

# Up-conversion of Photon Energy in Colloidal Clay Systems

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## ***Abstract***

The up-conversion (UC) of photon energy was attempted for the system of a colloidal clay dispersion through the mechanism of triplet-triplet annihilation. Tris(1,10-phenanthroline)ruthenium(II) ( $[\text{Ru}(\text{phen})_3]^{2+}$ ) and 9, 10-diphenylanthracene (DPA) were used as a donor and an acceptor, respectively. A used clay mineral was synthetic saponite. A medium was 1:1:0.1 (v/v) methanol/dichloromethane/water.  $\Delta$ - $[\text{Ru}(\text{phen})_3]^{2+}$  ( $4.9 \times 10^{-5}$  M) was adsorbed by SAP ( $3.8 \times 10^{-4}$  M) to 26 % CEC. The dispersion was irradiated by a laser light (0.5 mW) at 450 nm in the presence of DPA ( $4.2 \times 10^{-3}$  M). An emission with the peak around 430 nm was observed under air. It implied the Ru(II) complex adsorbed by a colloidal clay acted as a donor to achieve UC. Quantum yield of UC was estimated to be  $0.009 \pm 0.003$ . The effect of stereoselectivity was investigated when a chiral donor/acceptor pair was employed.

## ***Keywords***

Up-conversion; Synthetic saponite; Ruthenium(II) complex; 9,10-Diphenylanthracene; Stereoselectivity

## 1. Introduction

The up-conversion of photon energy is the process that an incident light is converted to an emission at shorter wavelength. The processes are investigated extensively with a purpose of achieving the conversion of solar light to shorter wavelength, the chemical reactions driven by visible light and the *in situ* sensing of biological samples (Yanai and Kimizuka, 2017; Joarder et al., 2018; Liu et al., 2018; Schmidt et al., 2014; Sasaki et al., 2017).

One approach for up-conversion is the sensitized triplet–triplet annihilation (denoted as TTA), in which two acceptor molecules having been excited to triplet states collide to be disproportionated to the generation of one molecule at a higher singlet level (Han et al., 2017; Li et al., 2021; Lu et al., 2017; Yanai and Kimizuka, 2017; Zhou, et al., 2020). Compared to the related approach of absorbing two photons simultaneously, sensitized TTA-based technologies do not necessarily require extremely high light intensities (Duan et al., 2013; El Roz and Castellano, 2017; Kerzig and Wenger, 2018; Singh-Rachford et al., 2008; Wu et al., 2011). They are much more promising for solar energy harvesting.

Recently a number of works have been reported to perform the up-conversion process by use of various macromolecules as a host fixing either a donor or an acceptor or both. The used hosts are organic polymers, gels and inorganic colloids (Kageshima et al., 2021; Kashino et al., 2021; Lee et al., 2022; Yang et al., 2021). Among the attempts, there is one paper reporting the use of a natural clay mineral (or montmorillonite) used as a host (Kishimoto, et al., 2020). The present work uses a synthetic saponite as a macromolecular host for the up-conversion. Comparing with montmorillonite, a synthetic

saponite includes no heavy metal ion, eliminating their quenching effects. The present attempt was motivated by our works demonstrating the unique role of clay minerals in photochemical reactions (Suzuki et al., 2009; Yamagishi et al., 1996a; Yamagishi and Sato, 2012; Yoshida et al., 2020; Yoshida et al., 2021). As a two-dimensional adsorbent, for example, a layered clay mineral is characterized by the following properties: (i) the surface density of an adsorbed molecule is high when it is ion-exchanged with a photo-reactive cation and (ii) the surface arrangement of such cations exhibits two-dimensional regularity. Due to these properties, photochemical reactions occurring on a clay surface attain the high efficiency of energy conversion, energy transfer and molecular recognition. It is demonstrated that the harvesting of photon energy is achieved at high efficiency when two kinds of emitting metal complexes are adsorbed on a clay surface (Sato et al., 2014; Tamura et al., 2015). This is due to the rapid energy transfer among adsorbed molecules. Some metal complexes such as cyclometalated Ir(III) complexes increase their emission efficiency when they are adsorbed by a clay mineral (Takimoto et al., 2018). Quenching by oxygen or solvent molecules is inhibited by the presence of exfoliated clay layers.

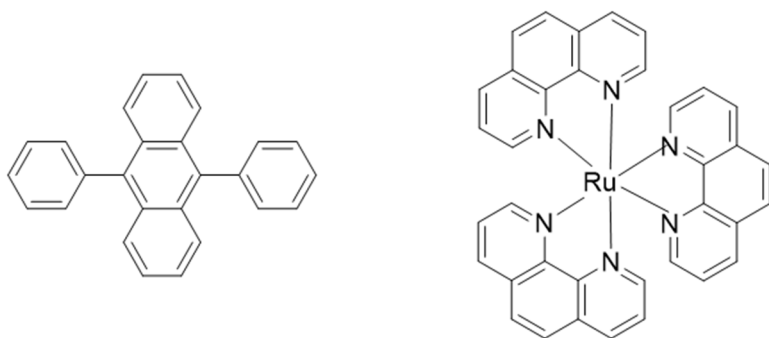
The above backgrounds motivated us to use a clay mineral as a medium for up-conversion. Using a colloidal dispersion of synthetic saponite, a laser light at 445 or 450 nm was up-converted to an emission at 430 nm by using tris(1,10-phenanthroline)ruthenium(II) as a donor and 1, 10-diphenylanthracene as an acceptor. Moreover, the use of a clay mineral was found to increase UC efficiency under the low concentration of an acceptor. Purposes of the present work are following: (i) to achieve UC under air atmosphere; (ii) to introduce molecular recognition for UC to be utilized for molecular sensing.

