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# Application of chiral cationic iridium(III) complexes for triplet–triplet annihilation up-conversion of photon energy in *R*-limonene

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Converting photon energy in a green solvent is a challenge for developing environmentally friendly technologies. Triplet–triplet annihilation up-conversion (TTA-UC) in *R*-limonene is one such attempt. Since *R*-limonene is a nonpolar medium, conventional organic compounds or neutral metal complexes are used as a donor. In this study, cationic chiral iridium(III) complexes are used for the first time. The studies were based on the finding that a cyclometalated cationic iridium(III) complex in a chiral form,  $\Delta$ - or  $\Lambda$ -[Ir(piq)<sub>2</sub>(dmbpy)]<sup>+</sup> (piqH = 1-phenyisoquinoline, dmbpy = 4,4'-dimethyl-2,2'-bipyridine), was soluble enough in *R*-limonene to perform TTA-UC. Conversely, its racemic form was barely soluble due to its high crystallinity. When an *R*-limonene solution containing chiral [Ir(piq)<sub>2</sub>(dmbpy)]PF<sub>6</sub> (ca. 2 × 10<sup>-5</sup> M) and DPA (0.3–2.6 mM) was irradiated with laser light at 445 nm, the up-conversion of photon energy to 430 nm was achieved with a quantum yield as high as 4.5% under air. Despite the slight difference in solubility between the enantiomers, no stereoselectivity was observed in TTA-UC. The effects of long alkyl chains attached to a donor molecule, or  $\Delta$ - or  $\Lambda$ -[Ir(piq)<sub>2</sub>(C<sub>n</sub>bpy)]<sup>+</sup> (C<sub>n</sub>bpy = 4,4'-nonyl (C<sub>9</sub>)- or 4,4'-nonyldecyl (C<sub>10</sub>)-2,2'-bipyridine), were investigated on the solubility and efficiency of TTA-UC.

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## Introduction

Recently there has been wide interest in the pursuit of an elucidation of the mechanism by which molecular systems convert photon energy in green solvents.<sup>1–4</sup> This is expected to solve energy supply problems without damaging environments. Among these investigations, triplet–triplet annihilation up-conversion (TTA-UC) has been studied using *R*-limonene as a representative green solvent.<sup>5–11</sup> *R*-limonene is a non-polar organic solvent that is reported to reduce the quenching effects of oxygen molecules in air due to the presence of a C=C bond.<sup>2</sup> Conventionally, emitting metal complexes with no charge, such as Pt-porphyrin complexes, have been used since they dissolve in *R*-limonene. These complexes attain a quantum yield of a few percent.<sup>2</sup>

Cyclometalated iridium(III) complexes (denoted as Ir(III) complexes) are extensively used as a donor in TTA-UC because they are highly emissive in the UV- visible region.<sup>12–25</sup> In fact, our group established the systems of triplet–triplet annihilation up-conversion (TTA-UC) of photon energy by use of various

types of Ir(III) complexes.<sup>25</sup> They are positively charged and are hybridized with inorganic polymers such as clay minerals. The systems achieve reasonable quantum yield of a few percentages even under air.<sup>25–28</sup>

Using these complexes in non-polar green solvents would expand the range of donors in TTA-UC systems. Motivated by this expectation, the present study attempted to use positively charged iridium(III) complexes. To overcome the issue of low solubility, we found that the chiral form of a positively charged Ir(III) complex was soluble enough in *R*-limonene. The used complex was  $\Delta$ - or  $\Lambda$ -[Ir(piq)<sub>2</sub>(dmbpy)]<sup>+</sup> (piqH = 1-phenyisoquinoline, dmbpy = 4,4'-dimethyl-2,2'-bipyridine). The racemic form of the same complex was hardly soluble probably due to high crystallinity. An *R*-limonene solution containing the chiral cationic complex as a donor and 9, 10-diphenylanthracene (DPA) as an acceptor, the quantum yield for TTA-UC attained as high as 4.5% under air. In this study, *R*-limonene was used instead of its antipodal enantiomer, because the formed was available in a purer form commercially.

