

# Luminescence Properties of Metal(II)-Diethyldithiocarbamate Chelate Complex Particles and Its Analytical Application

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In a suitable pH buffer solutions, sodium diethyldithiocarbamate (DDTC) reacts with some divalence metal ions M(II) to form (M-DDTC)<sub>n</sub> chelate complex nanoparticles, which exhibit different luminescence properties. There is a strongest luminescence peak at 470 nm for the Co(II)-DDTC system, three peaks at 330, 470, and 630 nm for the Cu(II)-DDTC system, three peaks at 420, 470, and 630 nm for the Cd(II)-DDTC system, four peaks at 350, 400, 435, and 470 nm for the Ni(II)-DDTC system, two peaks at 408 and 470 nm for the Pb(II)-DDTC system, two peaks at 415 and 470 nm for the Fe(II)-DDTC system. The different luminescence properties of (M-DDTC)<sub>n</sub> chelate complex nanoparticles was explained. Under the optimal conditions, the luminescence intensity of (Co-DDTC)<sub>n</sub> chelate complex nanoparticles at 470 nm ( $F_{470\text{ nm}}$ ) is linear to Co(II) concentration in the range of 0.012–1.44  $\mu\text{g/mL}$ . The detection limit is 0.0023  $\mu\text{g/mL}$ . A novel luminescence method has been proposed for the determination of cobalt in Vitamin B<sub>12</sub> samples, with satisfactory results.

**KEY WORDS:** Metal ion(II); DDTC; chelate complex nanoparticle; luminescence .

## INTRODUCTION

The fluorescence of nanoparticle in liquid phase is interesting to scientists in chemistry, physics, and bio-science. Firstly, the fluorescence of some nanosemiconductors such as CdS, CdSe, CdTe, ZnS/MnS was discovered and applied to several fields such as bioanalysis and luminescence materials [1–3]. Then, it has been found that some metal nanoparticles such as Au, Ag in liquid phase have fluorescence and resonance scattering effect [4–6]. Recently, It has been reported that some association complexes could aggregate automatically and form association nanoparticles by intermolecular forces and hydrophobic forces, which also exhibit fluorescence effect [7,8], and has been applied to analytical chemistry. It is

known that chelate complex has good stability and could be modified easily by chemical procedure, so it could be applied to material science and analytical science [9–12]. Up to date, the resonance scattering effect of chelate complex nanoparticle such as Al(III)-chrome azurol S has been studied [13], and was used to the selective determination of trace Al in water, but the fluorescence of chelate complex nanoparticles in water phase and its analytical application have not been reported.

Cobalt is an important trace element to human body and it is also a composition of Vitamin B<sub>12</sub>, so it is necessary to develop a simple, sensitive, and selective method for determination of cobalt. Fluorescence method has good sensitivity and selectivity. Several fluorescence methods have been reported for the determination of cobalt. Burns [14] determined cobalt spectrofluorimetrically by extraction as bis[1-(2-pyridylmethylene)-2-(2-pyridyl)hydrazide]-cobalt dimethoxyanthracenesuph-onate. However, the analytical time is long and the organic solvent is harmful to human body. Using a new fluorescence reagent of 5-(4-chlorophenylazo)-8-aminoquinoline, Cao [15] reported a fluorescence method for the determina-

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tion of 0.010–1.20  $\mu\text{g}/\text{mL}$  Co. However, the luminescence method of Co chelate complex nanoparticles has not been reported.

In this work, the luminescence properties of some M(II)–DDTC chelate complex nanoparticles including Co(II), Cu(II), Zn(II), Pb(II), Fe(II), and Cd(II) were considered. The luminescence mechanism of the chelate particle was proposed. A novel and sensitive luminescence method has been proposed for the determination of cobalt in real sample, with a detection limit of 0.0023  $\mu\text{g}/\text{mL}$  Co.

## EXPERIMENTAL

### Apparatus and Reagents

A  $1.00 \times 10^{-4}$  mol/L Co(II), Cd(II), Ni(II), Cu(II), and Pb(II) working solutions,  $2.00 \times 10^{-4}$  mol/L  $\text{FeCl}_3$  working solution,  $5.0 \times 10^{-3}$  mol/L sodium diethyldithiocarbamate (DDTC) solution (containing 6% ethanol) were prepared. A 0.50 mol/L  $\text{NH}_4\text{Cl}$  and 0.5 mol/L  $\text{NH}_3 \cdot \text{H}_2\text{O}$  solutions were used to prepare basic buffer solutions. A 0.2 mol/L NaAc and 0.2 mol/L HAc solutions were used to prepare acid buffer solutions with different pH. A 5.0 mg/L ascorbic acid (VC), 8.0 mol/L nitric acid, 30%  $\text{H}_2\text{O}_2$  were used. All reagents are analytically pure and the water is secondly distilled water.

