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Journal of Photochemistry and Photobiology A: Chemistry 104 (1997) 159–163

Journal of
PHOTOCHEMISTRY
AND
PHOTOBIOLOGY
A:CHEMISTRY

Investigation on the behavior of porphyrins at the surface of the colloidal silver particles

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Received 22 July 1996; accepted 7 October 1996

Abstract

The behavior of meso-tetra(4'-hydroxyphenyl) porphyrin (T(4-HP)P) and meso-5-(4'-hydroxyphenyl)-10,15,20-triphenylporphyrin (HPTPP) in a Ag sol system was investigated by UV-vis spectra, surface enhanced Raman scattering (SERS), fluorescence spectra and the measurements of luminescence lifetime. There was an obvious SERS effect when the porphyrins were adsorbed on the surface of colloidal silver particles. Meanwhile, a new peak was observed at about 460 nm in the absorption spectra. The evidence suggests that T(4-HP)P and HPTPP chemisorbed on the particle surface of Ag sol to produce complex like metalloporphyrins. The apparent association constants for the two porphyrins and silver sol were 3.16×10^4 M^{-1}, 2.79×10^4 M^{-1}, respectively. It was found that silver sol was a fluorescence quencher by which above 90% of the fluorescence emission of T(4-HP)P and HPTPP could be quenched. The mechanism for fluoresence quenching was proposed to be a static process based upon the measurements of fluorescence lifetimes. © 1997 Elsevier Science S.A.

Keywords: Surface enhanced Raman spectroscopy; Static fluorescence quenching; Porphyrins; Silver sol

1. Introduction

Colloidal silver has been proved to be a very useful substrate in surface enhanced Raman scattering spectra (SERS) experiments. A great amount of SERS experiments have been made in silver sol systems since the phenomenon was found by Fleischmann et al. [1] in 1974. Naturally, most attention was paid to the expoundation of the SERS mechanism and the relation between SERS spectra and structural chemistry, relatively less attention was paid to other effects of silver particles on the adsorbates, such as fluorescence quenching, which in some case is very important for the SERS measurement.

Porphyrins continue to be actively studied because of their importance in biochemistry, photochemistry, photosensitization and catalysis [2–7]. Therefore considerable interest has been shown in the structural characterization of porphyrins. The SERS technique was often used to carry out this aim [8–10]. Meanwhile, other changes in the properties of porphyrins caused by substrates, such as silver sol were often overlooked. The detail study on the fluorescence quenching of porphyrins by colloidal silver has never been reported.

In the present work, the SERS effect of meso-tetra(4'-hydroxyphenyl) porphyrin (T(4-HP)P) and meso-5-(4'-hydroxyphenyl)-10,15,20-triphenylporphyrin (HPTPP) adsorbed on colloidal silver particles was investigated and the fluorescence quenching of these porphyrins by silver sol was reported for the first time.

2. Experimental section

Meso-tetra(4'-hydroxyphenyl)porphyrin (T(4-HP)P) and meso-5-(4'-hydroxyphenyl)-10,15,20-triphenylporphyrin (HPTPP) were synthesized in our laboratory. The crude products were separated on chromatographic silica gel plates and purified by recrystallization. The purified products were identified by UV-vis, NMR and IR. The solutions of T(4-HP)P and HPTPP were prepared in ethanol 50% (v/v) at a concentration of 2.5×10^{-4} mol l^{-1}.

Silver sol was prepared by the reduction of $AgNO_3$ with $NaBH_4$, as described previously [10]. The silver sol was bright yellow with an average particle size of 10 nm determined by transmission electron microscopy (TEM) and had a plasmon absorption peak at about 390 nm [11]. The concentration of the prepared Ag sol was 5×10^{-4} mol l^{-1} and the pH value was around 8.5–9. All the reagents used in the experiments were analytical grade, and distilled deionized water was used.

