

# Supramolecular recognition of functional magnesium tetraphenylporphyrin with pyrrolidine for SO<sub>2</sub> capture

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**Abstract**—Supramolecular recognition of functional magnesium tetraphenylporphyrin (MgTPP) with pyrrolidine for SO<sub>2</sub> capture was investigated in CH<sub>2</sub>Cl<sub>2</sub> by steady-state fluorescence and UV-vis absorption spectroscopic techniques. The UV-vis spectra showed that the interaction of MgTPP with pyrrolidine resulted in red shift of 2 nm for MgTPP Soret absorption band. Once introduced, SO<sub>2</sub> competes with MgTPP for pyrrolidine, which eventually leads to the release of MgTPP. The fluorescence spectra suggested that MgTPP interacted with pyrrolidine to form 1 : 1 molecular adducts, and showed that the binding of MgTPP with pyrrolidine with the association constants (*K*<sub>assoc</sub>) of (0.86 to 1.19) is not only exothermic but enthalpy-driven with  $\Delta H = -15.805 \text{ kJ mol}^{-1}$ ,  $\Delta S = -52.727 \text{ J mol}^{-1} \text{ K}^{-1}$ , and  $\Delta G = -214.444 \text{ J mol}^{-1}$  at *T* = 296.15 K.

**Key words:** Magnesium Tetraphenyl Porphyrin (MgTPP), Pyrrolidine, Spectroscopy, Thermodynamic

## INTRODUCTION

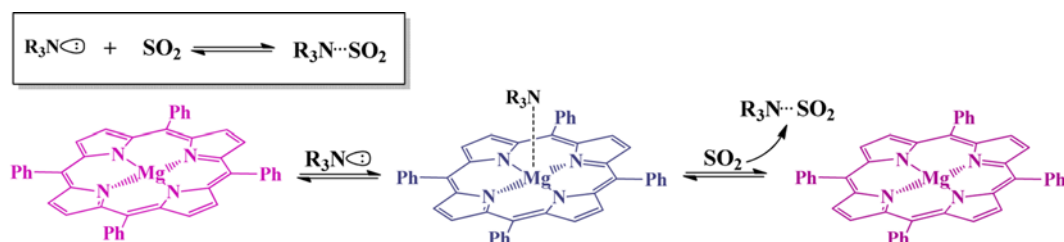
The emission of Sulfur dioxide (SO<sub>2</sub>) in flue gases from the burning of fossil fuels has drawn worldwide attention because it is a significant source of atmospheric pollution that threatens the environment and human health [1,2]. It has to be removed (selectively) from these gas streams for operational, economical or environmental reasons, and the chemical absorption called amine scrubbing using amine-based solvents is presently both the preferred option and probably the only commercially mature technology [3-5]. In this technology, SO<sub>2</sub> reacts with an amine absorption liquid *via* an exothermic, reversible reaction in a gas/liquid contactor. In the next step, the SO<sub>2</sub> is removed from the solvent in a regenerator at low pressure and/or high temperature resulting in significant vaporization and solvent loss, which leads to a significant decrease in plant performance and a concurrent increase in operating costs. Recently, attention has focused on replacing amine absorption liquid and controlling the lean amine temperature to reduce amine loss, but the price is loss of the acid gas loading capacity and the solvent regenerability [6,7]. In previous work, Rudkevich [8] used Zn-tetraphenylporphyrin (ZnTPP) as a detector for colorimetric detection of SO<sub>2</sub>. Once introduced,

SO<sub>2</sub> competes with ZnTPP for various amines. Zhang [9] investigated the photochemical reaction of MgTPP with SO<sub>2</sub>, and Dehghani [10] reported that meso-tetraphenylporphyrins interacted with SO<sub>2</sub> to form 2 : 1 (donor : acceptor) molecular complexes. These works presented more reference information for this research.