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## 89 2. Experimental

90 **2.1. Materials:** Racemic tris(1,10-phenanthroline)ruthenium chloride (denoted as  
91  $[\text{Ru}(\text{phen})_3]\text{Cl}_2$ ) was purchased from Tokyo Kasei Industries, Japan ([Chart 1, right](#)).  $\Delta$ -  
92  $[\text{Ru}(\text{phen})_3](\text{ClO}_4)_2$  and  $\Lambda$ - $[\text{Ru}(\text{phen})_3](\text{ClO}_4)_2$  were obtained as described previously  
93 ([Yamagishi et al., 1996b](#)). 9, 10-Diphenylanthracene (DPA) was purchased from Tokyo  
94 Kasei Industries, Japan ([Chart 1, left](#)). Synthetic saponite (SAP) was purchased Kunimine  
95 Industries (Japan). SAP was dissolved in an acid or alkali, and inductively coupled plasma  
96 optical emission spectrometry (ICP-OES) (SPS3520UV-DD, Hitachi High-  
97 Technologies) was then used to determine the composition formula of the smectites from  
98 the results of composition analysis for estimation of the absolute value of negative charge  
99 per unit. The composition formula was determined to be  
100  $\text{Na}_{0.45}(\text{Mg}_{3.11})(\text{Si}_{3.53}\text{Al}_{0.40})\text{O}_{10}(\text{OH})_2$ , and the measured cation exchange capacity (CEC)  
101 was 65 cmol(+)/kg. The synthesis and identification of a chiral acceptor (denoted as SS-  
102 DPA-BINOL) was described in [Supporting Information \(Fig. S4\)](#).

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105 **Chart 1.** Molecular structures of DPA (left) and  $[\text{Ru}(\text{phen})_3]^{2+}$  (phen = 1,10-  
106 phenanthroline) (right).

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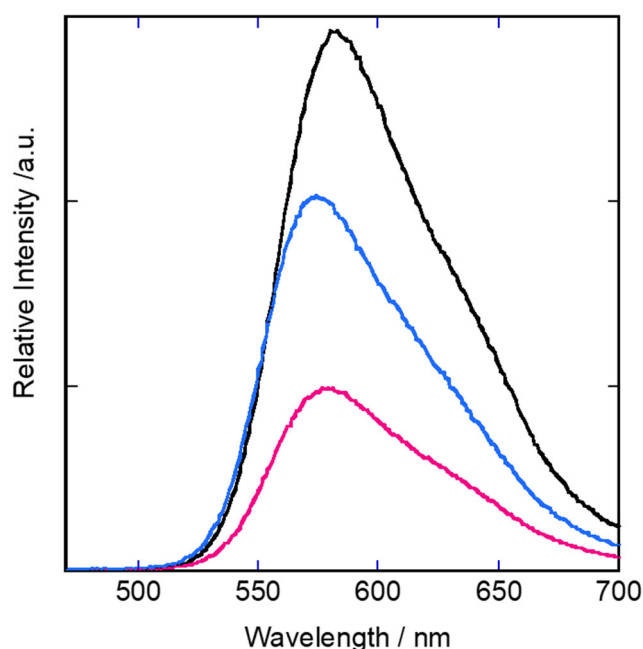
108 **2.2 Instruments:** UV-vis spectra were measured with a U-3810 spectrometer (Hitachi,  
109 Japan). Electronic circular dichroism spectra were measured a polarimeter J-720 (JASCO,  
110 Japan). Emission spectra were recorded with a RF-5300 fluorometer (Shimazu, Japan).  
111 Two systems were employed for the experiments of up-conversion. For recording the  
112 emission spectra from a sample containing a donor and an acceptor, the UC system (LSP-  
113 1000, Unisoku, Japan) was used. Excitation light at 445 nm was incident continuously  
114 from a CW laser at the emission power of 0.5 ~ 78 mW. 200  $\mu$ L of a sample solution was  
115 mounted in a glass tube of 4 mm in diameter. The signal was accumulated by averaging  
116 36 scans. For taking a photograph, 2 mL of a sample solution was mounted in a four-wall  
117 quartz cell. The excitation light at 450 nm was incident from a continuous laser, GPD  
118 Laser diode module (Power Technology, USA) at the emission power of 0.5 mW.  
119 Emission spectra were recorded by a high-resolution spectrometer BIM-6001 (BroLight  
120 Technology, China). The concentration of oxygen dissolved in a sample was measured  
121 with an optical oxygen meter FSO2-C1(Pyroscience, Germany). The oxygen sensor tip  
122 was placed at the bottom of a sample solution.

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### 124 **3. Results and Discussion**

125 **3.1. Quenching of emission from  $\Delta$ -[Ru(phen)<sub>3</sub>]<sup>2+</sup> by DPA:** TTA involves the process  
126 of energy transfer from an excited donor to an acceptor. The efficiency of the process was  
127 studied by quenching the emission from a donor by an acceptor. As a donor and an  
128 acceptor,  $\Delta$ -[Ru(phen)<sub>3</sub>](ClO<sub>4</sub>)<sub>2</sub> and DPA were used, respectively. The reason of using

the enantiomer (or  $\Delta$ -[Ru(phen)<sub>3</sub>]<sup>2+</sup>) instead of the racemic mixture is described later (Section 3.4). A solvent was a 1:1:0.1 (v/v) mixture of methanol, dichloromethane and water. A medium was a 1:1:0.1 (v/v) mixture of methanol, dichloromethane and water. The medium was selected from the viewpoints that [Ru(phen)<sub>3</sub>]<sup>2+</sup> ions and DPA were soluble and that SAP was well dispersed before adding [Ru(phen)<sub>3</sub>]<sup>2+</sup> ions. The excitation of  $\Delta$ -[Ru(phen)<sub>3</sub>]<sup>2+</sup> was performed by irradiating its solution sample by a light at 450 nm. Under nitrogen atmosphere, excited  $\Delta$ -[Ru(phen)<sub>3</sub>]<sup>2+</sup> emitted a light with the peak at 570 nm as shown in Fig. 1 (curve a). The intensity of the emission lowered by replacing nitrogen with air (curve b). Under air, oxygen molecules quenched excited  $\Delta$ -[Ru(phen)<sub>3</sub>]<sup>2+</sup>. On adding SAP, the intensity of emission recovered partially (curve c). This was because the exfoliated layers of SAP acted as a barrier against the attacking of oxygen molecules.



**Fig. 1.** Emission spectra of  $\Delta$ -[Ru(phen)<sub>3</sub>](ClO<sub>4</sub>)<sub>2</sub> ( $1.9 \times 10^{-5}$  M): (a) under nitrogen atmosphere (black curve); (b) under air (red curve); (c) under air in the presence of SAP ( $3.8 \times 10^{-4}$  M in CEC) (blue curve). An excitation wavelength was 450 nm. A medium was 1:1:0.1 (V/V) of dichloromethane/methanol/water.