## Results and discussion

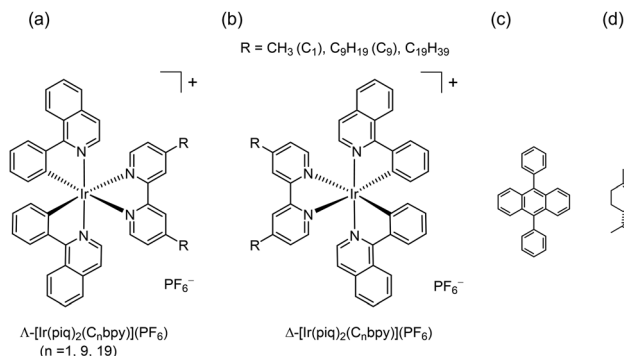
### Solubility of cationic iridium(III) complexes in *R*-limonene

In the present study, a cationic chiral Ir(III) complex,  $\Delta$ - or  $\Lambda$ -[Ir(piq)<sub>2</sub>(dmbpy)]<sup>+</sup>, was used as a donor in TTA-UC. The

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**Chart 1** Molecular structures of (a)  $\Delta$ - or (b)  $\Lambda$ -[Ir(piq)<sub>2</sub>(C<sub>n</sub>bpy)]<sup>+</sup> (piqH = 1-phenylisoquinoline, dmbpy = 4,4'-dimethyl-2,2'-bipyridine, C<sub>n</sub>bpy = 4,4'-nonyl (C<sub>9</sub>)- or 4,4'-nonyldecyl (C<sub>19</sub>)-2,2'-bipyridine), (c) DPA (or 9, 10-diphenylanthracene) and (d) *R*-limonene.

complex (Chart 1) was selected because it possessed a broad absorption band with the peak position at 430 nm and absorbed a laser light at 445 nm.<sup>26</sup> In order to see the effects of long alkyl chains, the complexes,  $\Delta$ - or  $\Lambda$ -[Ir(piq)<sub>2</sub>(C<sub>n</sub>bpy)]<sup>+</sup> (C<sub>n</sub>bpy = 4,4'-nonyl (C<sub>9</sub>)- or 4,4'-nonyldecyl (C<sub>19</sub>)-2,2'-bipyridine), were also studied. The preparation of enantiomeric [Ir(piq)<sub>2</sub>(dmbpy)]<sup>+</sup> and [Ir(piq)<sub>2</sub>(C<sub>9</sub>bpy)]<sup>+</sup> was reported previously.<sup>26–28</sup> The chromatographic resolution of [Ir(piq)<sub>2</sub>(C<sub>19</sub>-bpy)]<sup>+</sup> was achieved in the present work as shown in Fig. S1 (SI). The electronic circular dichroism (ECD) spectra of these enantiomers are shown in Fig. S1 and S2 (SI). The assignment of  $\Delta$ - or  $\Lambda$ -configuration was performed on the basis of their ECD spectra.<sup>26–31</sup>

Firstly chirality effects were studied on the solubility of [Ir(piq)<sub>2</sub>(dmbpy)]PF<sub>6</sub> in *R*-limonene. Fig. S3 (SI) shows that the temperature dependence of solubility of the racemic ( $\Delta\Lambda$ ),  $\Delta$ - and  $\Lambda$ -enantiomers of the complex. As a result, chirality influenced solubility in this solvent remarkably. At 273 K, for example,  $\Delta\Lambda$ -,  $\Delta$ - and  $\Lambda$ -enantiomers were soluble to  $0.8 \times 10^{-5}$  M,  $2.0 \times 10^{-4}$ , and  $2.5 \times 10^{-4}$  M, respectively. Usually, a racemate takes a stable antipodal pair in a crystalline state so that it is less soluble than an enantiomer.<sup>32,33</sup> Therefore, the higher solubility of the enantiomeric form compared to the racemic one was attributed to low crystallinity in the solid states. Slight difference was observed between the opposite enantiomers. It reflected stereoselective effects when chiral *R*-limonene molecules solvated  $\Delta$ - or  $\Lambda$ -[Ir(piq)<sub>2</sub>(dmbpy)]PF<sub>6</sub>, respectively.