A model of RF-540 spectrophotofluometer (Shimada, Japan) was applied to record luminescent spectrum. A model of H-600 transmission electron microscope (Electron Co., Japan) was used.

### Procedure

Taken a suitable volume of  $\text{NH}_3\text{--NH}_4\text{Cl}$  buffer solution, DDTC, and a certain volume of Co(II) (or  $\text{Cu}^{2+}$ ,  $\text{Cd}^{2+}$ ,  $\text{Ni}^{2+}$ ) working solution into a 5 mL comparison tubes orderly. Diluted it to 5 mL and mixed well. Transferred suitable amounts of solution into a cell and set it on the spectrophotofluometer. Fixed  $\lambda_{\text{ex}}$ , the fluorescence spectrum was got by scanning emission spectrum with high sensitivity. Fixed emission wavelength at which there is the strongest fluorescence intensity and obtained the excitation spectrum. The fluorescence intensity at the stronger emission wavelength and excitation wavelength was recorded.

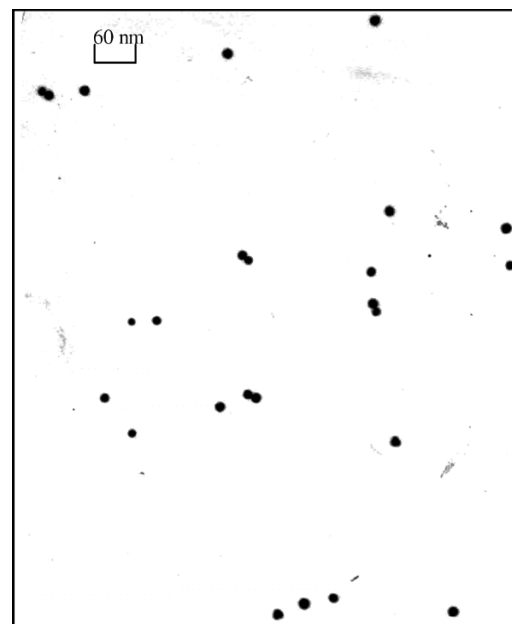
A 0.60 mL pH 4.8 buffer solutions HAc–NaAc buffer solutions, certain volume of Fe(III) working solution, 1.0 mL 5.0 mg/L VC solution, 0.60 mL  $5.0 \times 10^{-3}$  mol/L DDTC solution were orderly added into a 5 mL comparison tube. The following operation is similar to the Co(II).

A 0.60 mL pH 4.4 HAc–NaAc buffer solutions, certain volume of Pb(II) working solution, 0.30 mL  $5.0 \times 10^{-3}$  mol/L DDTC were added into a 5 mL comparison tube successively. The following operation is similar to the Co(II).

## RESULTS AND DISCUSSION

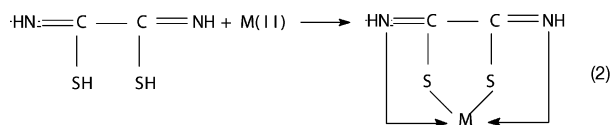
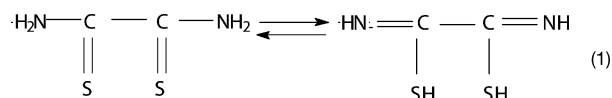
### Formation and Dissociation of Chelate Particles

DDTC contains two N and one S atoms that interact with M(II) and there is the equilibrium equation as follow Eq. (1) [16]. In a suitable pH buffer solutions, sodium diethyldithiocarbamate reacts with some divalence metal ions M(II) to form chelate which has not electric charge. The chelates can aggregate automatically to form chelate particles and yield solid–liquid interface and exhibits fluorescence since there are strong hydrophobic interaction and intermolecular force among chelates. Picture 1 indicates that the particle size of  $(\text{Co}\text{--DDTC})_n$  chelate particles is 20 nm. In organic solvent, however, chelate particles can be dissolved. As is shown in Fig. 1, with the increasing of organic solvent concentration, fluorescence intensity become more and more weak. When the concentration reaches certain level, there is almost not fluorescence. It can be explained that the fluorescence is interface fluorescence of the nanoparticles. With the



