## Emission properties of [Au(CN)<sub>2</sub>]<sup>-</sup> oligomers with cationic surfactants

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 $[Au (CN)_2]^-$  forms emissive oligomers due to aurollophilic interaction. The wavelength of the emission peak of the oligomers depends on the degree of oligomerization in aqueous solutions: 330 nm for the dimer, 390 nm for the trimer, and 430 nm for the tetramer [1]. Recently, we found that the emission quantum yields are considerably increased by adding tetraethylammonium cations to the solutions. [2]. In this study, we investigated the emission properties of aqueous solutions of [Au (CN)<sub>2</sub>]<sup>-</sup> and cationic surfactants with a long alkyl chain (TTA<sup>+</sup>, HTA<sup>+</sup>, and STA<sup>+</sup>, Fig.1).

Aqueous solutions of  $[Au (CN)_2]^-$  (1.0 mM) containing cationic surfactants (1.0 mM) showed emission peaks at 470 – 480 nm (Fig.2). Since the peak wavelength is longer than 430 nm, the 470-480-nm emission is originated by an excited pentamer and/or larger oligomers generated in solutions. In addition, the aqueous solutions containing STA<sup>+</sup> exhibited emissions with significantly longer lifetimes and higher emission quantum yields compared with those containing TTA<sup>+</sup> and HTA<sup>+</sup>(Table 1). The emission quantum yield of 1.0 mM [Au (CN)<sub>2</sub>]<sup>-</sup>

aqueous solutions containing 1.0 mM STA<sup>+</sup> is 0.56 (Table 1), though [Au (CN)<sub>2</sub>]<sup>-</sup> solutions containing 1.0 mM tetraethylammonium cation show little or no emission. In aqueous solutions of cationic surfactants such as STA<sup>+</sup>, molecular aggregates are formed by hydrophobic interaction between the cationic surfactants. A high-density positive charge of the aggregates would markedly stabilize excitedstate oligomers of [Au (CN)<sub>2</sub>]<sup>-</sup> and thereby increase the lifetime and emission quantum yields.

Table1 Peak wavelength ( $\lambda_{ex}$ =310 nm), emission lifetime( $\tau_{ave.}$ ) ( $\lambda_{ex}$ =337 nm) and quantum yields ( $\Phi_{em}$ ) for aqueous solutions of [Au(CN)<sub>2</sub>]<sup>-</sup> (1.0 mM) containing cationic surfactants(1.0 mM)

Cationic Surfactants	$\lambda_{em}$ /nm	<i>r <sub>ave.</sub></i> ∕ns	$\phi_{\rm em}$	
TTA(1.0 mM)	470	210	0.20	
HTA(1.0 mM)	470	213	0.22	
STA(1.0 mM)	480	810	0.56	



Figure1. Cationic surfactants



Figure 2. Emission spectra of  $[Au(CN)_2]^-$ (1.0 mM) and cationic surfactants(1.0 mM)aqueous solutions ( $\lambda_{ex} = 310$  nm)

[1] M. Iwamura et al., Phys. Chem. Chem. Phys., 2016, 18, 5103.

[2] R. Wakabayashi et al., Inorg. Chem., 2016, 55, 7739-7746.