



Intramolecular photo-substitution in the inclusion compound of mono[6-deoxy-6-(2-aminoethyl thio-1,2-dicyane ethylenylthio)]- β -cyclodextrin with cyclopentadienyl manganese tricarbonyl in DMF solution

Changsheng Lu^a, Zhaoping Ni^a, Wenlong Liu^a, Yang Zou^a, Jingli Xie^a, Chunlin Ni^a,
Huizhen Zhu^a, Qingjin Meng^{a,*}, Yuangen Yao^b

^a State Key Laboratory of Coordination Chemistry, Coordination Chemistry Institute, Nanjing University, Nanjing 210093, China

^b State Key Laboratory of Structural Chemistry, Fujian Institute of Research on the Structure of Matter, Fujian 350002, China

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Abstract

A novel host of β -cyclodextrin (β -CD) derivative, mono[6-deoxy-6-(2-aminoethyl thio-1,2-dicyane ethylenylthio)]- β -CD (**3**), and its inclusion compound **4** with cyclopentadienyl manganese tricarbonyl ($\text{CpMn}^{\text{I}}(\text{CO})_3$) have been prepared and characterized by spectroscopic methods. It is experimentally evident that the inclusion complexation stabilized the guest extremely when complex **4** was heated. Upon irradiation of inclusion compound **4** in DMF solution, an interesting intramolecular photo-substitution resulting in the formation of a self-stabilized compound mono[6-deoxy-6-(2-aminoethyl thio-1,2-dicyane ethylenylthio)]- β -CD- $\text{Mn}^{\text{II}}\text{Cp}(\text{DMF})_2$ (**7**) was observed. Based upon a double-recognition between the host and the organometallic guest, compound **7** became very stable in DMF solution.

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Keywords: Cyclopentadienyl manganese tricarbonyl; Mono[6-deoxy-6-(2-aminoethyl thio-1,2-dicyane ethylenylthio)]- β -CD; Inclusion compound; Intramolecular photo-substitution; Self-stabilized compound

1. Introduction

The organometallic guest encapsulated within a supramolecular host has developed into an active area of research [1]. Cyclodextrins (CDs) are macrocyclic oligosaccharides with hollow hydrophobic cavities that are well known to selectively bind a variety of organometallic molecules such as cyclopentadienyl (Cp) and η^6 -arene group [2]. Encapsulated half-sandwich complexes such as ($\eta^6\text{-C}_6\text{H}_6$)Cr(CO)₃ [3], CpFe(CO)₂X (X = Cl, Me) [4], CpMn(CO)₃ [5], and Cp'Mo($\eta^3\text{-C}_3\text{H}_5$)(CO)₂ (Cp' = Cp, C₅H₄SiMe₃ or indenyl) [6] have also been reported. Upon inclusion complexation with the hosts that are based on CDs, physical and

chemical properties of these organometallic guests have been modified effectively, for example, in their nonlinear optical properties [7] and ligand substitution/insertion reactions [4]. In our laboratory, the inclusion compound of an anion host, mono[6-deoxy-6-(2-sodium thio-1,2-dicyane ethylenylthio)]- β -CD (6-mnt- β -CD, (**1**)), with CpMn^I(CO)₃ has been reported [8]. And here, the inclusion compound **4** of a neutral CD host, mono[6-deoxy-6-(2-aminoethyl thio-1,2-dicyane ethylenylthio)]- β -CD (6-[NH₂-mnt]- β -CD, (**3**)), with CpMn^I(CO)₃ was prepared and investigated as well.

2. Results and discussion

2.1. The novel host 6-[NH₂-mnt]- β -CD (**3**)

The carbonyl stretching bands (1775.9 and 1727.1 cm⁻¹, respectively) were experimentally evident from

* Corresponding author. Tel.: +86-25-3592485; fax: +86-25-331-7761.

E-mail address: mengqj@netra.nju.edu.cn (Q. Meng).