We mainly focused on providing a new supramolecular approach for potentially reducing amine solvent loss. At first, pyrrolidine forms the coordination complexes with MgTPP before the absorption step. Once introduced, SO<sub>2</sub> competes with MgTPP for pyrrolidine, which eventually leads to the release of MgTPP (Fig. 1 and 2). After the desorption step, the released amines form adducts again with the regenerated MgTPP, which could reduce solvent loss and processing costs. The MgTPP amine-fixed agent could be recycled in the amine scrubbing, and the approach is simple and reliable. The UV-vis spectra showed that the interaction of MgTPP with pyrrolidine occurred more efficiently in CH<sub>2</sub>Cl<sub>2</sub> to form 1 : 1 molecular adducts at *T* = (291.15 to 306.15) K.

## EXPERIMENTAL

Fluorescence spectra were acquired using an F-4500 fluorescence



**Fig. 1.** An amine-fixed agent for SO<sub>2</sub> capture. MgTPP is initially coordinated to amines and then displaced by SO<sub>2</sub>.

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Fig. 2. Photograph of MgTPP (left), MgTPP+pyrrolidine (middle), and MgTPP+pyrrolidine+SO<sub>2</sub> (right).

spectrophotometer. UV-vis spectra were recorded on a Varian CARY 1E UV-vis spectrometer. All solid reagents were weighed using a Sartorius BS224S electric balance.

According to previous work [11-13], MgTPP was prepared using *meso*-tetraphenylporphyrin (H<sub>2</sub>TPP, >98%) purchased from Acros Organics (New Jersey, USA). All other reagents and solvents were reagent grade and used as received.

To discuss the interaction of MgTPP with pyrrolidine, we fixed the concentration of MgTPP at 19.51 μmol/L and designed the concentrations of pyrrolidine at different concentration gradient. All the experiments were carried at 291.15 K, 296.15 K, 301.15 K, and 306.15 K for 20 min using a constant temperature water SPY-III bath apparatus (accuracy: ±0.01 K).

## RESULTS AND DISCUSSION

When pyrrolidine was added to the solution of MgTPP in CH<sub>2</sub>Cl<sub>2</sub>, the color change of MgTPP solution from purple to blue (Fig. 2) could be due to the interaction of MgTPP with pyrrolidine. When SO<sub>2</sub> gas was bubbled through the solution, the color changed from blue to purple because the SO<sub>2</sub> gas may compete with MgTPP for pyrrolidine and cause the release of MgTPP. To confirm the the above reactions, UV-vis and fluorescence spectral technologies were used.

In a typical experiment, pyrrolidine was added to the MgTPP solution, and the absorbance changes were recorded (Fig. 3). The absorption spectra showed a typical Soret band at 424 nm, which was assigned to the Soret band of MgTPP arising from the  $a_{1u}(\pi) \rightarrow e_g^*(\pi)$  transition [14]. Similar Soret absorption peaks (B-bands) were observed for most porphyrinic compounds [15,16]. As expected, the solution changed from purple to blue, and a bathochromic shift