**Fig. 1.** Transmission electron microscope of  $(\text{Co}\text{--DDTC})_n$  chelate complex nanoparticles pH 9.5– $5.0 \times 10^{-4}$  mol/L DDTC– $6.0 \times 10^{-6}$  mol/L Co(II).

dissociation of chelate particles, interface disappear and fluorescence quench out,



$$n\text{M} - \text{DDTC} = (\text{M} - \text{DDTC})_n \quad (3)$$

### Excitation Spectrum

Fixed the emission wavelength at 470 nm, the excitation spectrum was obtained by scanning excitation wavelength from 200 to 700 nm. As shown in Fig. 2, there are two peaks at 200 and 470 nm for Co(II)-DDTC particle system. The peak at 200 nm is excitation peak and the other is resonance scattering peak. A 200 nm was chosen as excitation wavelength in the paper. The excitation spectra of other M(II)-DDTC particle systems are similar to the Co(II)-DDTC, but the strength is different. We also selected a 200 nm as their excitation wavelength for the Cd(II), Ni(II), Cu(II), and Pb(II) chelate complex nanoparticle systems.

### Fluorescence Spectrum

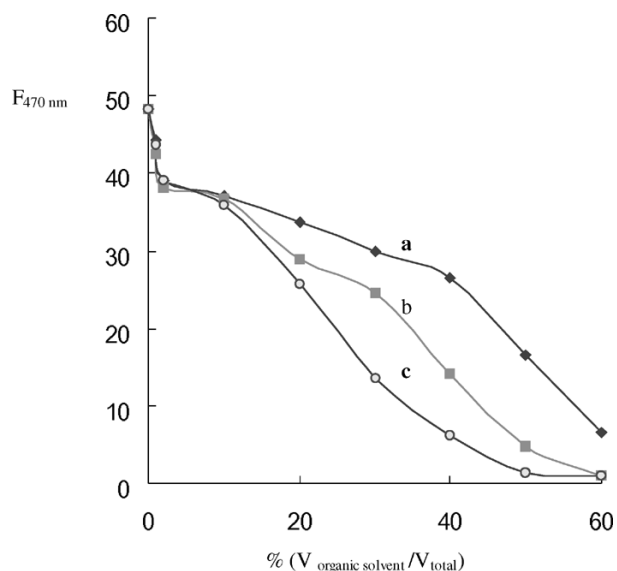
There is fluorescence for the metal ion and DDTC solutions. From Fig. 3, we can see that the Co(II)-DDTC chelate particles system exhibits a max luminescence peak at 470 nm. There are three peaks at 330, 470, and 630 nm for the Cu(II)-DDTC system, three peaks at 420, 470, and 630 nm for the Cd(II)-DDTC system, four peaks at 350, 400, 435, and 470 nm for the Ni(II)-DDTC system, two peaks at 408 and 470 nm for the Cu(II)-DDTC system, two peaks at 415 and 470 nm for the Fe(II)-DDTC system. Among them, Co(II)-DDTC, Pb(II)-DDTC chelate particle systems have the stronger luminescence intensity. As is shown in Fig. 3, the luminescence intensity of the system is very weak under the wavelength of 300 nm. It could be explained that there is strong molecular absorption of DDTC in the system under the wavelength.