Table 1
Spectroscopic and photophysical data for compounds 1–4

Complex ^a	UV λ_{\max} (nm) ^b	IR ν (cm ⁻¹)	¹ H-NMR δ (ppm)
CpMn ^I (CO) ₃	325	2025.1 1939.0	
Na ₂ mmt ^c	387.5	2194.9	
1 ^c	385.5	2189.7	4.82(H-1), 3.31(H-2), 3.63(H-3), 3.35(H-4), 3.55(H-5), 3.63(H-6)
2	342	2169.7 1775.9 1727.1	4.83(H-1), 3.30(H-2), 3.62(H-3), 3.35(H-4), 3.56(H-5), 3.62(H-6) 3.99(H-a) ^d , 3.72(H-a) ^d , 7.92(H-b) ^e , 7.87(H-b) ^e
3	342	2169.6	4.82(H-1), 3.30(H-2), 3.63(H-3), 3.35(H-4), 3.55(H-5), 3.63(H-6)
4	341	2169.5 2016.5 1940.2	4.82(H-1), 3.30(H-2), 3.63(H-3), 3.35(H-4), 3.55(H-5), 3.63(H-6) 5.03(H-c) ^f

^a Na₂mmt = 2-butenedinitrile-2,3-dimercapto disodium salt.

^b In DMF.

^c From Ref. [9].

^d Hydrogen atoms of the ethyl group.

^e Hydrogen atoms in the benzene ring of the phthalimide group.

^f Hydrogen atoms in the cyclopentadienyl ring of the organometallic guest.

the IR spectrum of mono[6-deoxy-6-(2-phthalimideethyl thio-1,2-dicyano ethylenylthio)]- β -CD (6-[NR₂-mnt]- β -CD, (**2**)) (Table 1). In addition, the introduction of β -bromoethylphthalimide to mnt group of complex **1** resulted in obvious shift, from 2189.7 to 2169.7 cm⁻¹, of the nitrile groups in that of complex **2**. So, it is logical to assume that the charge density has been lowered in mnt group with the conversion from complex **1** (anion host) to complexes **2** and **3** (neutral host). And the reasonableness of this assumption rests in the fact that the carbon atom signals of both the C=C bond and the nitrile groups have exhibited large downfield shifts (+6.83 and +1.74 ppm, respectively) in complex **3** compared with that of complex **1** (Table 2). Consistent with this observation, the electron spectra have shown obvious blue-shifts (about 43 nm) of the mnt group in complexes **2** and **3** compared with that in complex **1** (Table 1).

Parallels in the spectroscopic data of the hydrazinolysis, where complex **2** was converted to yield complex **3**, were very striking. The signal of amino group has been evidently observed (1.05 ppm, see Section 4) in ¹H-NMR spectrum of complex **3** in contrast with in that of complex **2**, despite the signals vanishing of the phthalimide group from both IR and ¹H-NMR spectra (Table 1). Therefore, the spectroscopic changes have suggested the formation of 6-[NH₂-mnt]- β -CD (**3**) in fact.

2.2. The inclusion compound 6-[NH₂-mnt]- β -CD/CpMn^I(CO)₃ (**4**)

All the spectroscopic data have experimentally indicated the formation of inclusion compound **4**. For example, proton signals of cyclopentadienyl ring (5.03 ppm) and CO signals (225.54 ppm, 2016.5 and 1940.2 cm⁻¹) of the guest (CpMn^I(CO)₃) have been clearly

observed from ¹H-NMR, ¹³C-NMR, and IR spectra of complex **4** (Tables 1 and 2), respectively. In addition, the carbonyl stretching bands of the guest have experienced obvious shifts upon inclusion complexation (from 2025.1 and 1939.0 to 2016.5 and 1940.2 cm⁻¹, respectively), as just the similar changes as in the samples of inclusion compounds β -CD/CpMn^I(CO)₃ and 6-mnt- β -CD/CpMn^I(CO)₃ [8]. And paralleling these observations, signals of all the carbon atoms in β -CD structure exhibited upfield shifts in complex **4** compared with that in complex **3**, which was able to be interpreted as the penetration of cyclopentadienyl group of the guest into cavity of the host.

Furthermore, the stoichiometry of complex **4** that was isolated as solid complex was determined by the comparison of peak areas of the host and guest molecules in ¹H-NMR spectrum. As expected, a one-to-one inclusion compound **4** has been obtained upon inclusion complexation in our experiment.