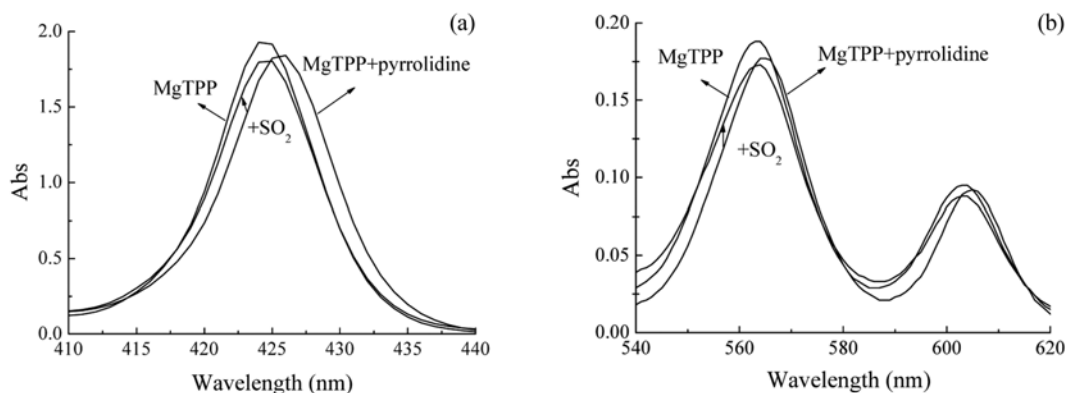


Fig. 3. Absorbance spectral changes ([MgTPP]:  $1.95 \times 10^{-5}$  mol/L, [pyrrolidine]: 0.94 mol/L, [SO<sub>2</sub>]: 5,000 ppm), (a) absorbance spectral change of Soret band; (b) absorbance spectral change of Q band.

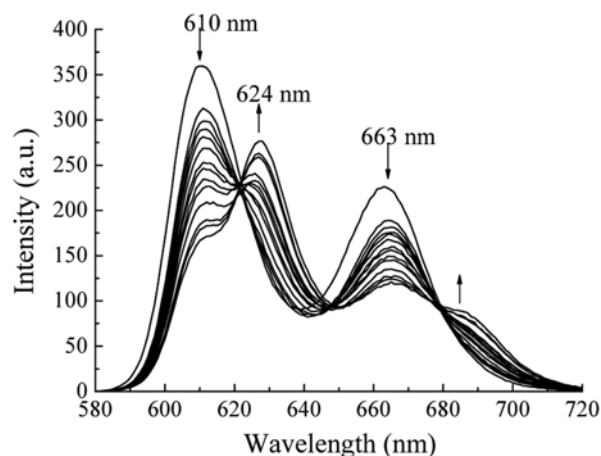


Fig. 4. Fluorescence emission spectral changes of MgTPP with increasing pyrrolidine concentrations at T=291.15 K.

of 2 nm was observed for the Soret band and Q band, suggesting the interaction of MgTPP with pyrrolidine to form the corresponding MgTPP-pyrrolidine adducts. When SO<sub>2</sub> gas was bubbled through the solution, the color changed from blue to purple, and the absorbance spectra returned to the position for free MgTPP (Fig. 3), confirming that the SO<sub>2</sub> gas competes with MgTPP for pyrrolidine, which eventually leads to MgTPP-pyrrolidine adducts dissociating and the adducts of the SO<sub>2</sub> with pyrrolidine being formed. The regenerated MgTPP could have formed adducts again with the released pyrrolidine when SO<sub>2</sub> was removed. MgTPP thus served as a recycled amine-fixed agent in amine scrubbing for SO<sub>2</sub> capture to reducing amine solvent losses.

Upon excitation at 550 nm, stable state fluorescence spectra with selective excitation of MgTPP were recorded and the maximum emission positions of Q\* at 610 nm and 663 nm were observed.

MgTPP is a potential amine-fixed agent, so the reaction mechanism of MgTPP with pyrrolidine was investigated by the fluorescence titrimetric method at the four temperatures of 291.15, 296.15, 301.15, and 306.15 K. Meanwhile, the concentration of MgTPP was fixed at 19.51 μmol/L and the concentrations of pyrrolidine were designed in the range of (0.000 to 0.938) mol/L for emission spectral measurements. The emission spectra of MgTPP were significantly quenched with stepwise addition of pyrrolidine at the four