The emission intensity decreased on adding DPA, indicating the occurrence of energy transfer from excited  $\Delta$ -[Ru(phen)<sub>3</sub>]<sup>2+</sup> to DPA. The results are analyzed in terms of the Stern-Volmer plots as below:

$$I_0/I = 1 + K_{SV}[\text{DPA}] \quad (1)$$

Here  $I_0$  and  $I$  are the intensity of the emission at 570 nm in the absence and presence of DPA.  $K_{SV}$  is the Stern-Volmer constant. In the absence of O<sub>2</sub>,  $K_{SV}$  is expressed by:

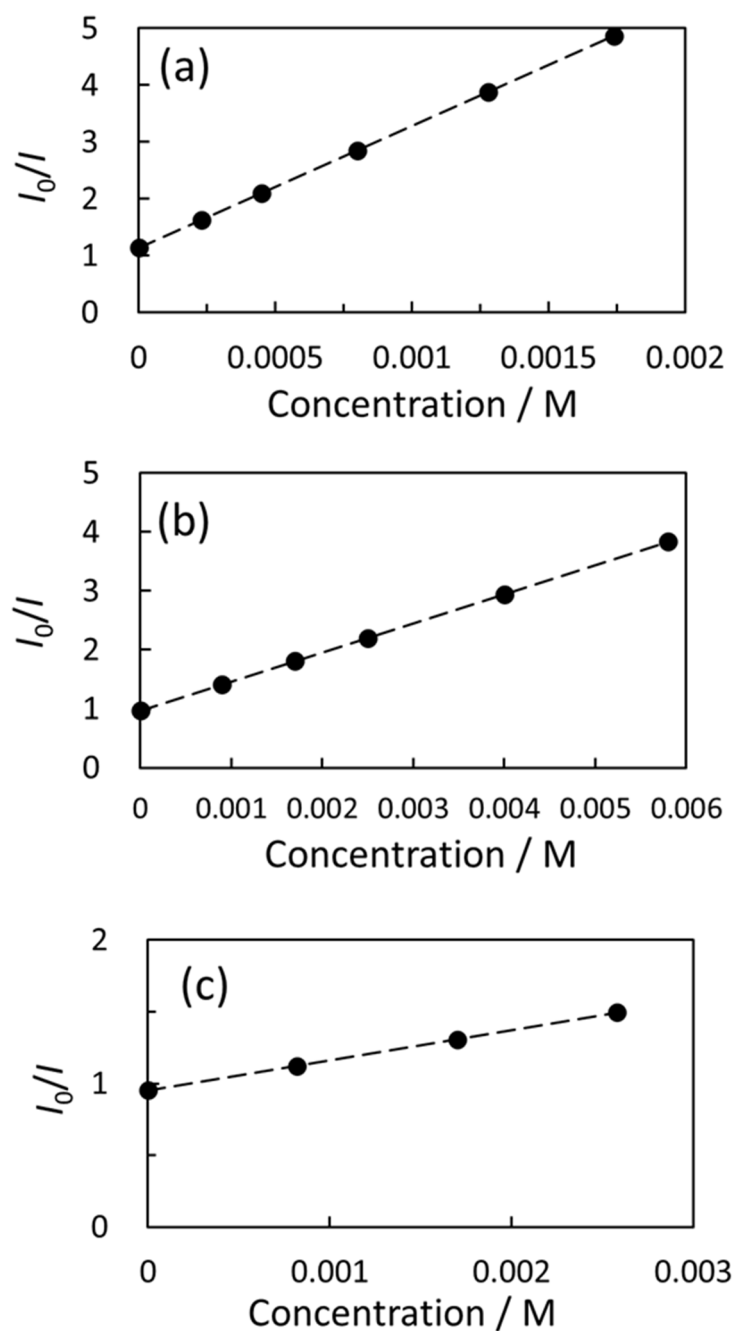
$$K_{SV} = k_q/k_r \quad (2)$$

Here  $k_r$  and  $k_q$  are the rate constants of spontaneous emission and quenching by DPA, respectively. In the presence of O<sub>2</sub>,  $K_{SV}$  is expressed by:

$$K_{SV} = k_q/k_r \times (1 + k_{qq}[\text{O}_2]/k_r)^{-1} \quad (3)$$

Here  $k_{qq}$  is the rate constant of quenching by O<sub>2</sub>. The concentration of oxygen (denoted as [O<sub>2</sub>]<sub>s</sub>) was obtained to be 2.2 mM, when the solvent was saturated with air. Figs. 2 (A), (B) and (C) are the results of quenching experiments under nitrogen atmosphere, air and air in the presence of SAP, respectively. For (B) and (C), the medium contained 2.2 mM of oxygen molecules. In the investigated three cases, the plots followed a linear relation. Table 1 gives the values of slopes (or  $K_{SV}$ ). The results implied that the energy transfer from excited  $\Delta$ -[Ru(phen)<sub>3</sub>]<sup>2+</sup> to DPA proceeded predominantly under air, when [DPA] was two times higher than [O<sub>2</sub>]<sub>s</sub> or c.a. 4 mM.





**Fig. 2.** The Stern-Volmer plots of the quenching of the emission from  $\Delta$ -[Ru(phen)<sub>3</sub>]<sup>2+</sup> ( $1.9 \times 10^{-5}$  M) excited at 450 nm: (a) under nitrogen atmosphere; (b) under air; (c) under air in the presence of SAP ( $3.8 \times 10^{-4}$  M in CEC). A medium was 1:1:0.1 (V/V) of dichloromethane/methanol/water.

**Table 1.** Stern-Volmer constants for the quenching of emission from excited  $\Delta$ -[Ru(phen)<sub>3</sub>]<sup>2+</sup> by DPA under various conditions.