Fig. 1 showed thermogravimetric (TG) and differential thermogravimetric (DTG) curves of pure CpMn^I(CO)₃, complexes **3** and **4**, respectively. In the sample of CpMn^I(CO)₃, only one peak arose at 147 °C, which was attributed to the decomposition of pure CpMn^I(CO)₃. The two peaks (around 61 and 317 °C, respectively) in the DTG curve of complex **3** corresponded to the dehydration and decomposition of 6-[NH₂-mnt]- β -CD. And in the case of complex **4**, two peaks were recorded either, one of which (around 65 °C) should be assigned to the dehydration process, and the other (around 317 °C) was related to the decomposition of the inclusion compound 6-[NH₂-mnt]- β -CD/CpMn^I(CO)₃. The complex **4** seemed to be thermally stable, and did not liberate the included manganese complex on heating up to 250 °C in fact. So, it can be easily concluded that after inclusion with the host,

Table 2
Partial ^{13}C -NMR spectroscopic data ^a for compounds **1**, **3**, **4** and **7**

Complex	C-1 (ppm)	C-2 (ppm)	C-3 (ppm)	C-4 (ppm)	C-5 (ppm)	C-6 (ppm)	C (ppm) ^b	C (ppm) ^c	C (ppm) ^d	C (ppm) ^e	C (ppm) ^f
1 ^g	102.05	72.12	73.15	81.62	72.49	59.95	80.94, 81.15	42.06	118.58		
3	102.03	72.13	73.13	81.62	72.49	60.01	82.68, 83.21	42.04	125.41		
4	102.01	72.09	73.09	81.58	72.44	59.95	82.65, 83.17	42.55		225.54	83.97
7	102.04	72.17	73.15	81.64	72.51	60.02					84.75

^a Spectra was recorded in DMSO- d_6 at 20 °C, and data were referenced to internal DMSO- d_6 (39.51 ppm); C-1 to C-6 refer to the carbon atoms of the β -CD structure.

^b Carbon atoms of the nitrile groups in mnt.

^c Carbon atoms of the ethyl group.

^d Carbon atoms of the double bond in mnt.

^e Carbon atoms of the carbonyl groups in the organometallic guest.

^f Carbon atoms in the cyclopentadienyl ring of the organometallic guest.

^g From Ref. [9].

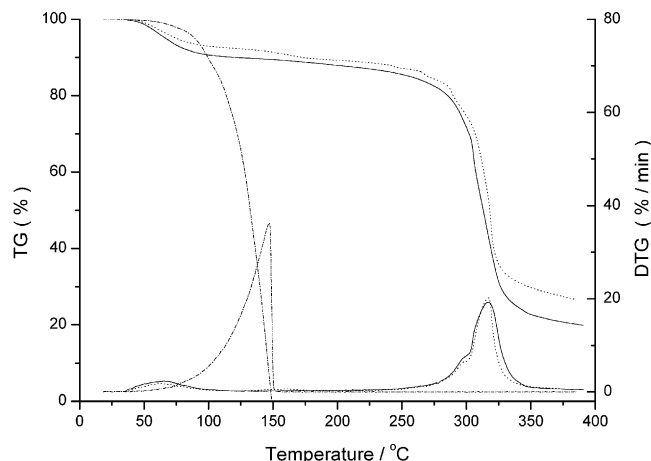


Fig. 1. TG and DTG curves of $\text{CpMn}^{\text{I}}(\text{CO})_3$ (.....), complex **3** (---), and complex **4** (—).

thermo-stability of the guest has been extremely improved. The decomposition temperature difference between a free guest and the guest in inclusion compound **4** was +170 °C (ΔT_{guest}). Thermal analyses of the inclusion compounds β -CD/ $\text{CpMn}^{\text{I}}(\text{CO})_3$ and 6-mnt- β -CD/ $\text{CpMn}^{\text{I}}(\text{CO})_3$ have been performed previously, and the ΔT_{guest} are +144 and +167 °C, respectively [8]. Therefore, it is evident that the host **3** exhibits more effective protection of the organometallic guest than do the pure β -CD and 6-mnt- β -CD (**1**).

2.3. Intramolecular photo-substitution of complex **4** in DMF solution

To date, all of the known photochemistry about $\text{CpMn}^{\text{I}}(\text{CO})_3$ in solution is consistent with the formation of $\text{CpMn}^{\text{I}}(\text{CO})_2\text{X}$, some of which have been obtained as fine crystals, as the principal result [10]. And virtually any nucleophile, X, can be used.