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PII S1010-6030(96)04521-2

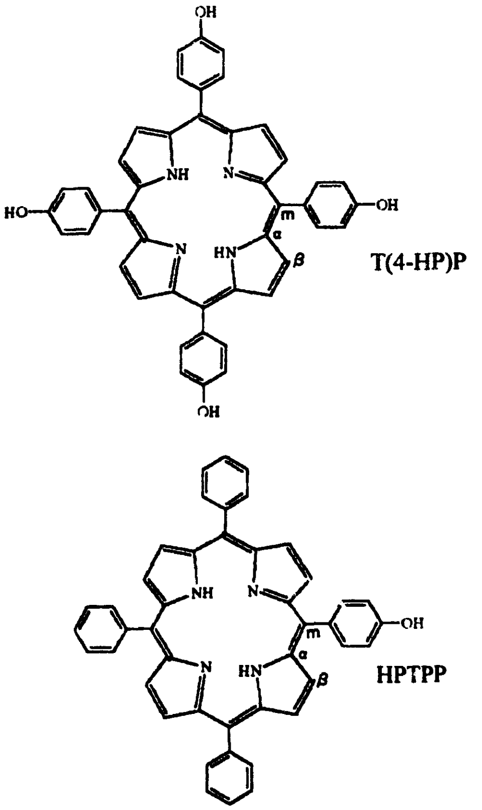

Fig. 1. The structures of T(4-HP)P and HPTPP.

The absorption spectra were measured on a Hewlett-Packard 8451A diode array UV-vis spectrophotometer. Raman spectra were recorded on a RTI-30 Raman spectrometer made in the Beijing second optical instrument plant. The line at 488.0 nm from an Ar^- laser was used as an excitation source with a power 100 mW. The scanning range was 200–1700 cm^{-1} and the scattered light was collected at an angle of 90°. A typical experiment for the measurement of Raman signal was repeated 5 times, and the average signal was processed with a computer. The time constant used for all measurements of Raman spectra was unity.

Emission spectra were measured by a Perkin–Elmer Ls-05 fluorescence spectrophotometer with a computer for data collection and reduction. The fluorescence lifetime measurements were carried on a multiplexed, time-resolved, single-photon-counting spectrofluorometer (HORIBA, model NAES-1100). Excitation was performed using the pulsed light of a hydrogen lamp. All experiments were carried out at room temperature. The structures of T(4-HP)P and HPTPP are shown in Fig. 1.

3. Results and discussion

3.1. UV-Vis spectra

As shown in Figs. 2 and 3, the absorption of the pure Ag sol had a single extinction maxium at 396 nm (dotted line); The UV-Vis spectra of the pure T(4-HP)P and HPTPP were similar (dashed line). Like most of porphyrin compounds, they both had a prominent absorption band near 420 nm called the Soret band or B band, and four small bands in the range of 510–650 nm called Q bands [11,12]. The similarity in the absorption spectra of the porphyrins is due to the structure of the porphyrin ring, which can be explained by the model of four orbitals [12,13]. Addition of T(4-HP)P and HPTPP (7.5×10^{-6} mol l^{-1}) into Ag sols of 7.5×10^{-5} mol l^{-1} respectively, produces obvious changes in the UV-Vis spectra (solid line in Figs. 2 and 3). The plasmon absorption of Ag sol at 390 nm shifted to a longer wavelength by about 10 nm and decreases in intensity. The intensity of absorption at longer wavelengths, however, was enhanced. In addition, a new peak appeared at about 460 nm.