### Effect of Buffer Solution

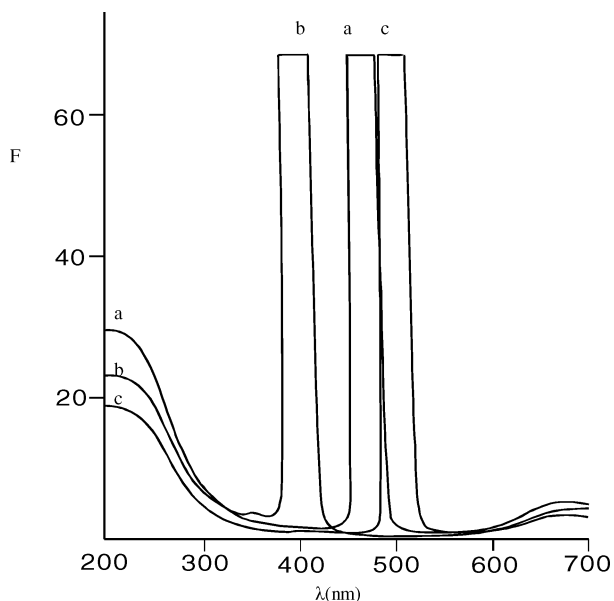
The experimental result shows that the luminescence intensity of chelate particles is more strong and stable when Cu(II), Cd(II), Ni(II), and Co(II) react with DDTC to form chelate particles in pH 9.5, 10.5, 10.0, and 10.5  $\text{NH}_3\text{-NH}_4\text{Cl}$  buffer solution, respectively. The effect of the buffer solution volume indicates that the condition is better when we choose 1.0 mL pH 9.5  $\text{NH}_3\text{-NH}_4\text{Cl}$  buffer solution, 2.0 mL pH 10.5  $\text{NH}_3\text{-NH}_4\text{Cl}$  buffer solution, 1.0 mL pH 10.0  $\text{NH}_3\text{-NH}_4\text{Cl}$  buffer solution, 1.0 mL pH 10.5  $\text{NH}_3\text{-NH}_4\text{Cl}$  buffer solution, respectively. The luminescence intensity of chelate particles is more strong and stable when Pb(II) and Fe(II) react with DDTC in pH 4.4 and 4.8  $\text{HAc-NaAc}$  buffer solution, respectively and the both better volumes are 0.60 mL.

### Effect of DDTC Concentration

The effect of DDTC concentration on the luminescence intensity of all systems was tested. As is shown from Fig. 4, the luminescence intensity of the system gets stronger with DDTC concentration at first. After it reached a value, the luminescence intensity became constant. In order to make the luminescence intensity of the system stronger, and that of the blank system weaker, a  $0.50 \times 10^{-3}$  mol/L DDTC for the Co(II) system,  $0.50 \times 10^{-3}$  mol/L DDTC for the Cu(II) system,  $0.50 \times 10^{-3}$  mol/L DDTC for the



**Fig. 2.** Effect of organic solvent on the  $F_{470 \text{ nm}}$  pH 9.5- $5.0 \times 10^{-4}$  mol/L DDTC- $6.0 \times 10^{-6}$  mol/L Co(II). (a)  $\text{CH}_3\text{OH}$ ; (b)  $\text{CH}_3\text{CH}_2\text{OH}$ ; (c)  $\text{CH}_3\text{COCH}_3$ .

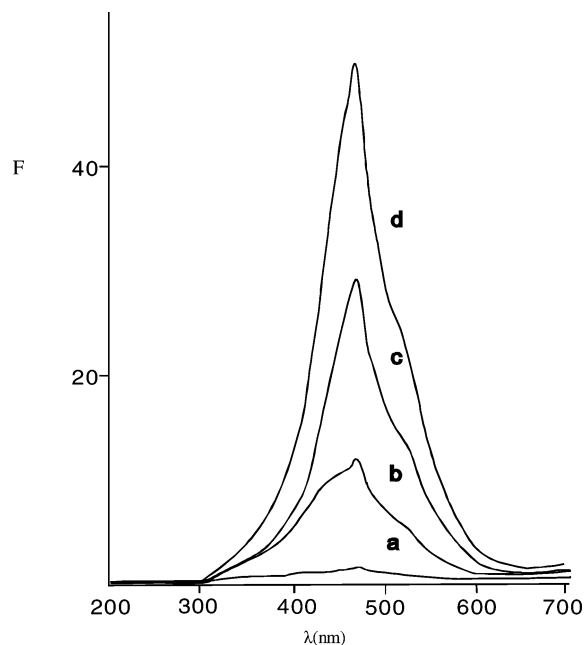


**Fig. 3.** Excited spectra of  $(\text{Co-DDTC})_n$  chelate nanoparticles pH 9.5–5.0  $\times 10^{-4}$  mol/L DDTC– $2.0 \times 10^{-6}$  mol/L Co(II) system. (a)  $\lambda_{\text{ex}} = 470$  nm; (b)  $\lambda_{\text{ex}} = 400$  nm; (c)  $\lambda_{\text{ex}} = 520$  nm.