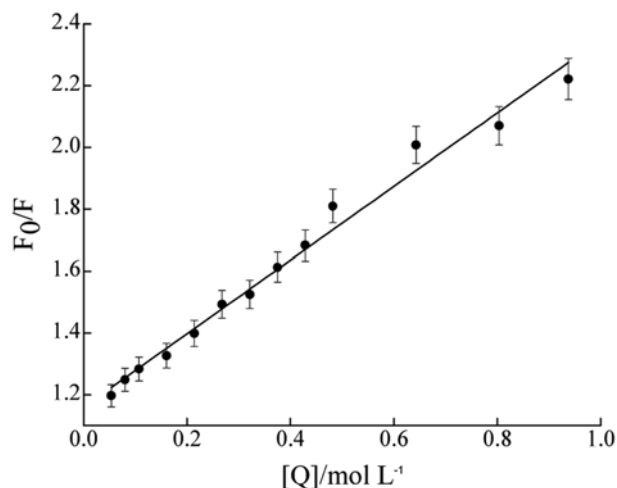


Fig. 5. Linear dependencies of  $F_0/F$  on  $[Q]$  ( $T=291.15$  K,  $K_{assoc}=1.190\pm0.044$ ,  $R^2=0.985$ ).

temperatures (Fig. 4 and supporting information 1). This could be attributed to electron transfer in the interaction of MgTPP with electron donor pyrrolidine molecules, because the pyrrolidine nitrogen with lone pair electrons is coordinated to the metal center of MgTPP [17].

The fluorescence intensities of MgTPP decrease with increasing concentration of pyrrolidine, which suggests that the binding of MgTPP with pyrrolidine is nonfluorescent. This phenomenon also proves that fluorescence quenching is static.

According to previous methods [18,19], the binding constants of MgTPP with pyrrolidine were calculated. In static quenching, the following formula can be obtained:

$$F_0/F = 1 + K [Q]^n \quad (1)$$

$$[M]_0/[M] = F_0/F \quad (2)$$

where  $[Q]$  denotes the concentration of free quencher of pyrrolidine,  $[M_0]$  denotes the total concentration of MgTPP, and  $[M]$  denotes the concentration of free MgTPP. A linear plot of  $F_0/F$  to  $[Q]$  indicates that one MgTPP molecule can bind one pyrrolidine molecule (see Fig. 5 and supporting information 2) to form stable 1 : 1 molecular adducts in CH<sub>2</sub>Cl<sub>2</sub>.

The fluorescence spectra of MgTPP-pyrrolidine binding were performed at  $T=(291.15$  to  $306.15)$  K. Thermodynamic parameters were estimated by the analysis of  $\ln K$  versus  $1/T$  plot (van't Hoff plot) obtained by the experimental data at the above temperatures. The gradient of this straight line of  $\ln K$  versus  $1/T$  is equal to  $-\Delta H/R$ , which indicates the values of  $\Delta H$ ,  $\Delta G$  and  $\Delta S$  can be calculated from the following relationships:

$$\Delta G = -RT \ln K = \Delta H - T\Delta S \quad (3)$$

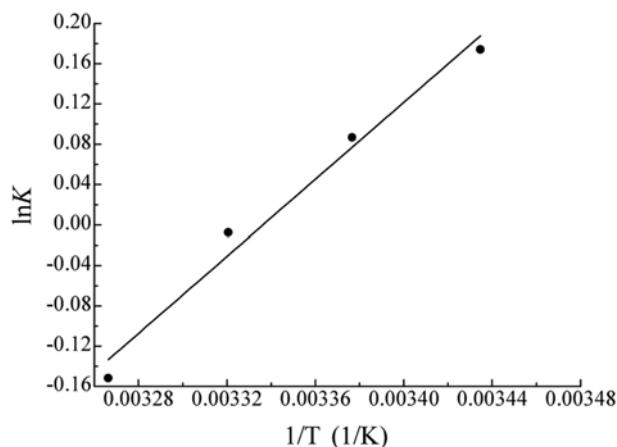


Fig. 6. van't Hoff plot of MgTPP-pyrrolidine (the regression equation:  $Y=-6.364+1907.469X$ ,  $R^2=0.981$ ).

By linear analysis, the van't Hoff plot for the binding of MgTPP to pyrrolidine is depicted in Fig. 6. The values of the thermodynamic parameters are shown in Table 1.