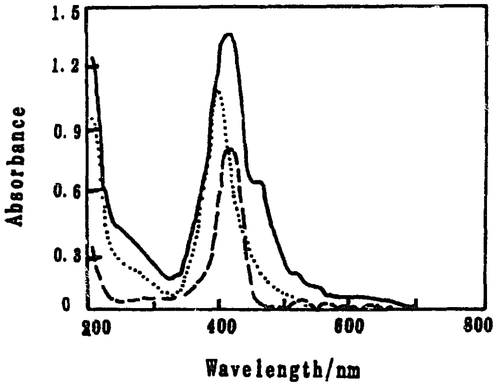

Fig. 2. Absorption spectra of T(4-HP)P, Ag sol and T(4-HP)P in colloidal silver with 3% (v/v) ethanol. pH = 7.5, [T(4-HP)P] = 7.5×10^{-6} M, [Ag] = 7.5×10^{-5} M. ······Ag, - - - T(4-HP)P, ———— Ag + T(4-HP)P.

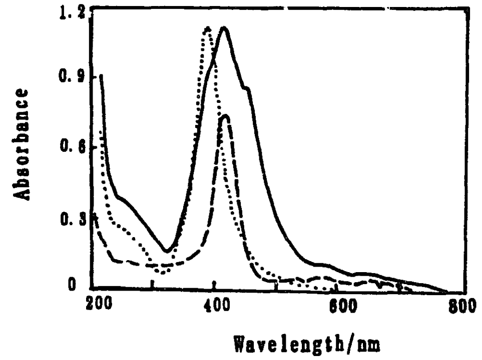

Fig. 3. Absorption spectra of HPTPP, Ag sol and HPTPP in colloidal silver with 3% (v/v) ethanol. pH = 7.5, [HPTPP] = 7.5×10^{-6} M, [Ag] = 7.5×10^{-5} M. ······Ag, - - - HPTPP, ———— Ag + HPTPP.

The above changes indicated that T(4-HP)P and HPTPP were adsorbed on the surface of the colloidal silver particles and formed new compounds at the interface by charge transfer between the adsorbates and silver in the ground state. This was also verified by the following SERS studies.

3.2. Raman scattering spectra

The Raman scattering spectra of T(4-HP)P and HPTPP in the solid state and in solutions with concentrations from 7.5×10^{-6} mol l^{-1} to 2.5×10^{-4} mol l^{-1} were measured.

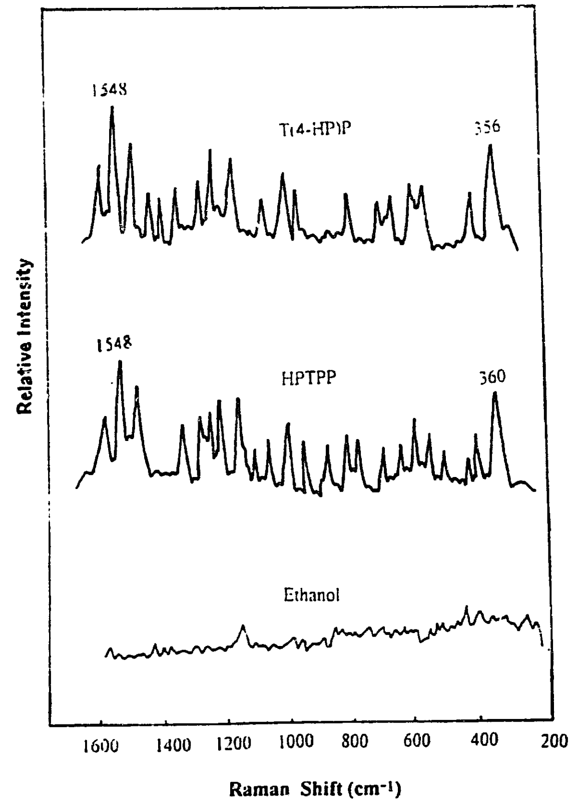

Fig. 4. The SERS spectra of T(4-HP)P and HPTPP on the particles of Ag sol. [T(4-)P] = [HPTPP] = 7.5 × 10^{-6} mol l^{-1} (with 3% (v/v) ethanol). [Ag] = 7.5 × 10^{-5} mol l^{-1}, pH = 7.5.

