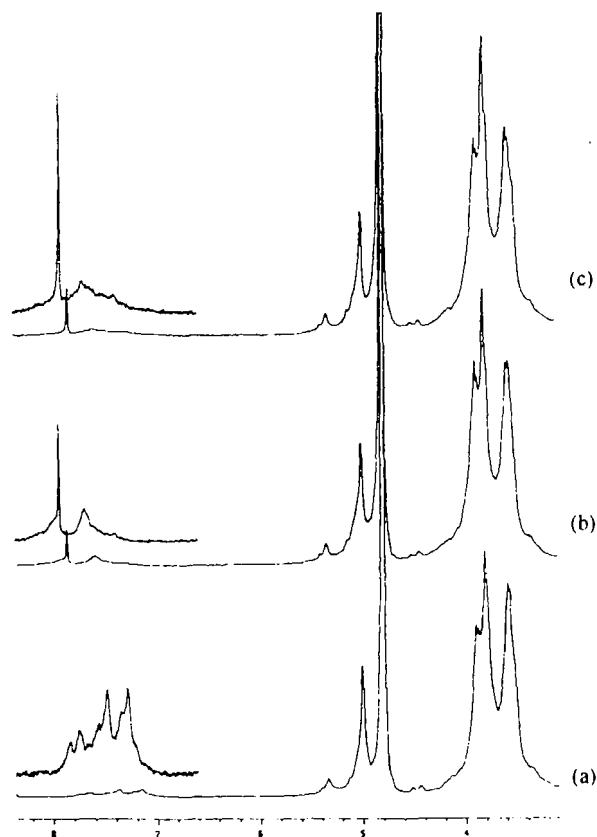


FIGURE 1  $^1\text{H}$  NMR spectra of *o*-phenylenediseleno bridged bis( $\beta$ -cyclodextrin)s **1** (a), Pt(IV) complex **2** (b) and Pd(II) complex **3** (c) in  $\text{D}_2\text{O}$ .

Pd ( $\delta 7.62$ – $7.86$ ), while the CD protons do not show appreciable shifts. Probably, the electron density of the aromatic ring is reduced by the ligation of the selenium atoms to Pt or Pd ions.

The thermal analyses of **1**–**3** also showed drastic changes upon complexation with Pt and Pd. In contrast to the physical mixture of **1** with Pt(IV) and Pd(II) ions, the complexes **2** and **3** show new phase-transition peaks in the DSC curve. The DSC curve for **1** has a small endothermic dehydration peak at  $82.5^\circ\text{C}$  and a small exothermic peak at  $181^\circ\text{C}$ , while the complexes **2** and **3** give two endothermic peaks at  $205.1$ ,  $207.7^\circ\text{C}$  and at  $248$ ,  $255.3^\circ\text{C}$ , respectively.

#### UV and CD Spectrum

As can be seen from Figure 2, the CD spectrum of modified  $\beta$ -cyclodextrin **1** in aqueous solution

showed a strong negative Cotton effect peak at  $259\text{ nm}$  ( $\Delta\epsilon = -6.76$ ). One possible explanation for this negative Cotton effect observed is the cooperative interaction of the  $^1L_a$  and  $^1L_b$  bands induced by the two cyclodextrin cavities. Due to the double seleno substituents on the benzene ring, the difference of the transition energy between the  $^1L_a$  band ( $237\text{ nm}$ ) and the  $^1L_b$  ( $277\text{ nm}$ ) band may be deduced obviously.

#### Fluorescence Spectral Titrations

As can be seen from Figure 3, in the titration experiments using differential fluorescence spectrometry, gradual addition of a known concentration of host (natural  $\beta$ -CD, **1** and **2**) to a dilute guest (ANS ammonium) solution ( $0.01\text{ mmol dm}^{-3}$ ) in phosphate buffer solution