From Fig. 5 and supporting information 2, MgTPP can interact with pyrrolidine to form 1 : 1 molecular adducts at  $T=(291.15$  to  $306.15)$  K. From Table 1, the  $K_{assoc}$  value of the interaction is 1.091 at  $T=296.15$  K, and In Rudkevich's work, the  $K_{assoc}$  value of SO<sub>2</sub> with pyrrolidine is  $2.0 \times 10^4$ , so SO<sub>2</sub> gas can compete with MgTPP for pyrrolidine easily. The thermodynamic data showed that interaction of MgTPP with pyrrolidine is not only exothermic but enthalpy-driven coordination reactions at temperatures of (291.15, 296.15, 301.15, and 306.15) K, and the interaction may spontaneously occur at the lower temperature.

## CONCLUSIONS

The UV-vis and fluorescence spectral results suggested MgTPP serving as a regenerated amine-fixed agent is now possible in amine scrubbing for SO<sub>2</sub> capture to reduce amine solvent losses utilizing its noncovalent chemistry with pyrrolidine. First, the MgTPP-pyrrolidine adducts were formed. Once introduced, SO<sub>2</sub> competes with MgTPP for pyrrolidine, which eventually leads to the release of MgTPP. After desorption, the released pyrrolidine forms adducts again with the regenerated MgTPP. In addition, we investigated reaction mechanisms and calculated the thermodynamic data for the MgTPP binding to pyrrolidine. The results suggested that MgTPP interacted with pyrrolidine to form 1 : 1 coordination complexes. The  $K_{assoc}$  indicated the binding ability between MgTPP and pyrrolidine is smaller than it is between SO<sub>2</sub> and pyrrolidine, proving that SO<sub>2</sub> can compete with MgTPP for pyrrolidine easily. All the experi-

Table 1. Thermodynamic parameters for MgTPP-pyrrolidine obtained from fluorescence measurements

T(K)	$K_{assoc}$	$\Delta G$ (J/mol)	$\Delta H$ (kJ/mol)	$\Delta S$ (J/mol K)
291.15	$1.190\pm0.044$	-421.075	$-15.805\pm0.734$	$-52.727\pm5.261$
296.15	$1.091\pm0.017$	-214.444	$-15.805\pm0.734$	$-52.727\pm5.261$
301.15	$0.993\pm0.021$	17.588	$-15.805\pm0.734$	$-52.727\pm5.261$
306.15	$0.860\pm0.031$	383.894	$-15.805\pm0.734$	$-52.727\pm5.261$

ments were carried out in the  $\text{CH}_2\text{Cl}_2$ , but the processes of amine scrubbing in the aqueous solution. We are working to modify the system using water soluble metalloporphyrins.

### ACKNOWLEDGEMENTS

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### SUPPORTING INFORMATION

Additional information as noted in the text. This information is available via the Internet at <http://www.springer.com/chemistry/journal/11814>.