System	$\Delta$ -[Ru(phen) <sub>3</sub> ] <sup>2+</sup> / M	SAP / M in CEC	$K_{SV}$ / M <sup>-1</sup>	$k_{qq}/k_r$
Under nitrogen	$1.9 \times 10^{-5}$	0	2100	—
In air	$1.9 \times 10^{-5}$	0	490	1500
Under nitrogen (SAP)	$1.9 \times 10^{-5}$	$3.9 \times 10^{-4}$	450	—
In air (SAP)	$1.9 \times 10^{-5}$	$3.9 \times 10^{-4}$	210	490

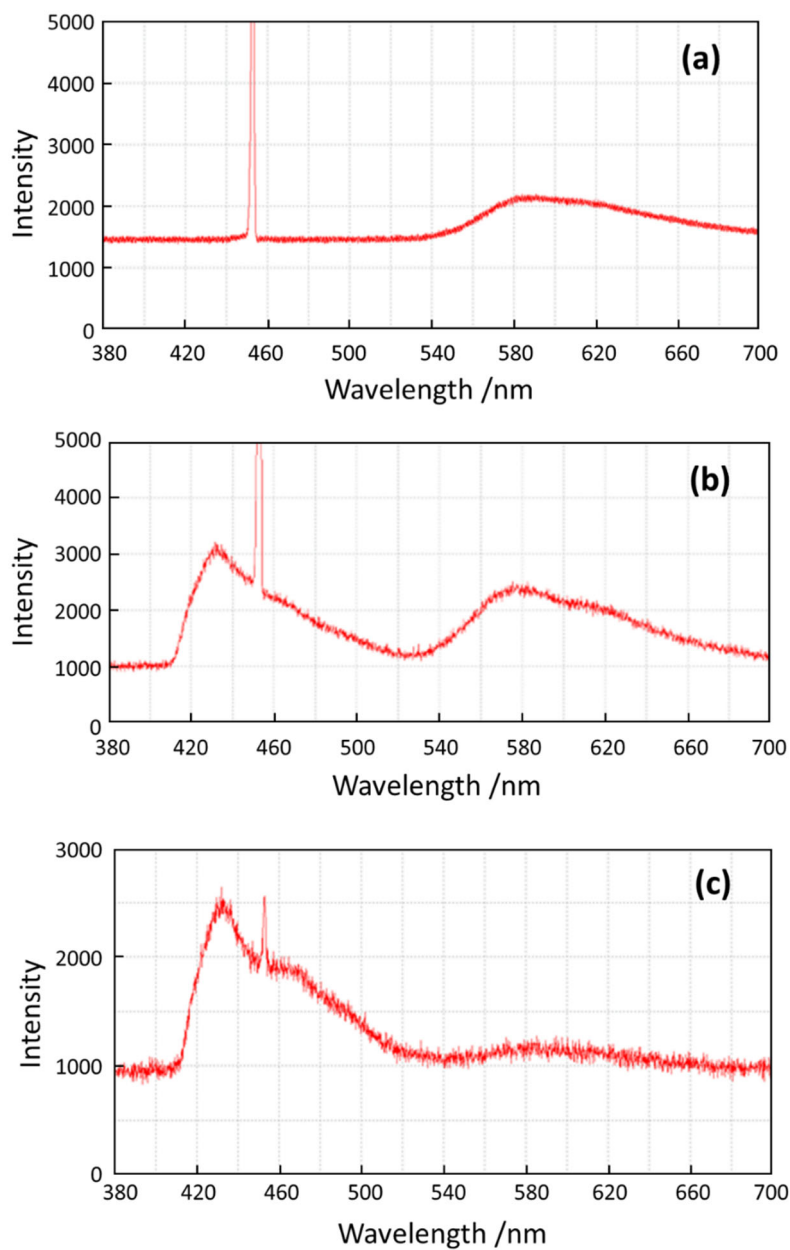
(\*) Excitation wavelength 450 nm

(\*\*) [DPA] =  $2 \times 10^{-4} \sim 6 \times 10^{-3}$  M

(\*\*\*) Temperature = 300 K

**3.2. Up-conversion of photon energy for a pair of  $\Delta$ -[Ru(phen)<sub>3</sub>]<sup>2+</sup> and DPA:** Up-conversion of photon energy was investigated for a pair of  $\Delta$ -[Ru(phen)<sub>3</sub>]<sup>2+</sup> (donor) and DPA (acceptor). Firstly, the homogeneous solution system of 1:1:0.1 (v/v) methanol/dichloromethane/water was investigated under air. A solution containing  $\Delta$ -[Ru(phen)<sub>3</sub>](ClO<sub>4</sub>)<sub>2</sub> ( $4.9 \times 10^{-5}$  M) was irradiated by a laser light at 445 nm. It gave an emission with a peak at 570 nm (Fig. 3 (a)). When DPA ( $4.2 \times 10^{-3}$  M) was added, a peak at 430 nm appeared (Fig. 3(b)). The emission was assigned to the transition from the singlet excited state of DPA. The intensity of the peak increased nearly quadratically with the intensity of a laser light (Fig. S1). The results implied that the up-conversion of photon energy from 445 nm to 430 nm was achieved for the used donor-acceptor pair. The photographic images of Figs. S2 (a) and (b) confirmed the color change of emission light from orange to blue on adding DPA.

Secondly the laser-irradiation experiments were performed on a colloidal dispersion of  $\Delta$ -[Ru(phen)<sub>3</sub>](ClO<sub>4</sub>)<sub>2</sub> ( $4.9 \times 10^{-5}$  M), DPA ( $4.2 \times 10^{-3}$  M) and SAP ( $3.8 \times 10^{-4}$  M in CEC) under air. The peak at 430 appeared on adding DPA, confirming the occurrence of up-conversion in the presence of SAP (Fig. 3(c)). For the system containing colloidal particles of SAP, the emission spectra were recorded within 10 minutes after preparing the sample. SAP particles coagulated to a negligible extent within this period. When the dispersion was left for more than 1 hour, yellow-colored colloidal particles precipitated at the bottom of the cell (Fig. S2 (c)). The upper solution was nearly colorless, indicating that the whole Ru(II) complexes were bound to clay particles. When a laser light at 450 nm was irradiated onto the yellow-colored particles, white emission was observed (Fig. S2 (d)). The results confirmed that the up-conversion took place through excited Ru(II) complexes bound to clay particles.



**Fig. 3.** The emission spectra recorded in the up-conversion experiments: (a) a laser light at 445 nm was incident on a solution containing  $\Delta$ -[Ru(phen)<sub>3</sub>]<sup>2+</sup> ( $4.9 \times 10^{-5}$  M) under air; (b) DPA ( $4.2 \times 10^{-3}$  M) was added to a sample (a); (c) SAP ( $3.8 \times 10^{-4}$  M in CEC) was added to a sample (b). A medium was 1:1:0.1 (v/v) of dichloromethane/methanol/water.