The results showed that the Raman signals under these conditions were too weak to be measurable. Nevertheless, clear Raman spectra could be obtained (as shown in Fig. 4) when Ag sol was added into the porphyrins solutions. This indicated that there was an obvious SERS effect when the porphyrins adsorbed on the surface of the silver particles. Fig. 4 shows the SERS spectra of T(4-HP)P and HPTPP at concentrations of 7.5 × 10^{-6} mol l^{-1} in colloidal silver (7.5 × 10^{-5} mol l^{-1}). In the experiments, the ethanol concentration was kept constant so that the interferences of ethanol could be reduced. The Raman shifts, relative intensity and assignments are listed in Table 1. From Fig. 4 and Table 1, it is easy to see that there are several strong scattering bands at 1586, 1548, 1492(1490), 1240(1238) and 360(356) cm^{-1}. These bands were assigned to υ_{ring}, $\upsilon_{\text{C-N}}$, $\upsilon_{\text{C-C}}$, δ_{ring} and $\delta_{\text{C-H}}$ vibrations (υ, δ represent strenching and in-plane deformation vibration, respectively) [9–14]. That means the phenyl and porphyrin rings of the adsorbed T(4-HP)P and HPTPP were near to the surface of the silver particles. In addition, the vibration band in the range of 200–300 cm^{-1}, assigned to the vibrations of Ag-N or Ag-O was not enhanced. It was believed that T(4-HP)P and HPTPP adsorbed with the porphyrin ring lies parallel to the surface of the silver particles. Bands at 1346, 425, 355 cm^{-1} are characteristic of metalloporphyrins [8–10]. Similar peaks appeared at 1354, 428(420), and 360(358) cm^{-1} in our experiments. Therefore, T(4-HP)P and HPTPP might undergo Ag incorporation during the adsorption on the silver surface. This is in agreement with the results of the absorption spectra. The formation of metalloporphyrins caused the plasmon absorption of Ag sol to redshift, and resulted in a new peak appearing at about 460 nm. The incorporation into the porphyrin ring changed the surface electronic state of the silver particles, resulting in the shift of the plasmon absorption of the silver sol.

Table 1
Ranan shifts, relative intensity and assignment for the vibration of T(4-HP)P and HPTPP

HPTPP cm^{-1}	*RI*	T(4-HP)P cm^{-1}	*RI*	Assignment
1590	0.64	1588	0.67	phenyl ring
1548	1.0	1548	1.0	$\upsilon(C_\beta\text{-}C_\beta)+\delta(C_\beta\text{-H})$
1492	0.81	1490	0.78	$\upsilon(C_\alpha\text{-}C_\beta)+\delta(C_\beta\text{-H})$
		1434	0.46	
		1416	0.43	
1354	0.56	1354	0.47	$\upsilon(C_\alpha\text{-N})+\delta(C_\beta\text{-H})$
1284	0.63	1280	0.54	$\upsilon(C_\alpha\text{-N})$
1264	0.63			
1240	0.71	1238	0.7	
1172	0.71	1172	0.67	
1126	0.4			
1082	0.47	1078	0.39	$\delta(C_\beta\text{-H})$
1018	0.56	1006	0.57	$\upsilon(C_\alpha\text{-}C_m)$
968	0.45	966	0.45	
892	0.41			phenyl ring
826	0.46	812	0.41	
808	0.43			
720	0.40	716	0.37	
664	0.40	674	0.37	
620	0.56	618	0.48	prophyrin deformation
576	0.46	576	0.43	
526	0.36			
452	0.30			
428	0.46	420	0.42	porphyrin deformation
360	0.84	356	0.71	

Note: The relative intensity (*RI*) is normalized. υ represents strenching vibration, δ represents in-plane deformation vibration.

In examining the assignments of Raman bands, it is obvious that the enhancement is mainly for the υ and δ rather than the γ vibration (γ represents out-plane deformation). As we know, υ and δ vibrations do not change the conjugation of the system, which is favorable for the charge transfer between the adsorbate and substrate. This indicates there being chemical enhancement caused by a short range charge transfer for the SERS effect of T(4-HP)P and HPTPP on the Ag surface.