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## Supporting Information

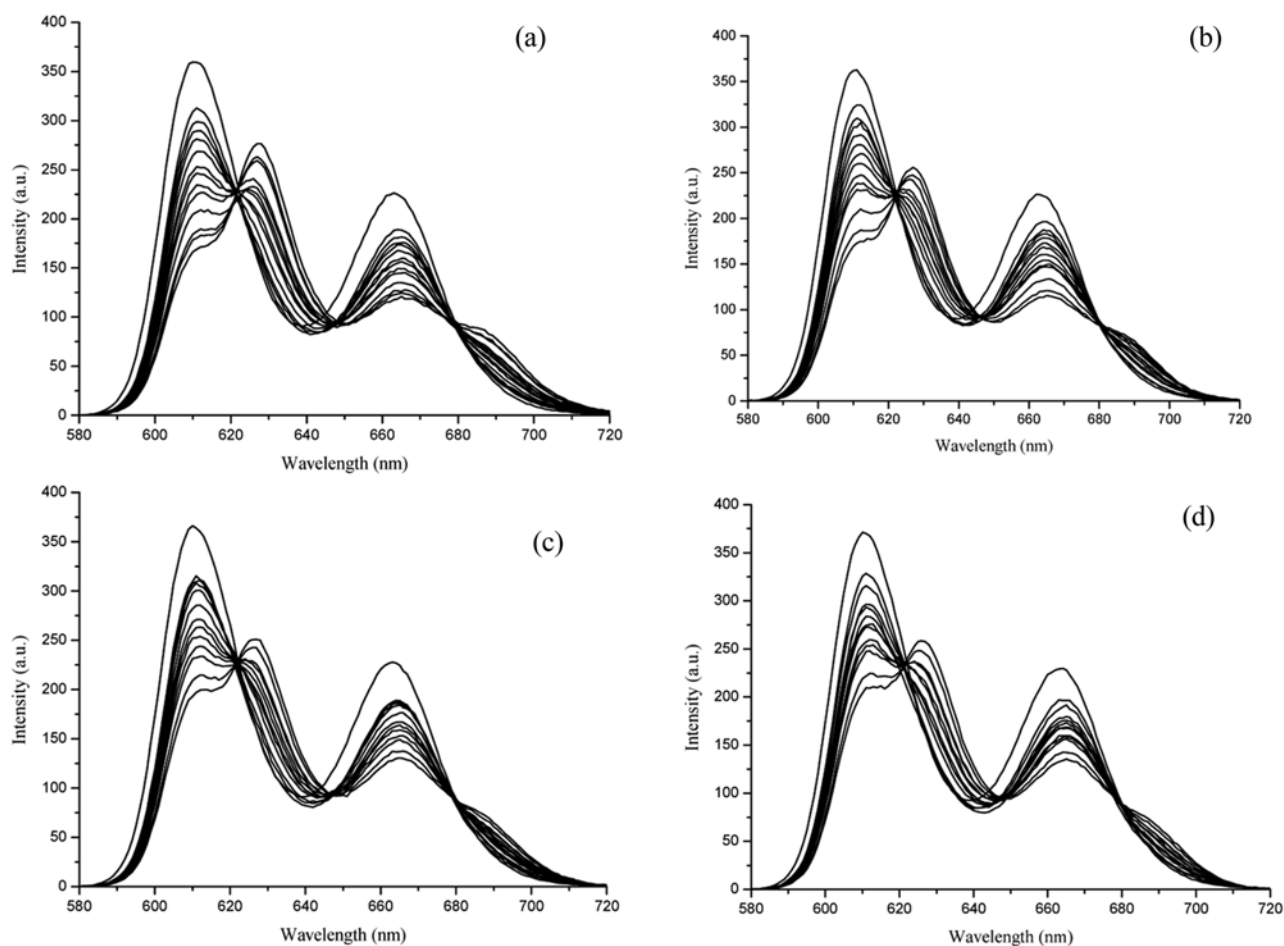
### Supramolecular recognition of functional magnesium tetraphenylporphyrin with pyrrolidine for SO<sub>2</sub> capture