Upon irradiation under sunlight, $\text{CpMn}^{\text{I}}(\text{CO})_3$ solution in DMF is ready to undergo photo-substitution of CO to precipitate substituted derivative, which has been observed in our experiment. However, upon irradiation of inclusion compound **4** solution, 6-[NH₂-mnt]- β -CD/ $\text{CpMn}^{\text{I}}(\text{CO})_3$ in DMF, the color of the solution gradually turned brown while a continuous release of CO from the solution was observed. But no precipitates were found.

Fig. 2 showed the absorption spectra, of inclusion compound **4** solution in DMF under sunlight at 20 °C, as a function of irradiation time (the irradiation time interval was 5 min each). The peak at around 341 nm decreased gradually with the increasing irradiation time. However, no absorption maximum was formed during the measuring range after 1-h irradiation, in addition to an absorption shoulder arising at around 300 nm. In view of the previous researches [10], proper assignments of the electronic spectra of $\text{CpMn}^{\text{I}}(\text{CO})_3$ in solution by

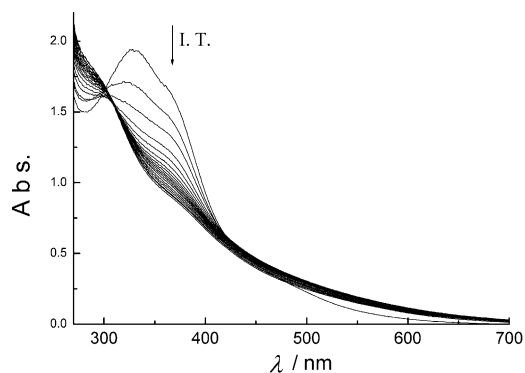


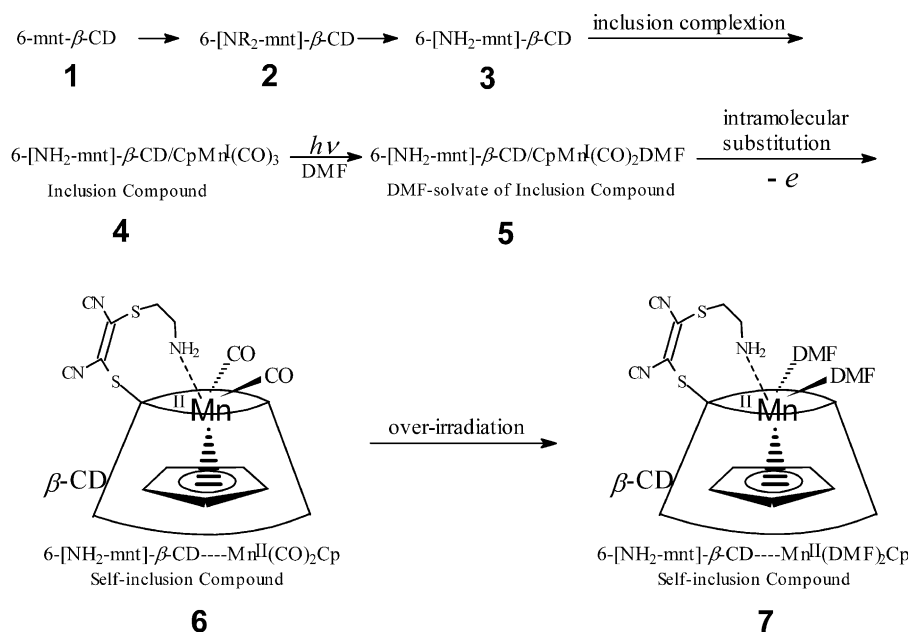
Fig. 2. Absorption spectra of inclusion compound **4** in DMF solution at various irradiation times (IT).