In comparing the SERS spectrum of T(4-HP)P with that of HPTPP (Fig. 4), it is found that their Raman shifts are very similar. This can be explained by their similar structure. However, examining the vibration bands under 1000 cm^{-1}, shows the SERS spectra of HPTPP is more complicated than that of T(4-HP)P. These bands were assigned to the δ_{ring} vibration. There are two different substituting groups (phenyl and hydroxyphenyl rings) in the HPTPP molecule, resulting in a more complicated SERS spectrum than that of T(4-HP)P.

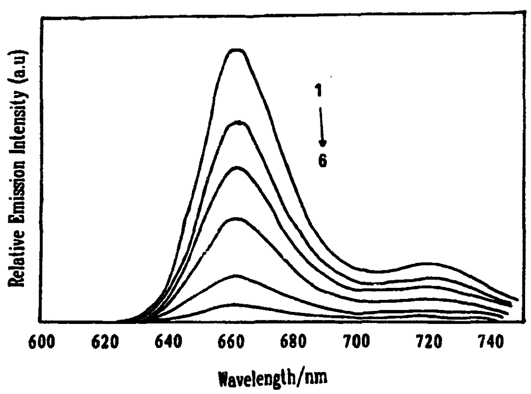

Fig. 5. Fluorescence emission spectra of 7.5×10^{-6} mol l^{-1} T(4-HP)P in 50 v/v% ethanol at various concentrations of Ag sol. (1) 0 mol l^{-1}; (2) 1.25×10^{-5} mol l^{-1}; (3) 2.5×10^{-5} mol l^{-1} (4) 5×10^{-5} mol l^{-1}; (5) 1×10^{-4} mol l^{-1}; (6) 1.5×10^{-4} mol l^{-1}. Excitation wavelength 395 nm.

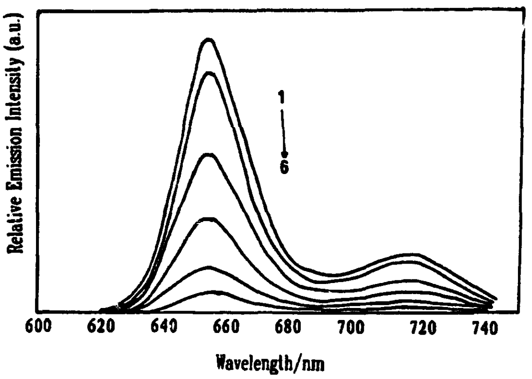

Fig. 6. Fluorescence emission spectra of 7.5×10^{-6} mol l^{-1} HPTPP in 50% v/v ethanol at various concentrations of Ag sol. (1) 0 mol l^{-1}; (2) 1.25×10^{-5} mol l^{-1}; (3) 2.5×10^{-5} mol l^{-1} (4) 5×10^{-5} mol l^{-1}; (5) 1×10^{-4} mol l^{-1}; (6) 1.5×10^{-4} mol l^{-1}. Excitation wavelength 395 nm.

3.3. Emission spectra

The fluorescence emission spectra of both T(4-HP)P and HPTPP exhibited a maximum around 660 nm (Figs. 5 and 6). The maximum of the excitation spectra of T(4-HP)P and HPTPP in 50% (v/v) ethanol matched well with their absorption maximum (dashed line shown in Figs. 2 and 3). As shown in Figs. 5 and 6, the fluorescence intensity obviously decreased with the successive addition of Ag sol to the solution of T(4-HP)P or HPTPP. More than 90% of the emission of T(4-HP)P or HPTPP (7.5×10^{-6} mol l^{-1}) can be quenched by 1.5×10^{-4} mol l^{-1} colloidal silver. The marked fluorescence quenching was perhaps due to the quenching of the excited singlet state of the porphyrins. The above quenching behavior is similar to the reported fluorescence quenching of dyes by semiconductor colloids [15–17]. From the UV-spectra and the results of SERS, it is obvious that the porphyrins are chemically adsorbed on the surface of the colloidal silver particles. The process can be expressed in the following equation:

$$\text{Porphyrin} + \text{Ag} = [\text{Porphyrin}\cdots\cdots\text{Ag}] \qquad (1)$$

There is an equilibrium between the adsorbed and unadsorbed porphyrin molecules with an apparent association constant K_a.