Cd(II) system,  $0.50 \times 10^{-3}$  mol/L DDTC for the Fe(II) system,  $0.50 \times 10^{-3}$  mol/L DDTC for the Ni system,  $0.30 \times 10^{-3}$  mol/L DDTC for the Pb system,  $0.60 \times 10^{-3}$  mol/L DDTC in Fe system were chosen for use.

### Linear Relationship

Under optimal conditions, different concentration of metal ions were tested and the working curve of different system was drawn according the relationship between metal ion concentration and its corresponding luminescence intensity. As is shown in Table I, there is good linear relationship between metal ion concentration and  $\Delta F$  value. The most sensitive analytical system is the Co system, and was chosen for use.



**Fig. 4.** Luminescence spectra of  $(\text{Co-DDTC})_n$  chelate nanoparticles. (a) pH 9.5–5.0  $\times 10^{-4}$  mol/L DDTC; (b) a– $2.0 \times 10^{-6}$  mol/L Co(II); (c) a– $6.0 \times 10^{-6}$  mol/L Co(II); (d) a– $1 \times 10^{-5}$  mol/L Co(II).

### Effect of Coexistent Substance

Effect of some kinds of ions and substances on the determination of  $0.353 \mu\text{g/mL}$  Co(II) has been tested. When the relative error is in range of  $\pm 5\%$ , allowable value of coexistent substance is as in Table II. Most common ions have no effect on the determination, but  $\text{Fe}^{3+}$ ,  $\text{Zn}^{2+}$ ,  $\text{Cd}^{2+}$ ,  $\text{Mn}^{2+}$ , and  $\text{Pb}^{2+}$  have disturbance. This interfering can be eliminated by addition of 0.004 mol/L EDTA solution.

### Sample Analysis

Took 2.0 mL Vitamin B<sub>12</sub> injections to a 50 mL beaker exactly, let Co(II) be released from Vitamin B<sub>12</sub> by nitrofication process, then transferred it to 25 mL volume flask, and diluted to scale by water. According to

**Table I.** Analytical Features for the M-DDTC Chelate Particle Systems

M(II)	Linear range ( $\mu\text{g/mL}$ )	Regression equation (c, $\mu\text{g/mL}$ )	Relative coefficient	Detection limit ( $\mu\text{g/mL}$ )
$\text{Cu}^{2+}$	0.025–1.52	$\Delta F = 63.2c + 0.09$	0.9982	0.0025
$\text{Cd}^{2+}$	0.044–6.29	$\Delta F = 43.6c - 5.65$	0.9979	0.0036
$\text{Ni}^{2+}$	0.011–1.34	$\Delta F = 80.8c + 0.44$	0.9998	0.0017
$\text{Pb}^{2+}$	0.082–4.96	$\Delta F = 42.3c - 2.65$	0.9988	0.029
$\text{Fe}^{2+}$	0.055–1.11	$\Delta F = 45.6c + 1.19$	0.9959	0.051
$\text{Co}^{2+}$	0.012–1.44	$\Delta F = 169c - 1.44$	0.9990	0.0023

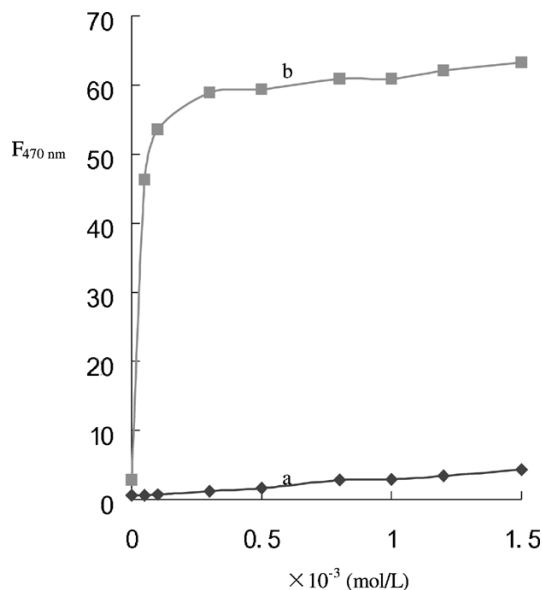
**Table II.** Tolerance of Coexistent Substances (CS) ( $0.353 \mu\text{g/mL Co}$ )