The effects of long alkyl chains were investigated for the complexes of  $\Delta$ - or  $\Lambda$ -[Ir(piq)<sub>2</sub>(C<sub>n</sub>bpy)]<sup>+</sup> (C<sub>n</sub>bpy = 4,4'-nonyl (C<sub>9</sub>)- or 4,4'-nonyldecyl (C<sub>19</sub>)-2,2'-bipyridine). These complexes were soluble to more than  $10^{-4}$  M at room temperature even in the form of racemates. Reasons might lie in poor crystallinity since the long alkyl chains were possible to take various conformations in solid states with nearly the same free energy. The enantiomers were even more soluble to more than  $10^{-3}$  M at room temperature.

### Energy transfer in *R*-limonene

The enantiomeric forms of [Ir(piq)<sub>2</sub>(dmbpy)]PF<sub>6</sub> were used for studying the photochemical processes in *R*-limonene. The

racemate was hardly soluble so that it was unable to provide sufficient emission under the irradiation of a laser light. When a solution of an enantiomeric Ir(III) complex in the solvent was irradiated at 445 nm, emission was observed with the dual peaks around 590 nm and 630 nm. The duality suggested the emissions from two excited triplet state with different vibrational levels. The intensity of the emission decreased upon the addition of DPA. It indicated that the photon energy was transferred from excited  $\Delta$ - or  $\Lambda$ -[Ir(piq)<sub>2</sub>(dmbpy)]<sup>+</sup> to DPA. The same experiments were performed using  $\Delta$ - or  $\Lambda$ -[Ir(piq)<sub>2</sub>(C<sub>n</sub>bpy)]<sup>+</sup> ( $n = 9$  or  $19$ ). Their emission spectra are given in Fig. S4–S6 (SI).

Fig. 1 shows the plots of the  $I_0/I$  ratios against the DPA concentration (Stern–Volmer plots) at 300 K under air, where  $I_0$  and  $I$  denote the intensities of emission at 590 nm in the absence and presence of DPA, respectively. The plots were constructed according to the following equation:

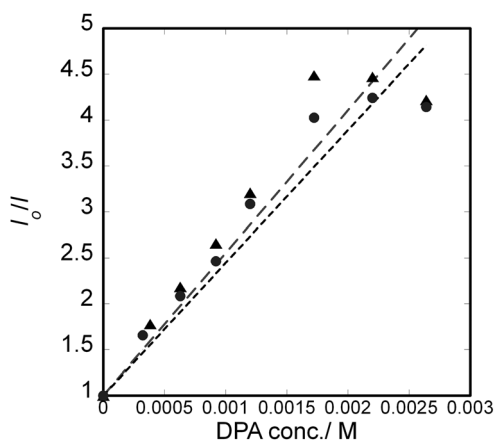
$$I_0/I = 1 + K_{SV}[DPA], \quad (1)$$

In the absence of oxygen, the slope of the plot (or  $K_{SV}$ ) corresponds to  $k_q/k_r$ , where  $k_q$  and  $k_r$  are the bimolecular quenching and irradiation rate constants, respectively. In the presence of oxygen, quenching occurs competitively between DPA and oxygen. Under the situations. Eqn (1) is modified to:

$$K_{SV} = k_q / \{k_r + k_{qox}[O_2]\}, \quad (2)$$

where  $k_{qox}$  and  $[O_2]$  are the bimolecular quenching rate constant by an oxygen molecule and its molar concentration, respectively.

According to the results in Table 1, it was concluded that energy transfer occurred from excited Ir(III) complexes to DPA. A small difference in  $k_q/k_r$  was observed between the  $\Delta$ - and  $\Lambda$ -enantiomers. It might be caused by the stereoselectivity effects in solvating a chiral complex in *R*-limonene. Besides, It was noted that the slope of a plot ( $K_{SV}$ ) was more than two times higher than that observed previously for the similar Ir(III) complex and DPA as a donor/acceptor pair in the medium of 1 : 1 (v/v) dichloromethane/methanol/water (or  $K_{SV} = 600 \text{ M}^{-1}$ ).<sup>24</sup>



**Fig. 1** S–V plots for a pair of  $\Delta$ - (filled triangle) or  $\Lambda$ -[Ir(piq)<sub>2</sub>(dmbpy)]<sup>+</sup> (filled circle) and DPA in *R*-limonene. The solution was irradiated by a laser light at 445 nm. The intensity of emission was measured at 590 nm.