the visible light irradiation highly depend on whether the entering group, X, is a π -acceptor ligand or a simple ligand that binding to the central metal atom only via σ interactions. The electronic spectral data have strongly supported the assignment of the absorption maximum, in the case of X = π -acceptor ligand, as $M \rightarrow \pi^*XCT$. Otherwise, when X = simple ligand such as amino or THF, the notion has been adopted that the electronic absorption are LF bands associated with d–d transitions [10]. So, the absorption maximum situated at around 306 nm in the sample of 6-mnt- β -CD/CpMn^I(CO)₃ system upon irradiation [8] could be ascribed as $Mn \rightarrow \pi^*mntCT$, where the entering group (mnt) has just worked as a π -acceptor ligand. And in our experiments, as showed in Scheme 1, the entering ligand that we used was amino group. It was close to the central manganese atom upon the effect of inclusion complexation, and substantially underwent a photo-substitution process from DMF-solvate **5** to the self-

inclusion compound **6**, which has been experimentally recorded in Fig. 2. Therefore, in the case of complex **4**, the appearance of the absorption shoulder around 300 nm would consequently be assigned as LF bands, which suggested in fact the formation of an N–Mn bonding between the host and guest. Because of the larger energy gap existing in the LF bands than that in the $Mn \rightarrow \pi^*mntCT$, the absorption maximum would exhibit blue-shift in the case of complex **4** compared with that of 6-mnt- β -CD/CpMn^I(CO)₃ system, which was able to favor the interpretation of the absorption shoulder in electronic spectrum.

Moreover, electrochemical investigations of CpMn^I(CO)₂X have shown that strong nucleophilic ligands can facilitate the one-electron oxidation of CpMn^I(CO)₂X, and stabilize the Mn^{II} metal center effectively to yield CpMn^{II}(CO)₂X at last [11]. In our experiment, low-spin Mn^{II} signals were observed in ESR spectrum from the irradiated brown solution of complex **4** in DMF (Fig. 3).

So, it is reasonable to assume that the primary result of photo-substitution of inclusion compound **4**, 6-[NH₂-mnt]- β -CD/CpMn^I(CO)₃, in DMF solution was the dissociative loss of CO and the formation of DMF-solvate, 6-[NH₂-mnt]- β -CD/CpMn^I(CO)₂DMF **5** (Scheme 1) [12]. Furthermore, the coordinated DMF in the DMF-solvate **5** was substituted by the amino group attached to the host to yield the intramolecular photo-substituted product 6-[NH₂-mnt]- β -CD–CpMn^I(CO)₂. Finally, the photochemically generated compound 6-[NH₂-mnt]- β -CD–CpMn^I(CO)₂ experienced one-electron oxidation to give the product 6-[NH₂-mnt]- β -CD–CpMn^{II}(CO)₂ **6**. The release of CO from the DMF solution of inclusion compound **4** was



Scheme 1. Proposal mechanism of the intramolecular photo-substitution process.

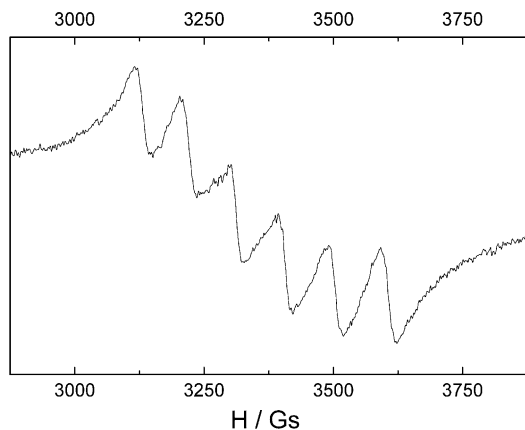


Fig. 3. ESR spectrum of inclusion compound **4** in DMF solution upon irradiation in sunlight for 3 h.

observed after minutes of irradiation (vide supra). And the one-electron oxidation, that is the transformation from Mn^{I} to Mn^{II} , was confirmed by the ESR spectrum (Fig. 3). Further evidence in favor of this intramolecular photo-substitution was provided by electron spectra (vide supra). Although the amino group that we used in the experiment is not a strong nucleophile, it has experimentally favored the one-electron oxidation of 6-[NH_2 -mnt]- β -CD- $\text{CpMn}^{\text{I}}(\text{CO})_2$ to yield 6-[NH_2 -mnt]- β -CD- $\text{CpMn}^{\text{II}}(\text{CO})_2$ (**6**), despite by far the less photo-sensitive of the transformation from Mn^{I} to Mn^{II} species than in that of the 6-mnt- β -CD/ $\text{CpMn}^{\text{I}}(\text{CO})_3$ system [8].