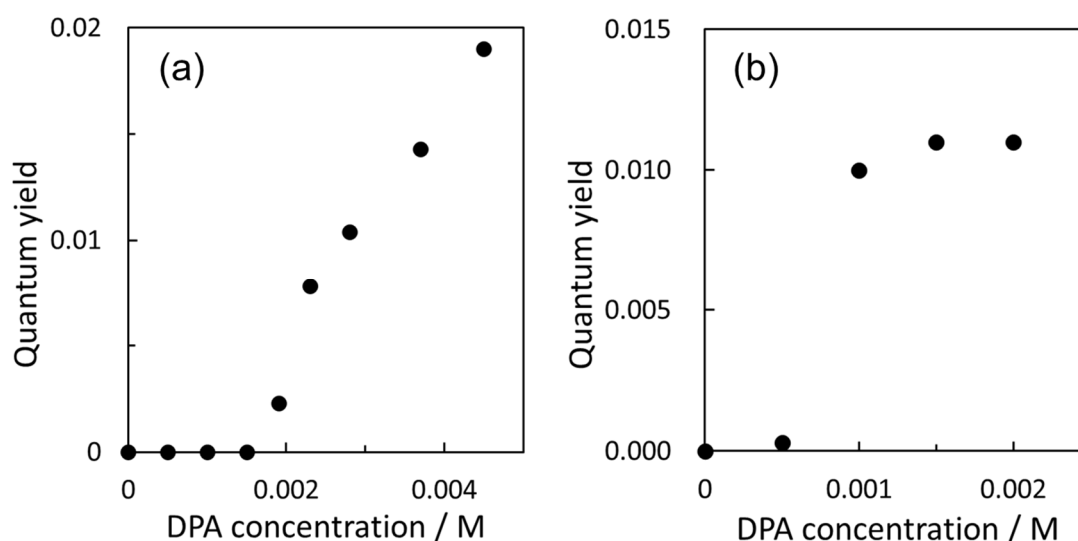
The quantum yield of up-conversion was calculated according to the following equation (Ji et. al., 2011):

$$\Phi_{uc} = 2 \Phi_{std} (A_{std}/A_{sam})(I_{std}/I_{sam})(E_{sam}/E_{std})(\eta_{sam}/\eta_{std})^2 \quad (4)$$

Here  $\Phi_{uc}$  and  $\Phi_{std}$  are the quantum yields of  $\Delta$ -[Ru(phen)<sub>3</sub>]<sup>2+</sup> and the standard compound ([Ru(4,4'-dimethylbipyridine)<sub>3</sub>]<sup>2+</sup>) used as a donor,  $A_{std}$  and  $A_{sam}$  the absorbances of the standard and samples solutions at 445 nm, respectively,  $E_{std}$  and  $E_{sam}$  the band areas with the peak at 430 nm,  $I_{std}$  and  $I_{sam}$  the intensities of a laser light irradiated on the standard and sample solutions, and  $\eta_{std}$  and  $\eta_{sam}$  the refractive indexes of the standard and sample solutions, respectively. The difference of the refractive indexes was neglected. Taking a dichloromethane solution of tris(4,4-dimethylbipyridine) ruthenium(II) chlorides as a standard solution and  $\Phi_{std} = 0.015 \pm 0.005$  from the literature (Ji et. al., 2011), the quantum yield of up-conversion for  $\Delta$ -[Ru(phen)<sub>3</sub>]<sup>2+</sup> was obtained to be  $0.018 \pm 0.005$  and  $0.009 \pm 0.003$  in the absence and in the presence of SAP ( $3.8 \times 10^{-4}$  M in CEC), respectively. Thus the adsorption of a used donor by SAP resulted in the decrease of the quantum yield of up-conversion to 50%. The lowering of the quantum yield might be caused by the situations that a part of bound  $\Delta$ -[Ru(phen)<sub>3</sub>]<sup>2+</sup> complexes were not accessible to DPA, since they were intercalated between SAP layers.

**3.3. Effects of clay adsorption on up-conversion efficiency:** The effects of clay adsorption on up-conversion efficiency were investigated. Under the constant concentration of  $\Delta$ -[Ru(phen)<sub>3</sub>](ClO<sub>4</sub>)<sub>2</sub> ( $4.9 \times 10^{-5}$  M), the intensity of emission at 430 nm (denoted as  $I_{430}$ ) was measured on adding DPA in the absence or presence of SAP. As shown in Fig. 4 (a), the quantum yield as measured in terms of  $I_{430}$  started to rise at [DPA] =  $1.5 \times 10^{-3}$  M in the absence of SAP.  $I_{430}$  continued to increase until [DPA] was  $6.0 \times 10^{-3}$

M. Contrarily  $I_{430}$  rose already at  $[DPA] = 5.0 \times 10^{-4}$  M in the presence of SAP ( $3.8 \times 10^{-4}$  M in CEC) (Fig. 4 (b)).  $I_{430}$  attained the saturated value at  $[DPA] = 1.5 \times 10^{-3}$  M. The results indicated that SAP had the effect of lowering the critical concentration of DPA to realize the up-conversion. One plausible mechanism is that DPA was attracted to SAP particles due to its hydrophobic properties. This resulted in the increase of the effective concentration of DPA around excited  $\Delta$ -[Ru(phen)<sub>3</sub>]<sup>2+</sup> on a clay surface. The tendency was particularly prominent in the vicinity of the SAP surface ion-exchanged with  $\Delta$ -[Ru(phen)<sub>3</sub>]<sup>2+</sup>. The situations are schematically shown in Fig. S3.