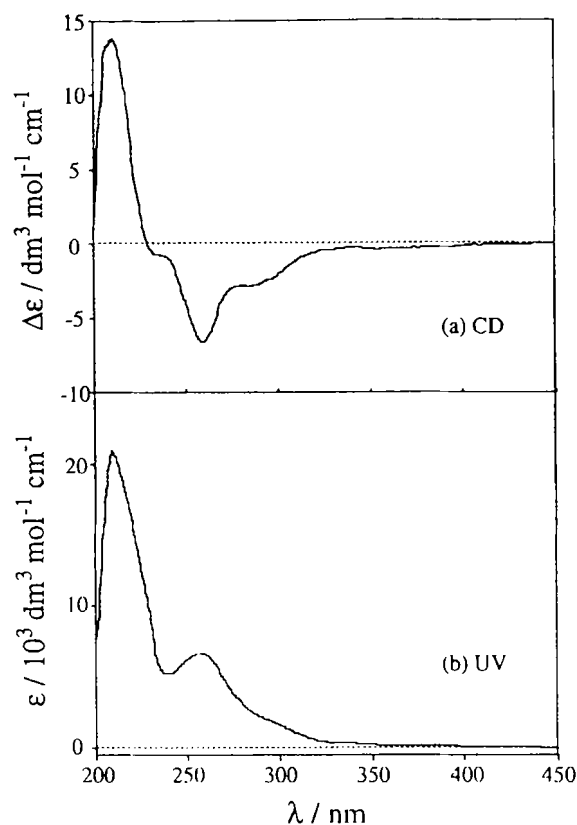


FIGURE 2 UV and CD spectra of *o*-phenylenediseleno bridged bis( $\beta$ -cyclodextrin)s **1** ( $1 \times 10^{-4} \text{ mol dm}^{-3}$ ) in phosphate buffer solution at  $25.0^\circ\text{C}$ .

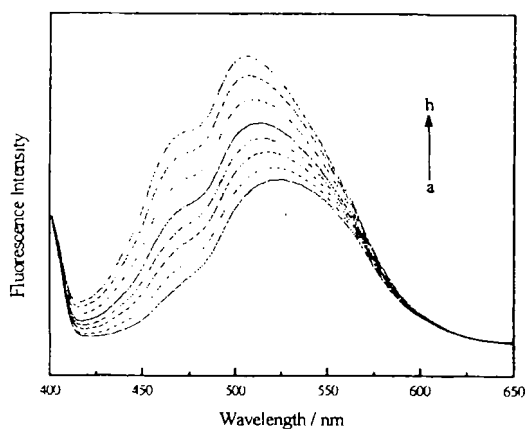


FIGURE 3 The fluorescence spectrum of ANS ammonium in the presence of *o*-phenylenediseleno bridged bis( $\beta$ -cyclodextrin)s platinum(IV) complex **2** at various concentrations at  $25.0^\circ\text{C}$ . The concentration of ANS ammonium is  $1 \times 10^{-5} \text{ mol dm}^{-3}$ . The concentrations of **2** increase in the range of  $0 - 2.258 \times 10^{-4} \text{ mol dm}^{-3}$  from *a* to *b*.

caused significant increases in intensity. Somewhat unexpectedly and interestingly, although platinum(IV) is a well-known quencher of fluorescence, the fluorescence intensity of ANS ammonium gradually increased with the addition of varying concentration of host **2**. Typical fluorescence spectral changes upon addition of host **2** to ANS ammonium solution are shown in Figure 3. With the assumption of a 1:1 stoichiometry, the inclusion complexation of ANS ammonium (G) with  $\beta$ -cyclodextrin derivatives (H) is expressed by Eq. (1).



The stability constant ( $K_s$ ) of inclusion complex formed can be determined using a non-linear

least squares method according to the curve fitting Eq. (2) [9].

$$\Delta F = \left\{ \alpha([H]_0 + [G]_0 + 1/K_s) \pm \sqrt{\alpha^2([H]_0 + [G]_0 + 1/K_s)^2 - 4\alpha^2[H]_0[G]_0} \right\} / 2 \quad (2)$$

where  $[G]_0$  and  $[H]_0$  refer to the total concentration of ANS ammonium and  $\beta$ -cyclodextrin derivatives, respectively;  $\alpha$  is the proportionality coefficient, which may be taken as a sensitivity factor for the fluorescence change;  $\Delta F$  denotes the change in the fluorescence spectrum of ANS ammonium upon stepwise addition of the host  $\beta$ -cyclodextrin derivative. For each host compound examined, the plot of  $\Delta F$  as a function of  $[G]_0$  give an excellent fit, verifying the validity of the 1:1 complex stoichiometry assumed above. As shown in Figure 4, where the  $\Delta F$  values are plotted against the  $[G]_0$  values to given an excellent fit, no serious deviations are found in the curve fitting. The complex stability constants ( $K_s$ ) obtained by the curve fitting are listed in Table I, along with the free energy change of complex formation ( $-\Delta G^\circ$ ).