The observed fluorescence intensity (I) of the porphyrins in Ag sol is dependent on the fluorescence intensity of the unadsorbed (I_0) and the adsorbed (I') molecules of the porphyrins, as shown in the following equation:

$$I = (1-\alpha)I_0 - I' \qquad (2)$$

which can be transformed to:

$$I_0 - I = (I_0 - I') \qquad (3)$$

where α is the fraction of porphyrins associated with Ag sol. If the concentration of Ag sol is relatively high, the following formula could be obtained:

$$\alpha = K_a[\text{Ag}]/(1+K_a[\text{Ag}]) \qquad (4)$$

Substituting Eq. (4) into the Eq. (3) yields:

$$\frac{1}{I_0-I} = \frac{1}{I_0-I'} + \frac{1}{K_a(I_0-I')[\text{Ag}]} \qquad (5)$$

If the fluorescence quenching is entirely due to the association between the porphyrins and the colloidal silver, then by Eq. (5), there should be a linear dependence of $1/(I_0-I)$ on the reciprocal concentration of Ag sol. Fig. 7 shows such a dependence for both T(4-HP)P and HPTPP. From the slope and intercept, the apparent constants for the association of T(4-HP)P and HPTPP with silver sol can be obtained. They are 3.16×10^4 M^{-1} and 2.79×10^4 M^{-1}, respectively. Obviously, $\alpha_{T(4\text{-HP})P} > \alpha_{HPTPP}$. This can be explained by their molecular structure. There are four hydroxyphenyl groups on

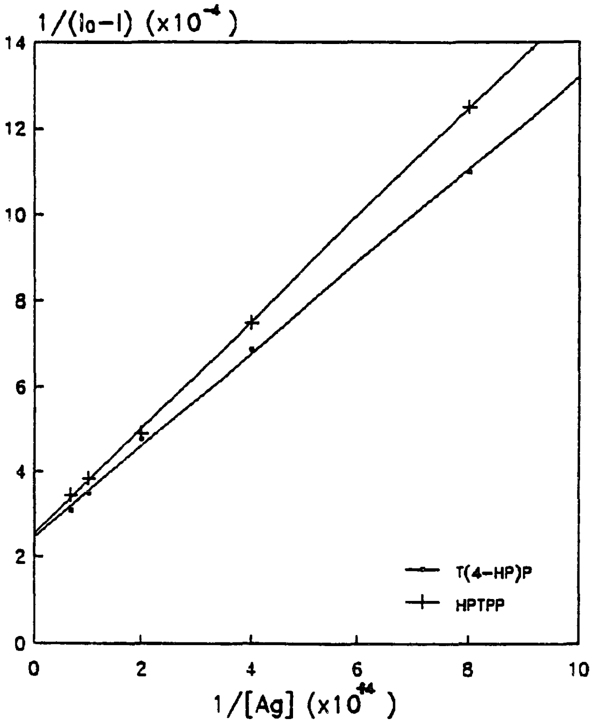

Fig. 7. Dependence of $1/(I_0-I)$ on the reciprocal concentration of Ag sol in 50 v/v% ethanol.