**Table 1** Results for SV plots in *R*-limonene for the enantiomeric forms of iridium(III) complexes under air<sup>a</sup>

Ir(III) complexes	$K_{SV}$ or $k_q/k_r$ ( $M^{-1}$ ) for $\Delta$ -isomer	$K_{SV}$ or $k_q/k_r$ ( $M^{-1}$ ) for $\Lambda$ -isomer	$\tau$ ( $\mu s$ ) for $\Delta$ -isomer <sup>b</sup>	$k_q$ ( $M^{-1} s^{-1}$ ) for $\Delta$ -isomer
$[\text{Ir}(\text{piq})_2(\text{dmbpy})]^+$	1554	1446	0.22	$7.06 \times 10^9$
$[\text{Ir}(\text{piq})_2(\text{C}_9\text{bpy})]^+$ ( $n = 9$ )	2550	3276	0.27	$9.44 \times 10^9$
$[\text{Ir}(\text{piq})_2(\text{C}_{19}\text{bpy})]^+$ ( $n = 19$ )	1457	1191	0.28	$5.20 \times 10^9$

<sup>a</sup> The experimental conditions are described in the text. <sup>b</sup> The lifetime under air.

The results reflected that *R*-limonene reduced substantially the competitive quenching by oxygen molecules.

With a purpose of examining the effects of long alkyl chains, the same experiments were performed for a pair of  $[\text{Ir}(\text{piq})_2(\text{C}_n\text{bpy})]^+$ /DPA ( $n = 9$  or  $19$ ) (Fig. S7 in SI). As summarized in Table 1, the presence of alkyl chains in donors affected little the efficiency of energy transfer. The UV-vis spectra were shown in Fig. S8 in SI.

The lifetime of a used complex ( $\tau$ ) was measured in the same medium (Fig. S9 in SI). Under air,  $\tau$  is expressed by:

$$\tau = \{k_r + k_{\text{ox}}[\text{O}_2]\}^{-1}. \quad (3)$$

Using the measured lifetime ( $\tau$ ),  $k_q$  was calculated according to the eqn (4)

$$k_q = K_{SV}/\tau. \quad (4)$$

The results are summarized in Table 1. The obtained values of  $k_q$  were compared with the bimolecular rate constant for a diffusion-controlled encounter mechanism (denoted by  $k_{\text{diff}}$ ).  $k_{\text{diff}}$  was calculated to be  $=7.09 \times 10^{-9} M^{-1} s^{-1}$  according to the following theoretical eqn (2).<sup>4</sup>

$$k_{\text{diff}} = \frac{8RT}{3\eta}, \quad (5)$$

where  $R$ ,  $T$ , and  $\eta$  are the gas constant, absolute temperature, and solvent viscosity (0.932 mPa s taken from the literature),<sup>34</sup> respectively. It was concluded that  $k_q$  and  $k_{\text{diff}}$  were of the same order, indicating that the energy-transfer from an excited iridium(III) complex to a DPA molecule occurred through a diffusion-controlled encounter reaction. Lifetimes were also measured under nitrogen atmosphere (denoted by  $\tau_N$ ). Since no oxygen was present,  $\tau_N$  was equal to  $k_r$ , leading to:

$$k_{\text{ox}}[\text{O}_2] = 1/\tau - 1/\tau_N. \quad (6)$$

The results are shown in Fig. S9. In case of  $[\text{Ir}(\text{piq})_2(\text{dmbpy})]^+$  and  $[\text{Ir}(\text{piq})_2(\text{C}_9\text{bpy})]^+$ , the removal of oxygen resulted in the significant elongation of lifetime, while no influence was observed for  $[\text{Ir}(\text{piq})_2(\text{C}_{19}\text{bpy})]^+$ .