### Molecular Binding Ability

Extensive studies of molecular recognition by cyclodextrins have shown that an important characteristic of the complexation is simultaneous operation of several weak forces working between the guest and host, which determine how the size and shape of a guest molecule fit into the host cavity [10]. Cyclodextrin dimers possessing two hydrophobic cavities can form more stronger complex with suitable guest molecules than natural cyclodextrin through multipoint recognition mechanism. As can be seen from Table I, the stability constants of the complexes formed by three hosts with ANS

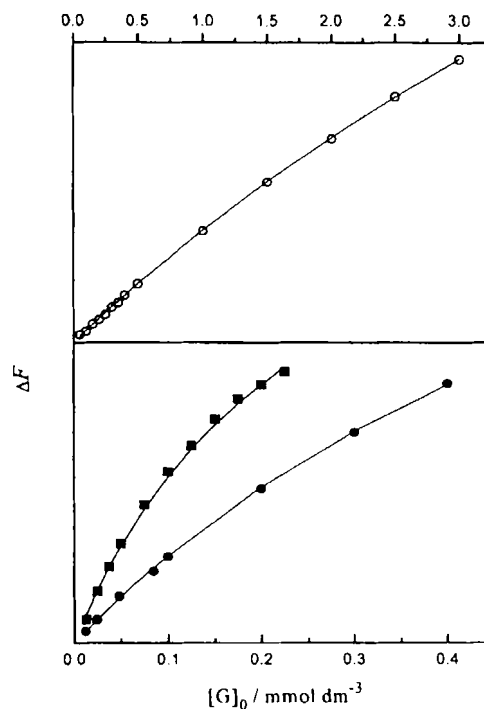


FIGURE 4 Curve fitting analyses, according to Eq. (2), for complexations of natural  $\beta$ -CD ( $\circ$ ) ( $0-3 \times 10^{-3} \text{ mol dm}^{-3}$ ), **1** ( $\bullet$ ) ( $0-4.014 \times 10^{-4} \text{ mol dm}^{-3}$ ) and **2** ( $\blacksquare$ ) ( $0-2.258 \times 10^{-4} \text{ mol dm}^{-3}$ ) with ANS ammonium ( $1 \times 10^{-5} \text{ mol dm}^{-3}$ ) at  $25^\circ\text{C}$ .

TABLE I The stability constants ( $\log K_s$ ) and the Gibbs free energy changes ( $-\Delta G^\circ$ ) for 1:1 inclusion complexation of ANS ammonium with  $\beta$ -cyclodextrin and host **1** and **2** in  $0.1 \text{ mol} \cdot \text{dm}^{-3}$  phosphate buffer solution (pH = 7.20) at  $25^\circ\text{C}$ <sup>a</sup>

Host	Guest	$K_s$	$\log K_s$	$-\Delta G^\circ / \text{kJ mol}^{-1}$
$\beta$ -CD	ANS ammonium	103	2.01	11.5
<b>1</b>	ANS ammonium	1280	3.11	17.7
<b>2</b>	ANS ammonium	4020	3.60	20.6

<sup>a</sup>  $\lambda_{\text{Ex}} = 350 \text{ nm}$ ,  $\lambda_{\text{Em}} = 524 \text{ nm}$ .

ammonium are in the order of  $2 > 1 > \text{natural } \beta\text{-CD}$ , which can be ascribed to the structural difference between three hosts. The *o*-phenylene-diseleno bridged bis(cyclodextrin)s **1** displayed much higher, nearly 12.4 times calculated from the stability constants  $K_s$ , molecular binding ability to ANS ammonium than natural  $\beta$ -cyclodextrin through simultaneous inclusion

complexation of two cyclodextrin cavities. According to the model of bridged cyclodextrins binding guest molecules possessing two hydrophobic groups, [11,12] the benzene ring and naphthene ring of ANS must be embedded into the two cyclodextrin cavities, respectively. As shown in Table I, the platinum(IV) complex 2 showed the strongest binding ability to ANS ammonium, suggested that the stability constant of 2 with ANS ammonium enlarged 3 times than that of bridged cyclodextrins 1. One reasonable explanation is the triple recognition mechanism of host 2. The platinum(IV) ion introduced to the bridge chain can not only adjust the orientation of the two cyclodextrin cavities to fit the shape of guest molecule, but also be taken as a new point to recognize the sulfonic acid group of the ANS through electrostatic interaction. These results obtained indicated that multipoint recognition mechanism plays a crucial role in inclusion complexation of cyclodextrin derivatives.

#### SUPPLEMENTARY MATERIAL AVAILABLE

The DSC curves of  $K_2PtCl_6$ ,  $PdCl_2$ , compounds 1–3 and the IR spectrums of 1–3 (8 pages).

#### Acknowledgements

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