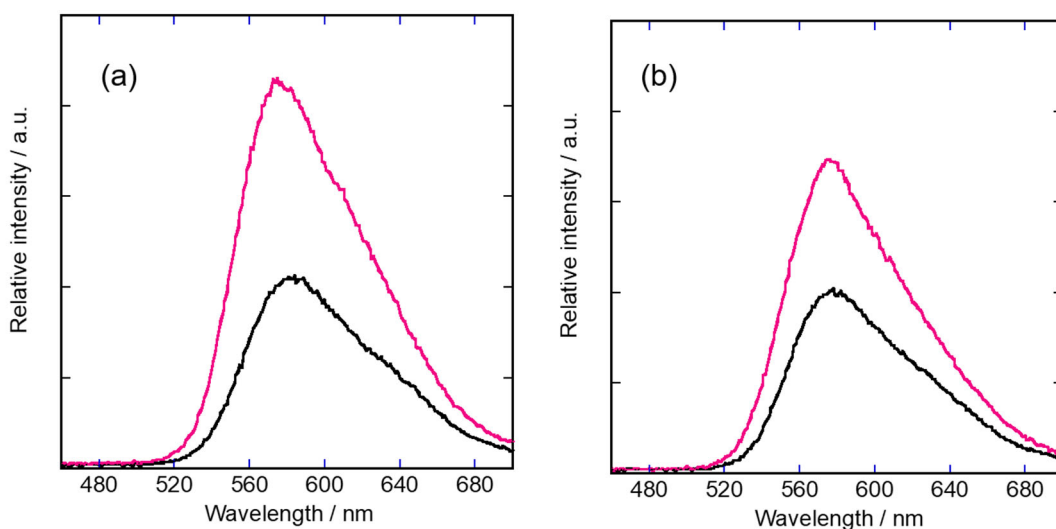


**Fig. 4.** The dependence of the quantum yield of up-conversion, when DAP was added to the following samples: (a) a solution containing  $\Delta$ -[Ru(phen)<sub>3</sub>](ClO<sub>4</sub>)<sub>2</sub> ( $4.9 \times 10^{-5}$  M); (b) a dispersion containing  $\Delta$ -[Ru(phen)<sub>3</sub>](ClO<sub>4</sub>)<sub>2</sub> ( $4.9 \times 10^{-5}$  M) and SAP ( $3.8 \times 10^{-4}$  M in CEC). A medium was 1:1:0.1 (v/v) of dichloromethane/methanol/water.

### 3.4 Effect of optical purity of [Ru(phen)<sub>3</sub>]<sup>2+</sup> on up-conversion efficiency: Figs. 5 (a) and

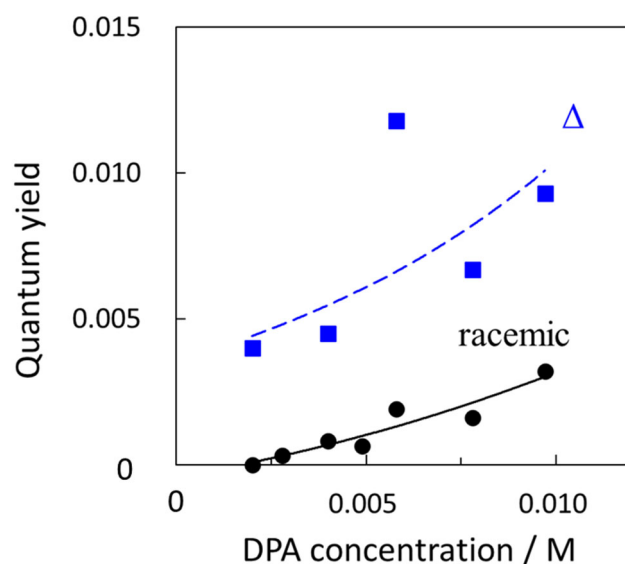
(b) compared the emission spectra, when the complex was adsorbed by SAP in the form

of either a pure enantiomer (or  $\Delta$ -form) or a racemic mixture. A medium was 1:1:0.1 (V/V) dichloromethane/methanol/water. For both cases, the emission intensity at 570 nm from excited  $[\text{Ru}(\text{phen})_3]^{2+}$  ( $1.90 \times 10^{-5}$  M) increased on adding SAP ( $3.8 \times 10^{-4}$  M in CEC) under air. The degree of increase was larger for  $\Delta$ - $[\text{Ru}(\text{phen})_3]^{2+}$  (80% increase) than for racemic  $[\text{Ru}(\text{phen})_3]^{2+}$  (40 % increase). The difference was rationalized in terms of the mechanism that racemic  $[\text{Ru}(\text{phen})_3]^{2+}$  tended to form a tight pair of  $\Delta$ - and  $\Lambda$ -enantiomers, while enantiomeric  $[\text{Ru}(\text{phen})_3]^{2+}$  exists as an isolated species on a clay surface. In case of a racemic mixture, the formation of a tight  $\Delta/\Lambda$  pair resulted in lowering emission intensity due to self-quenching. The observe chirality effect on adsorption was assisted by the previous theoretical simulations (Sato et. al., 1992).



**Fig. 5.** Emission spectra of  $[\text{Ru}(\text{phen})_3](\text{ClO}_4)_2$  ( $1.9 \times 10^{-5}$  M) in the presence of SAP ( $3.8 \times 10^{-4}$  M in CEC): (a)  $[\text{Ru}(\text{phen})_3](\text{ClO}_4)_2$  added as a  $\Delta$ -formed enantiomer; (b)  $[\text{Ru}(\text{phen})_3](\text{ClO}_4)_2$  added as a racemic mixture. Excitation wavelength was 450 nm. A medium was 1:1:0.1 (v/v) of dichloromethane/methanol/water. Black curve: no SAP added, red curve: SAP ( $3.8 \times 10^{-4}$  eq/L) added.

Figs. 6 (A) and (B) compares the efficiency of up-conversion, when  $[\text{Ru}(\text{phen})_3]^{2+}$  ( $4.9 \times 10^{-5}$  M) was adsorbed by SAP ( $3.8 \times 10^{-4}$  M in CEC) as a donor in the form of either a pure enantiomer (or  $\Delta$ -form) or a racemic mixture. A medium was a 1:1:0.1 (v/v) dichloromethane/methanol/water. In case of  $\Delta$ - $[\text{Ru}(\text{phen})_3]^{2+}$ , the up-conversion was realized at  $[\text{DPA}] = 2.0 \times 10^{-3}$  M, while, in case of racemic  $[\text{Ru}(\text{phen})_3]^{2+}$ , the up-conversion occurred at the concentration of DPA higher than  $5.0 \times 10^{-3}$  M.  $I_{430}$  was higher for  $\Delta$ - $[\text{Ru}(\text{phen})_3]^{2+}$  than for racemic  $[\text{Ru}(\text{phen})_3]^{2+}$  in the range of  $[\text{DPA}] = 2 \sim 10 \times 10^{-3}$  M. One possibility for the observed effects was that the energy transfer from excited  $[\text{Ru}(\text{phen})_3]^{2+}$  to DPA took place less effectively when  $[\text{Ru}(\text{phen})_3]^{2+}$  formed a tight racemic pair on a clay surface than when the molecule formed an isolated enantiomeric species. The present results implied that a donor is preferred to be used as a pure enantiomer when it has a tendency of forming a racemic pair.