#### TTA-UC of photon energy by Ir(III) complexes in *R*-limonene

TTA-UC of photon energy in *R*-limonene was investigated for the pair of  $\Delta$ - (or  $\Lambda$ )- $[\text{Ir}(\text{piq})_2(\text{dmbpy})]^+$  as a donor and DPA as an acceptor. Firstly, a  $\text{CH}_2\text{Cl}_2$  solution containing the standard pair,  $[\text{Ru}(\text{dmbpy})_3]^{2+}$ ( $\text{dmbpy} = 4,4'$ -dimethylbipyridine)/DPA, was irradiated at 445 nm under air using a laser pulse. The results of laser irradiation on the system are shown in SI. Next, an *R*-limonene solution of  $\Delta$ - or  $\Lambda$ - $[\text{Ir}(\text{piq})_2(\text{dmbpy})]^+$ PF<sub>6</sub> was

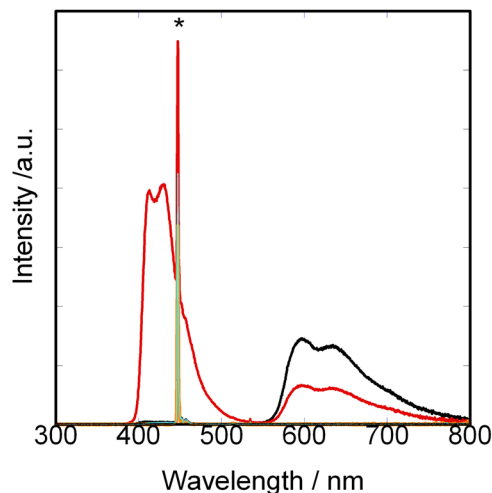
irradiated under the same conditions. The results are shown in Fig. 2 and 3.

In case of the pair of  $\Delta$ - (or  $\Lambda$ )- $[\text{Ir}(\text{piq})_2(\text{dmbpy})]^+$ /DPA, dual peaks appeared around 430 nm on adding DPA. The concomitant decrease of intensity was observed at the dual peaks around 590 nm (black and red curves in Fig. 2). The results indicated that TTA-UC of photon energy occurred for this pair. A reason for the dual nature of the induced UC band remained to be clarified. It might imply that the up-converted emission took place from two different singlet states in DPA. A reason was unclear, either, why the ratio of peak intensity of two dual peaks varied with the increase of concentration of added DPA as shown in Fig. S4 (SI).

The quantum yield of up-conversion was calculated using the following equation,<sup>35</sup>

$$\Phi_{(\text{uc,ref})} = 2\Phi_{\text{std}}(A_{\text{std}}/A_{\text{sam}})(I_{\text{std}}/I_{\text{sam}})(E_{\text{sam}}/E_{\text{std}})(n_{\text{sam}}/n_{\text{std}})^2 \quad (7)$$

where  $\Phi_{(\text{uc,ref})}$  and  $\Phi_{\text{std}}$  are the quantum yields of  $\Delta$ - or  $\Lambda$ - $[\text{Ir}(\text{piq})_2(\text{dmbpy})]^+$  and the standard compound ( $[\text{Ru}(\text{dmbpy})_3]^{2+}$ ) used as the donor, respectively;  $A_{\text{std}}$  and  $A_{\text{sam}}$  the absorbances of the standard and sample solutions at 445 nm, respectively;  $E_{\text{std}}$  and  $E_{\text{sam}}$  are the band areas of the peak at approximately 430 nm (400–440 nm);  $I_{\text{std}}$  and  $I_{\text{sam}}$  are the laser light intensities irradiated on the standard and measured samples, respectively. The standard and sample solutions have refractive indices of 1.42 and 1.47, respectively, and are labelled as  $n_{\text{std}}$  and  $n_{\text{sam}}$ . The difference in the



**Fig. 2** A laser light was irradiated onto a *R*-limonene solution containing DPA and  $\Delta$ - $[\text{Ir}(\text{piq})_2(\text{dmbpy})]^+$  under air. The concentration of DPA was 0 mM (black) and 0.63 mM (red), respectively. The concentration of Ir(III) complex was  $2.4 \times 10^{-5} M$ . The orange and sky blue lines are only *R*-limonene and DPA in *R*-limonene, respectively. A scattered part of a laser light is indicated by \*(asterisk).