Over-irradiation of the solution of inclusion compound **4** in DMF resulted in the disappearance of CO signals in ^{13}C -NMR spectra, which suggested a total release of CO from the mono-substituted product 6-[NH_2 -mnt]- β -CD- $\text{CpMn}^{\text{II}}(\text{CO})_2$ [13]. The over-irradiated solution **7** was brown and very stable in air for more than 1 year. Concentration of this solution under reduced pressure gave a brown powder. IR spectrum of the powder showed the presence of the carbonyl signal of DMF (1658.5 cm^{-1}), but no CO signals (around 2000 cm^{-1}) were observed at all. ^1H -NMR spectra of the powder showed additional three hydrogen atoms at δ 2.47 (6H), 2.62 (6H) and 7.55 (2H) ppm, compared with that of inclusion compound **4**. These results suggested the formation of a DMF-solvate 6-[NH_2 -mnt]- β -CD- $\text{Mn}^{\text{II}}\text{Cp}(\text{DMF})_2$ (**7**) upon over-irradiation, which has greatly encouraged the above-assumed intramolecular photo-substitution process.

For the over-irradiated solution **7**, downfield shifts of carbons in both the β -CD moiety and the cyclopentene ring of the guest were observed. For example, the signals of C-5 shifted from 72.44 (in compound **4**) to 72.51 ppm (in compound **7**), the signals of carbons in the cyclopentene ring shifted from 83.97 (in compound **4**) to 84.75 ppm (in compound **7**), and the signals of carbons of the ethyl groups shifted from 42.04 (in compound **4**)

to 42.55 ppm (in compound **7**). In addition, the signals of amino group shifted from 1.05 (in complex **3**) to 1.77 ppm (in complex **7**) in ^1H -NMR spectra. These revealed the lowering of charge density of the central organomanganese and the charge transfer from the amino group to the organomanganese fragment in β -CD cavity, which were able to be interpreted as the oxidation from $\text{Mn}^{\text{I}} \rightarrow \text{Mn}^{\text{II}}$ and the formation of an N-Mn bonding, respectively.

In compound **7**, the metal coordination recognition brings about the binding of amino group of the host to Mn^{II} center, and the hydrophobic recognition brings about the inclusion of organomanganese fragment with β -CD cavity. Therefore, it is the double-recognition that has made compound **7** self-stabilized in solution.

3. Conclusion

We prepared a β -CD derivative, 6-[NH_2 -mnt]- β -CD (**3**), and its inclusion compound with an organometallic guest, $\text{CpMn}^{\text{I}}(\text{CO})_3$. The new host in the inclusion compound 6-[NH_2 -mnt]- β -CD/ $\text{CpMn}(\text{CO})_3$ (**4**) exhibited better guest-binding ability, and was thermally more beneficial to protect the included guest than the pure β -CD and 6-mnt- β -CD (**1**). In addition, intramolecular photo-substitution in the inclusion compound 6-[NH_2 -mnt]- β -CD/ $\text{CpMn}^{\text{I}}(\text{CO})_3$ in DMF solution was explored. This intramolecular photo-substitution finally brought about a double-recognition between the host and the organometallic guest.

4. Experimental

4.1. Physical measurements and materials

A Bruker IFS66V FT-IR spectrophotometer was used, and the measurements were made by the KBr disk method. The UV spectra were recorded on a Shimadzu UV-3100 spectrometer. All ^{13}C -NMR and ^1H -NMR spectra were recorded on a Bruker AVANCE-300 spectrometer in $\text{DMSO}-d_6$ solution at $15\text{ }^\circ\text{C}$. Elemental analysis was determined by a Perkin-Elmer 240C elemental analyzer. TG analysis curves were recorded on an American SDT-2960 thermal analyzer. The ESR spectrum was recorded using a (JEOL) JES-IXG spectrometer at 100 KHz modulation. Mn^{2+} in MgO was used as the standard sample. Ethanol, acetone and THF were of analytically pure grade. DMF was distilled under reduced pressure in N_2 atmosphere before use. 2-(2-Bromoethyl)-1H-isoindole-1,3(2H)-dione (β -bromoethylphthalimide) was obtained commercially (Nanjing Chemical Products Factory) and recrystallized before use. 6-Mnt- β -CD was synthesized

according to the methods described in the literatures [8,9].