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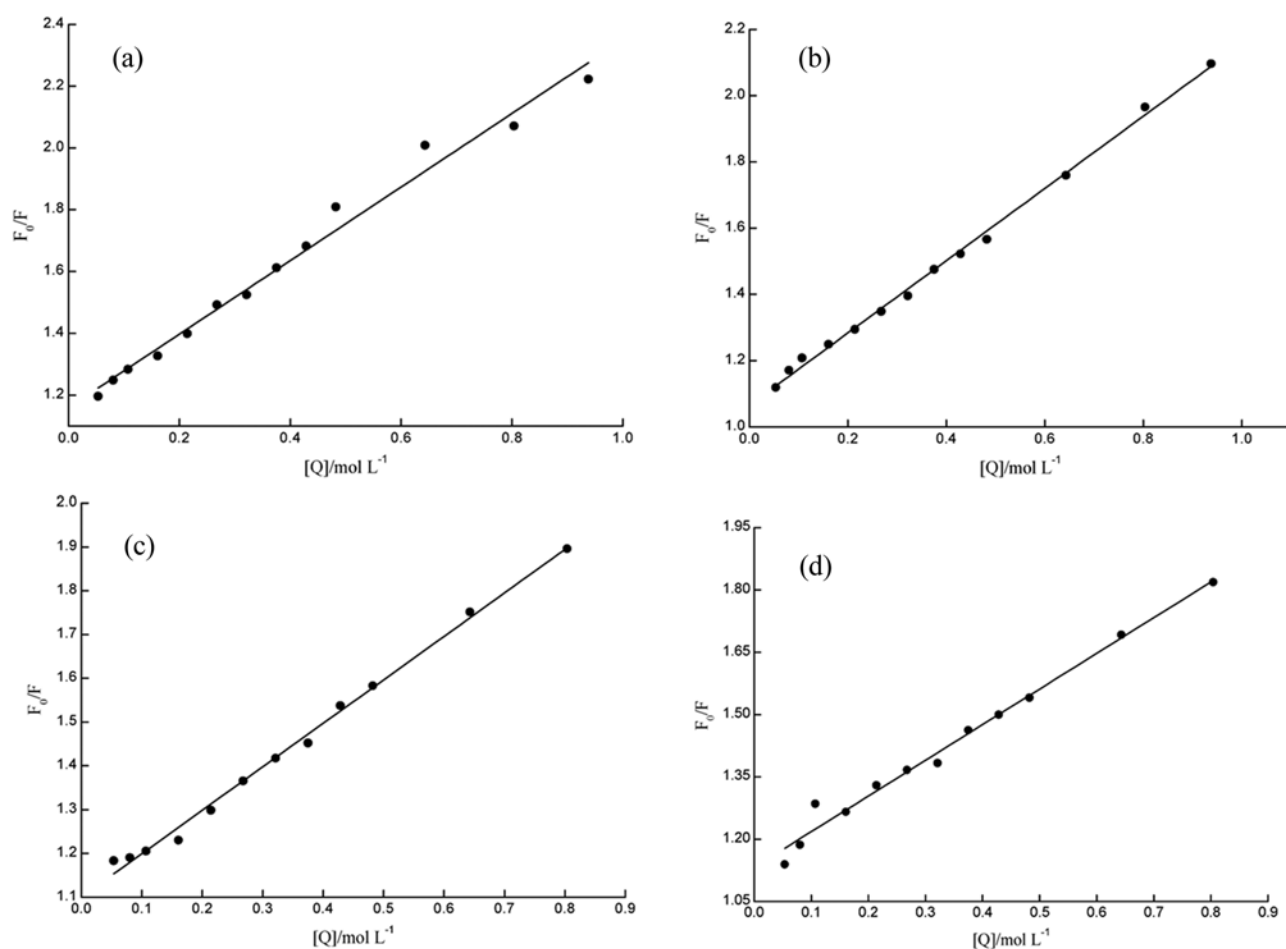
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#### 1. Fluorescence emission ( $\lambda_{\text{ex}}=550$ nm) spectral changes of MgTPP with increasing pyrrolidine concentration



**Fig. 1.** Fluorescence emission ( $\lambda_{\text{ex}}=550$  nm) spectral changes of MgTPP with increasing pyrrolidine concentrations ((a) T=291.15 K; (b) T=296.15 K; (c) T=301.15 K; (d) T=306.15 K).

## 2. Linear dependencies of $F_0/F$ on $[Q]$ at various temperature



**Fig. 2. Linear dependencies of  $F_0/F$  on  $[Q]$  at 291.15 K ((a)  $R^2=0.985$ ,  $K_{\text{assoc}}=1.190\pm0.044$ ), 296.15 K ((b)  $R^2=0.997$ ,  $K_{\text{assoc}}=1.091\pm0.017$ ), 301.15 K ((c)  $R^2=0.995$ ,  $K_{\text{assoc}}=0.993\pm0.021$ ), 306.15 K ((d)  $R^2=0.986$ ,  $K_{\text{assoc}}=0.860\pm0.031$ ).**