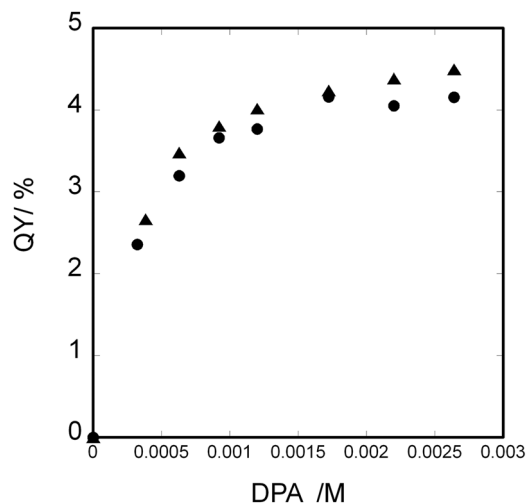


Fig. 3 The DPA dependence of the TTA-UC quantum yield ( $QY = \Phi_{(uc,ref)}$ ) for the system of  $\Delta$ - or  $\Lambda$ -[Ir(piq)<sub>2</sub>(dmbpy)]<sup>+</sup> (donor) and DPA (acceptor) in *R*-limonene under air. Solid triangle and solid circles are for  $\Delta$ - or  $\Lambda$ -enantiomers, respectively.

refractive indices was taken into account. Taking  $\Phi_{std} = 1.2\%$  from the literature<sup>23</sup> for a dichloromethane solution of [Ru(dmbpy)<sub>3</sub>]<sup>2+</sup>/DPA as the standard (Fig. S10 in SI), the quantum yields of up-conversion was determined to be 4–4.5% for the  $\Delta$ - or  $\Lambda$ -[Ir(piq)<sub>2</sub>(dmbpy)]<sup>+</sup>/DPA pair, respectively (Fig. 3). The quantum yields are summarized in Table 2. The same experiments were performed using  $\Delta$ - or  $\Lambda$ -[Ir(piq)<sub>2</sub>(C<sub>n</sub>bpy)]<sup>+</sup> ( $n = 9$  or  $19$ ). Their emission spectra are given in Fig. S5 and S6 (SI). No significant difference was observed for the opposite enantiomers of the donor.

When the power of the laser light was varied, the quantum yield increased quadratically in the initial region, followed by linear increase in the high-laser-power region (Fig. S11 in SI). These results are in agreement with the known dependence of TTA-UC efficiency on laser power.<sup>15</sup>

The same experiments were performed for a pair of [Ir(piq)<sub>2</sub>(C<sub>n</sub>bpy)]<sup>+</sup>/DPA ( $n = 9$  or  $19$ ) as shown in Fig. S5 and S6 (SI). The results are also included in Table 2. It was concluded that the presence of long alkyl chains in a donor lowered the efficiency of TTA-UC. The presence of alkyl chains might interfere the proximity of the donor/acceptor pair in *R*-limonene.

## Experimental section

### Materials

A cationic cyclometalated Ir(III) complex,  $\Delta$ - or  $\Lambda$ -[Ir(piq)<sub>2</sub>(C<sub>n</sub>bpy)]<sup>+</sup> (piqH = 1-phenylisoquinoline, C<sub>n</sub>bpy = 4,4'-dialkyl-2,2'-bipyridine;

dialkyl = dimethyl (C<sub>1</sub>), dinonyl (C<sub>9</sub>), and dinonyldecyl (C<sub>19</sub>) were prepared and optically resolved into  $\Delta$ - and  $\Lambda$ -enantiomers, as described previously.<sup>26–28</sup> The chromatogram in resolving racemic [Ir(piq)<sub>2</sub>(C<sub>19</sub>bpy)]PF<sub>6</sub> is shown in Fig. S1 (SI). The circular dichroism spectra of resolved [Ir(piq)<sub>2</sub>(dmbpy)]<sup>+</sup>, [Ir(piq)<sub>2</sub>(C<sub>9</sub>bpy)]<sup>+</sup> and [Ir(piq)<sub>2</sub>(C<sub>19</sub>bpy)]<sup>+</sup> are shown in Fig. S1 and S2 (SI). DPA was purchased from Tokyo Kasei Ind. Co. (Japan). *R*-limonene was purchased from FUJIFILM Wako Pure Chemical Corporation without purification.