4.2. Synthesis of 6-[NR₂-mnt]-β-CD (2)

To a solution of 6-mnt-β-CD (1) (1.0 g, 0.68 mmol) in DMF (20 ml) was added β-bromoethylphthalimide (0.25 g, 0.98 mmol), and the mixture was stirred at 65 °C for 4–6 h under a N₂ atmosphere. After cooling down to room temperature, the solution was concentrated under reduced pressure to remove the solvent. Then by addition of acetone (30 ml) to the residue, the solid was collected and recrystallized from water to give the final product (0.9 g, 82%) as yellow deposits. Anal. Calc. for C₅₆H₇₇O₃₆N₃S₂·11H₂O: C, 41.25; H, 6.12; N, 2.58. Found: C, 41.40; H, 6.21; N, 2.49%. UV: λ_{max} nm (DMF): 342 (ε, M⁻¹ cm⁻¹, 9700). IR (ν, cm⁻¹): 2169.7(w), 1775.9(s), 1727.1(s). ¹H-NMR (288 K, DMSO-*d*₆) δ 3.30, 3.35, 3.56, 3.62, 3.72, 3.99, 4.49, 4.83, 5.69, 5.76, 7.87, 7.92 ppm.

4.3. Synthesis of 6-[NH₂-mnt]-β-CD (3)

The precipitate of 6-[NR₂-mnt]-β-CD (2) (1.0 g, 0.61 mmol) was hydrazinolized with 30 ml 0.1 M hydrazine hydrate at 65 °C for 2 h, and the clear solution was evaporated under reduced pressure. The residue was then added to stirred ethanol (100 ml) to precipitate product 3 as pale-brown deposits (0.8 g, 86%). Anal. Calc. for C₄₈H₇₅O₃₄N₃S₂·12H₂O: C, 37.97; H, 6.57; N, 2.77. Found: C, 38.11; H, 6.43; N, 2.82%. UV: λ_{max} nm (DMF): 342 (ε, M⁻¹ cm⁻¹, 6700). IR (ν, cm⁻¹): 2169.6(w). ¹H-NMR (288 K, DMSO-*d*₆) δ 1.05, 3.30, 3.35, 3.55, 3.63, 4.46, 4.82, 5.68, 5.72 ppm. ¹³C-NMR (288 K, DMSO-*d*₆) δ 42.06, 60.01, 72.13, 72.49, 73.13, 81.62, 82.68, 83.21, 102.03, 125.41 ppm.

4.4. Preparation of inclusion compound 6-[NH₂-mnt]-β-CD/CpMn^I(CO)₃ (4)

The inclusion compound of 6-[NH₂-mnt]-β-CD (3) with CpMn^I(CO)₃ was prepared by coprecipitation method [8,9]. 6-mnt-β-CD (0.5 g, 0.33 mmol) was dissolved in water (40 ml), and then was added CpMn^I(CO)₃ (0.16 g, 0.81 mmol). After stirring at 40 °C for 2 h, the solution was cooled to room temperature and a pale-brown solid precipitated, which was then collected by filtration and washed twice with water and THF. Finally, drying of this solid in air for 4 h gave the inclusion compound as a pale-brown powder (0.22 g, 40%). Anal. Calc. for C₅₆H₈₀O₃₇N₃MnS₂·10H₂O: C, 39.88; H, 5.98; N, 2.49%. Found: C, 40.12; H, 5.89; N, 2.63%. UV: λ_{max} nm (DMF): 342 (ε, M⁻¹ cm⁻¹, 6100). IR (ν, cm⁻¹): 2169.5(w), 2016.5(s),

1940.2(s). ¹H-NMR (288 K, DMSO-*d*₆) δ 1.14, 3.30, 3.35, 3.55, 3.63, 4.48, 4.82, 5.03, 5.69, 5.74 ppm. ¹³C-NMR (288 K, DMSO-*d*₆) δ 42.04, 59.95, 72.09, 72.44, 73.09, 81.58, 82.65, 83.17, 102.01, 225.54 ppm.

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