Coexistent substance	Tolerance [CS]/[Co]	Relative error (%)
Ca <sup>2+</sup>	1200	4.0
EDTA	1890	-4.4
Mg <sup>2+</sup>	280	4.3
Al <sup>3+</sup>	15	4.9
CO <sub>2</sub> <sup>3+</sup>	960	-1.8
PO <sub>4</sub> <sup>3+</sup>	180	-4.2
K <sup>+</sup>	1200	-4.1
Br <sup>-</sup>	310	-5.0
Na <sup>+</sup>	920	-5.0
Ac <sup>-</sup>	110	1.3
F <sup>-</sup>	800	-4.3
I <sup>-</sup>	250	-4.3
Fe <sup>3+</sup>	5	4.2
Cd <sup>2+</sup>	7	4.0
Zn <sup>2+</sup>	13	5.0
Mn <sup>2+</sup>	10	4.3
Ba <sup>2+</sup>	100	-3.5
Pb <sup>2+</sup>	8	1.6
VC	500	-4.7
Gly	400	-2.1
Val	80	5.0
Citrate	8500	4.6
CH <sub>3</sub> CHOCH <sub>3</sub>	160	-4.1
CH <sub>3</sub> CH <sub>2</sub> OH	380	-4.8

experimental method, took 1 mL sample solution to detect. The result is as given in Tables III and IV. Recovery is in the range of 99.3–99.7% and the relative standard deviation is in the range of 2.30–2.95%.

### Relationship Between Interface Formation of Chelate Particle and Fluorescence Spectrum

Under experimental metal concentration condition, since all systems are colorless, it is reasonable to neglect the effect of absorption on fluorescence in the visible light region. Figs. 1, 3, and 5 indicate that there is relationship



**Fig. 5.** Effect of DDTC concentration on the luminescence intensity of the Co(II) system. (a) pH 9.5– $5.0 \times 10^{-4}$  mol/L DDTC; (b) a– $6.0 \times 10^{-6}$  mol/L Co(II).

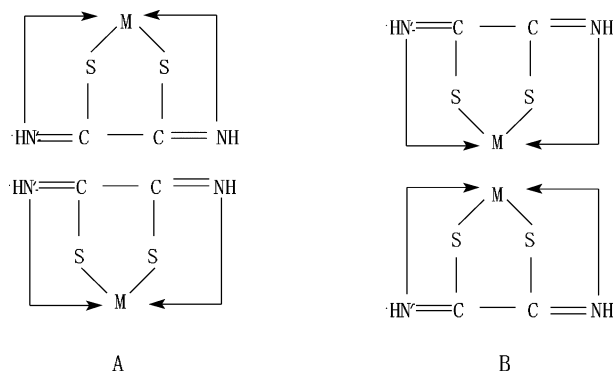
between the creation of fluorescence and solid–liquid interface. The different metal systems have different fluorescence spectra, which show that the surface structure and its composition of the chelate particle are different. The difference lies in the metal ions by ingredient analysis of  $(M\text{-DDTC})_n$  particle. We have known that the metal ion may be situated at the surface or in the body. When metal ion lies in the body of particles, the DDTC may be at the particle surface and their fluorescence shape should be similar. However, the results show that this is not the case. When metal ions are situated at particle surface as in Fig. 6A, different systems will produce different fluorescence spectra when it is excited by light since the

**Table III.** Analytical Result of Co in Sample

Sample (V <sub>B12</sub> )	Found ( $\mu\text{g/mL}$ )	Mean found ( $\mu\text{g/mL}$ )	RSD (%)	Content (%)
1#	1.74, 1.77, 1.74, 1.78, 1.64	1.73	2.30	4.34
2#	1.67, 1.65, 1.73, 1.65, 1.73	1.67	2.95	4.18
3#	1.68, 1.66, 1.74, 1.75, 1.74	1.71	2.34	4.29

**Table IV.** The Recovery

Sample	Addition ( $\mu\text{g}$ )	Recovery ( $\mu\text{g}$ )	Average magnitude ( $\mu\text{g}$ )	Recovery (%)
1#	0.353	0.352, 0.342, 0.343, 0.362, 0.362	0.353	99.7
2#	0.353	0.338, 0.357, 0.367, 0.340, 0.353	0.351	99.3
3#	0.353	0.340, 0.358, 0.365, 0.340, 0.356	0.352	100.3



**Fig. 6.** The surface composition of (M-DDTC)<sub>n</sub> particles. (A) The M atoms on the surface; (B) The DDTC molecules on the surface.

metal ions are different and their surface electrons are different. It is in accordance with the experimental result.

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