### Instruments

UV-vis spectra were collected using a U-3810 spectrometer (Hitachi, Japan) or UV-vis spectrophotometer (V-730, JASCO Co., Japan). Electronic circular dichroism spectra were measured using a polarimeter J-720 (JAPSCO Co., Japan). An LSP-1000 instrument (Unisoku Co., Japan) was used to measure TTA-UC. A CW laser with an emission power of 0.0–51 mW was used for continuous irradiation at the excitation wavelength of 445 nm. Each sample (0.4 mL) was mounted into a glass tube with a diameter of 5 mm. Signals were accumulated by averaging five scans. Emission decay profile was monitored on irradiating a sample solution by a laser pulse at 355 nm. The emission signals at 600 nm were averaged for 128 pulses. The obtained curves were analyzed under the assumption of a single-exponential decay.

### Solubility measurements

1–5 mg of an enantiomeric or racemic Ir(III) complex as a PF<sub>6</sub> salt was placed in a 5 mL vial. 1 mL of *R*-limonene was added and stirred. The sample was placed for one day at given temperature. The mixture was centrifuged. The residue of an unresolved complex was ascertained to be present at the bottom. The UV-vis spectrum of a filtrate was measured using a quartz cell of 2 mm optical path. The concentration of a solubilized iridium(III) complex was determined from the absorbance at 430 nm ( $\epsilon = 4800$ ).

## Conclusions

Triplet-triplet annihilation up-conversion (TTA-UC) was performed in *R*-limonene for the donor/acceptor pair of  $\Delta$ - (or  $\Lambda$ -) [Ir(piq)<sub>2</sub>(dmbpy)]<sup>+</sup>/DPA. The chiral forms of the complex were soluble enough to detect emission. As a result, the UC quantum efficiency of 4.5% was achieved under air. No difference in efficiency was observed between the opposite enantiomers. Attaching two long alkyl chains to the iridium(III) complex increased solubility while decreasing the efficiency of TTA-UC by about 3%.

## Author contributions

Akihiko Yamagishi: writing – original draft, conceptualization, validation, methodology, investigation, and data curation. Jun Yoshida: writing – reviewing, and editing, conceptualization, validation, visualization, investigation, data curation, funding acquisition, and formal analysis. Hisako Sato: writing – original

Table 2 The quantum yield (QY) for the ATT-UC of photon energy

Ir(III) complexes	$\Phi_{(uc,ref)}$ (QY) for $\Delta$ -isomer (%)	$\Phi_{(uc,ref)}$ (QY) for $\Lambda$ -isomer (%)
[Ir(piq) <sub>2</sub> (dmbpy)] <sup>+</sup>	4.5	4.2
[Ir(piq) <sub>2</sub> (C <sub>n</sub> bpy)] <sup>+</sup> ( $n = 9$ )	3.6	3.3
[Ir(piq) <sub>2</sub> (C <sub>n</sub> bpy)] <sup>+</sup> ( $n = 19$ )	3.3	2.6

draft, conceptualization, data curation, methodology, investigation, and funding acquisition.

## Conflicts of interest

There are no conflicts to declare.

## Data availability

The data supporting this article have been included as part of the supplementary information (SI) and the digital data of this study are available from the corresponding authors upon reasonable request. Supplementary information: chromatogram for optical resolution; electronic circular dichroism spectra; solubility; emission spectra of *R*-limonene solution containing Ir(III) complex and DPA under air; S–V plots of *R*-limonene solution; UV-vis spectra containing Ir(III) complex and DPA; lifetime of Ir(III) complexes; standard emission spectra; dependence of up-conversion efficiency on the intensity of laser light. See DOI: <https://doi.org/10.1039/d5cp03773e>.

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