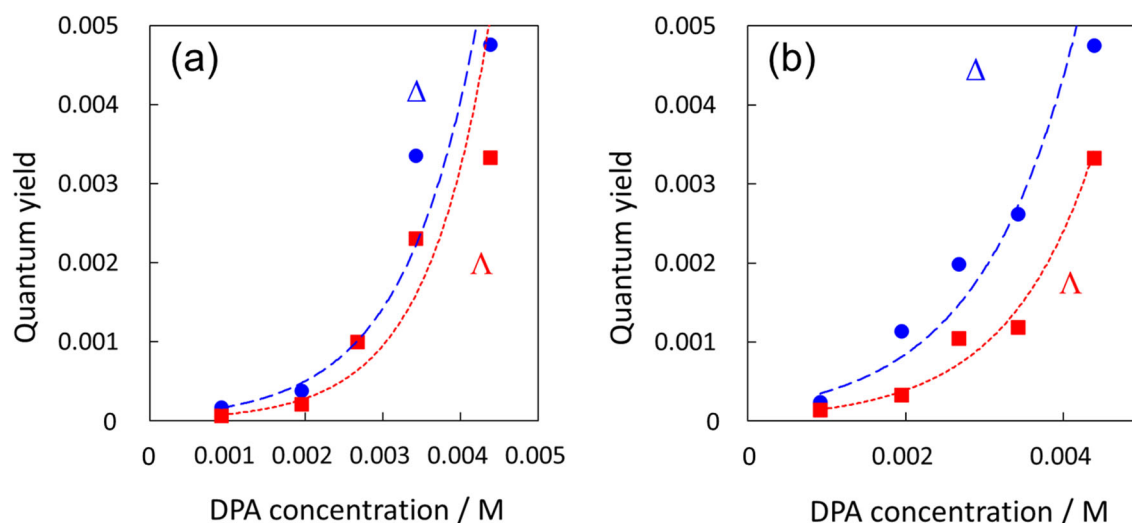
**Fig. 6.** The dependence of the quantum yield of up-conversion on  $[\text{DPA}]$ , when  $[\text{Ru}(\text{phen})_3]^{2+}$  ( $4.9 \times 10^{-5}$  M) was added as a pure enantiomer or a racemic mixture in the presence of SAP ( $3.8 \times 10^{-4}$  M in CEC): (a)  $\Delta$ - $[\text{Ru}(\text{phen})_3](\text{ClO}_4)_2$ ; ■, (b)



racemic-[Ru(phen)<sub>3</sub>](ClO<sub>4</sub>)<sub>2</sub>; •. A medium was 1:1:0.1 (v/v) of dichloromethane/methanol/water.

**3.5 Stereoselectivity in the up-conversion for a chiral donor/acceptor pair:** In order to pursue the possibility to achieve stereoselectivity, the up-conversion was investigated for the pair of a chiral donor and a chiral acceptor in the presence of SAP.  $\Delta$ - or  $\Lambda$ -[Ru(phen)<sub>3</sub>]<sup>2+</sup> was used as a chiral donor. As a chiral acceptor, a molecule with two DPA moieties connected to 1,1'-binaphthol was used (Fig. S4). The compound is denoted as SS- or RR-DPA-BINOL, depending on the chirality of a central binaphthyl group, respectively. Here a 1,1'-binaphthyl group was chosen because 1,1'-binaphthol was known to interact with [Ru(phen)<sub>3</sub>]<sup>2+</sup> stereoselectively on a clay surface (Yamagishi et al., 1996).

Up-conversion was studied for the donor/acceptor pair of  $\Delta$ - or  $\Lambda$ -[Ru(phen)<sub>3</sub>]<sup>2+</sup> and SS-DPA-BINOL. The quantum yield of up-conversion was measured on increasing the concentration of SS-DPA-BINOL. The results are shown in Figs. 7 (a) and (b). In the absence of SAP, no significant difference was observed in the up-conversion efficiency between  $\Delta$ -[Ru(phen)<sub>3</sub>]<sup>2+</sup>/SS-DPA-BINOL and  $\Lambda$ -[Ru(phen)<sub>3</sub>]<sup>2+</sup>/SS-DPA-BINOL (Fig. 7 (a)). In the presence of SAP (3.8×10<sup>-4</sup> M in CEC), the up-conversion efficiency was higher by 20 ~ 40 % for  $\Delta$ -[Ru(phen)<sub>3</sub>]<sup>2+</sup>/SS-DPA-BINOL than for  $\Lambda$ -[Ru(phen)<sub>3</sub>]<sup>2+</sup>/SS-DPA-BINOL (Fig. 7 (b)). The results implied that the fixation of a donor molecule on a clay surface resulted in enhancing chiral selectivity during the courses of donor/acceptor energy transfer and/or TTA of excited acceptors. The results might open the possibility of developing chiral sensing on the basis of the up-conversion of colloidal clay systems.



**Fig. 7.** The dependence of the quantum yield of up-conversion on the concentration of SS-DPA-BINOL as a chiral acceptor, when Δ- or Λ- $\text{Ru}(\text{phen})_3]^{2+}$  ( $4.9 \times 10^{-5}$  M) was used as a chiral donor: (a) no SAP added; (b) SAP added to  $3.8 \times 10^{-4}$  M in CEC). A medium was 1:1:0.1 (v/v) of dichloromethane/methanol/water.

#### 4. Conclusions

The possibility of achieving the up-conversion of photon energy in systems containing colloidal particles of synthetic saponite was explored. As a donor-acceptor pair, Δ-tris(1,10-phenanthroline)ruthenium(II)/1,10-diphenylanthracene was used. It was confirmed that an incident laser light at 450 nm was converted to emission at 430 nm through the triplet-triplet annihilation of excited donors in the presence of a clay mineral. The effects of the optical purity of the used Ru(II) complex were examined. Stereoselectivity was pursued through the use of a synthesized chiral acceptor molecule.