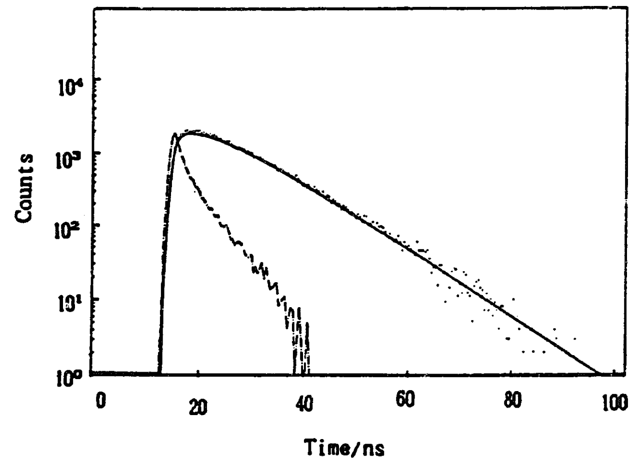

Fig. 8. Fluorescence decay and normalized instrument response curves for T(4-HP)P in 50% (v/v) ethanol at 298 K. Excitation was at 395 nm and the emission was recorded at 659.5 nm. Solid line is a calculated decay curve fitted to a single-exponential decay law with the following parameters: $A = 0.176$, $\tau = 9.83$ ns and reduced $\chi^2 = 1.16$.

Table 2

Former exponential factor (A), fluorescence life-time (τ/ns) and reduced χ^2 for the luminescence decay of T(4-HP)P and HPTPP at various concentrations of silver sol

[Ag]/mol/l	T(4-HP)P			HPTPP		
	A	τ	χ^2	A	τ	χ^2
0	0.176	9.83	1.16	0.185	10.8	1.24
1.25×10^{-5}	0.205	9.74	1.34	0.163	10.9	0.984
2.5×10^{-5}	0.186	9.88	0.934	0.183	10.9	1.12
5.0×10^{-5}	0.164	9.86	1.08	0.185	11.0	1.01
1.0×10^{-4}	0.193	9.88	1.02	0.174	10.9	1.09

the T(4-HP)P molecule and the electron density of hydroxyphenyl is richer than that of phenyl resulting in easier transfer of electrons between silver particles and T(4-HP)P compared to HPTPP.

3.4. Quenching mechanism analysis

It is well known that the emission life-time can be used to probe the mechanism of the fluorescence quenching process. It is determined to be static quenching if the lifetime doesn't change with the addition of a quencher [18]. Fig. 8 shows the luminescence decay of T(4-HP)P in 50% ethanol, which exhibited a single exponential decay with a lifetime of 9.86 ns. In the presence of Ag sol, the luminescence of T(4-HP)P showed a similar decay, and the lifetime was nearly constant, ~9.86 ns. The same observations as noted above were made for HPTPP. That is, T(4-HP)P and HPTPP, with or without the Ag sol, all showed the monoexponential kinetic fit of the emission decay equation: $F(t) = A\exp(-t/\tau)$. Some parameters are listed in Table 2.

The lifetimes of T(4-HP)P and HPTPP were almost unchanged even if the fluorescence was quenched by Ag sol, therefore, the quenching is a kind of static quenching. This indicates that T(4-HP)P and HPTPP in the ground state associated with silver particles results in fluorescence quenching, which is in good agreement with the results observed in the SERS and the absorption experiments. Interface complexes, i.e. metalloporphyrins, are formed between T(4-HP)P (or HPTPP) and the silver particles.

4. Conclusions

T(4-HP)P and HPTPP chemisorbed on the surface of colloidal silver particles showed new peaks at about 460 nm in absorption spectra. Meanwhile, obvious SERS effects could be determined. The fluorescence of T(4-HP)P and HPTPP could be efficiently quenched by Ag sol, and the quenching process was static quenching. These results showed that an interface-complex formed between T(4-HP)P (or HPTPP) and the silver particles in the solution of T(4-HP)P or HPTPP and the silver sol. The degree of association between Ag sol and T(4-HP)P was greater than with HPTPP.

Acknowledgements

The authors are grateful to the National Natural Science Foundation of China and Eastman Kodak Company for their financial support of this work.

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