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## Supporting Information

# Up-conversion of Photon Energy in Colloidal Clay Systems

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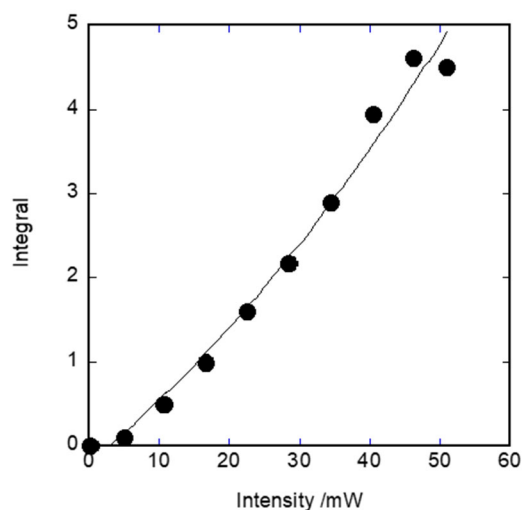
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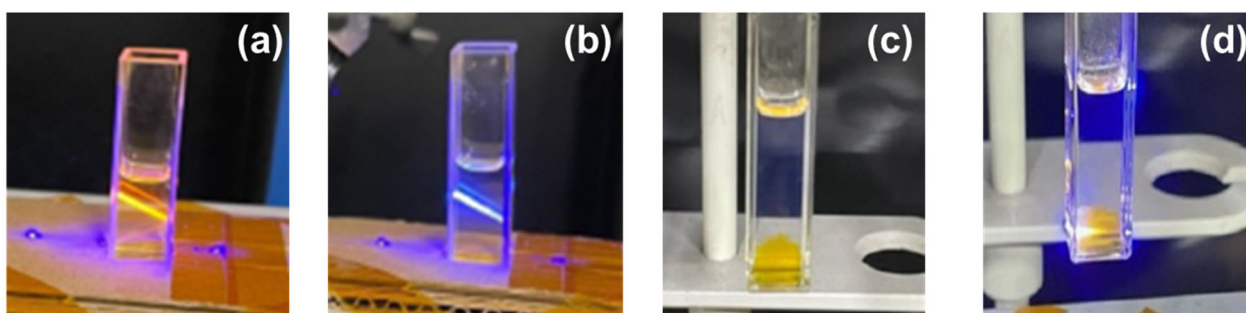
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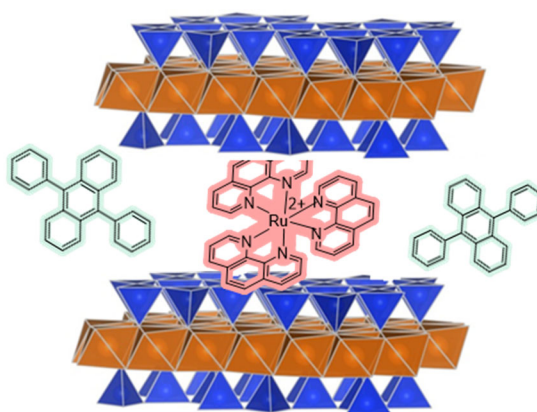
**Fig. S1.** The dependence of the up-conversion efficiency on the intensity of an incident light. The vertical axis is the laser power at 450 nm and the horizontal axis the area of the band at 430 nm (in arbitrary unit). The experimental conditions are following:  $\Delta$ -[Ru(phen)<sub>3</sub>]<sup>2+</sup> ( $4.9 \times 10^{-5}$  M), DPA ( $4.2 \times 10^{-3}$  M) and a medium 1 : 1 : 0.1 (V/V) of dichloromethane/methanol/water. The atmosphere was under air.

**S2. The phtographic images of the experiments on the up-conversion of homogenous and clay-dispersion systems**



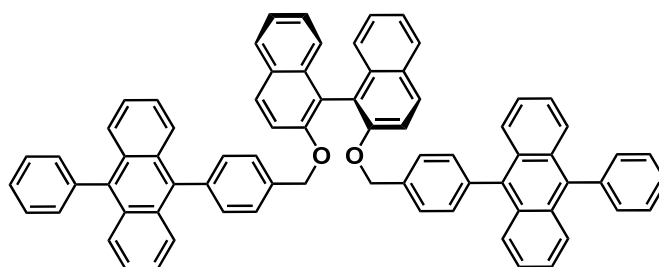
**Fig. S2.** The photographic images of the samples in the up-conversion experiments: (a) a laser light at 450 nm was incident on sample (a) in Figure3; (b) a laser light at 450 nm was incident on sample (b) in Figure 3; (c) sample (c) in Figure 3 was left for one hour; (d) a laser light at 450 nm was incident on sample (c) in this figure.

**S3. The schematic drawing showing the effects of clay exfoliated layers on concentrating DPA molecules**



**Fig. S3.** The schematic image showing the gathering of PDA molecules around a SAP particles ion-exchanged with  $\Delta$ -[Ru(phen)<sub>3</sub>]<sup>2+</sup>.

**S4. The synthesis and identification of a chiral acceptor for stereoselective up-conversion**



*S*-9-phenyl-10-(4-((7'-((4-(10-phenylanthracen-9-yl)benzyl)oxy)-[1,1'-binaphthalen]-7-yl)oxy)phenyl)anthracene

**Fig. S4.** The molecular structure of a chiral acceptor (abbreviated as *SS*-DPA-BINOL in the text). The compound was identified by means of  $^1\text{H}$ -NMR,  $^{13}\text{C}$ -NMR and mass spectrum. The results are following:

$\delta\text{H}$ (400 MHz :  $\text{CDCl}_3$ ) 5.29 (4H, d,  $J = 6.8$  Hz), 7.20-7.32 (20H, m), 7.36 (3H, m), 7.45 (3H, d,  $J = 6.8$  Hz), 7.54-7.66 (16H, m), 7.92 (2H, d,  $J = 9.2$  Hz), 8.04 (2H, d,  $J = 9.2$  Hz)

$\delta\text{C}$ (100 MHz :  $\text{CDCl}_3$ ) 71.7, 116.5, 121.2, 124.1, 125.1, 125.2, 125.3, 125.8, 126.6, 126.8, 126.9, 127.0, 127.2, 127.6, 127.7, 128.1, 128.5, 129.7, 129.8, 129.9, 130.0, 131.2, 131.3, 134.5, 136.9, 137.0, 137.2, 138.2, 139.2, 154.5

FAB-MS  $m/z = 970$  (Calc. for : 970.38)