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**SUSTAINABLE JET FUELS FROM CO₂ BY
MICRO-ALGAL CELL FACTORIES IN A ZERO
WASTE APPROACH**

ALFAFUELS

**Deliverable number & title: D4.3 – Triplet
sensitizer QD performance**

Lead Beneficiary: UU

**Authors: Sindhuja Vajravel, Martin Axelsson,
Haining Tian, and Henrik Ottosson**

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Contributors		
Authors	Organisation name	E-mail
Sinhuja Vajravel	Uppsala University	sindhuja.vajravel@kemi.uu.se
Martin Axelsson	Uppsala University	martin.axelsson@kemi.uu.se
Haining Tian	Uppsala University	haining.tian@kemi.uu.se
Henrik Ottosson	Uppsala University	henrik.ottosson@kemi.uu.se
Reviewers	Organisation name	E-mail
Ylva Bruce	RISE Processum AB	ylva.bruce@ri.se
Charilaos Xiros	RISE Processum AB	charilaos.xiros@ri.se

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1. Executive summary

This report outlines the synthesis and characterization of potential photocatalysts for converting isoprene, a fuel precursor, into dimers, which serve as jet fuel molecules. The work follows the objectives set in the ALFAFUELS project.

The primary goal was to synthesize lead halide quantum dots (QDs), a class of perovskite nanomaterials with promising photocatalytic properties for isoprene dimerization. Among the different halide-based QDs, cesium lead bromide (CsPbBr_3) was identified as the most suitable candidate due to its bandgap energy, which aligns well with isoprene for efficient photocatalytic conversion.

CsPbBr_3 QDs were synthesized, purified, and processed into a form suitable for catalytic conditions. The materials were then characterized using various spectroscopic techniques to confirm their optical properties, ensuring that the synthesized QDs matched the expected characteristics.

The successful synthesis and characterization of these materials lay the foundation for further development of the photochemical reaction of isoprene, a crucial step in producing the final jet fuel product.

2. Acronyms and abbreviations

<i>Term</i>	<i>Abbreviation</i>
Quantum dot	QD
Cesium Lead Bromide	CsPbBr_3
Lead Halide Perovskite (X = Halide Ion)	PbX_3
Ultraviolet-visible	UV-Vis
Photoluminescence	PL
Excitation Wavelength	λ_{exc}
Oleic Acid	OA
Oleyl Amine	OLA

1-Octadecene	ODE
Triplet Energy Transmitter	TET
Light-Emitting Diode	LED
Gas Chromatography-Mass Spectrometry	GC-MS
Proton Nuclear Magnetic Resonance Spectroscopy	¹ H NMR
Full Width at Half Maximum	FWHM
National Television System Committee (color standard)	NTSC
Sustainable Aviation Fuel	SAF

3. Introduction

This document describes Deliverable 4.3, which focuses on the synthesis of quantum dots, one type of photocatalyst proposed in the ALFAFUELS project. To obtain the final jet fuel from photosynthetically produced isoprene by cyanobacteria, a key step is the light-induced dimerization process. These cyanobacteria can convert water and CO₂ into small hydrocarbons, including isoprene (1, 2). Isoprene has the advantage of being easily separated due to its high volatility and does not interfere with cell metabolism as larger molecules do. The catalyst that enables the photodimerization reaction must have certain properties, such as strong sunlight absorption, high photostability, long-lived excited states, efficient charge transport, and versatility in design, along with sufficient energy to facilitate the reaction. Ideally, the catalyst should also be inexpensive, easy to prepare, and abundant to enable scalable production.

A class of material that could fulfil all of the requirements are cesium lead bromide quantum dots (CsPbBr₃-QD). CsPbBr₃-QDs are a type of lead halide (PbX₃) perovskite nanomaterial with a size range of 1-100 nm. The bandgap can be tuned by halide ratio, as larger halide anions increase cell volume and decrease bandgap, covering the visible spectrum (3,4,5) (Figure 1). The halide ratio is determined by the starting materials or post-synthesis anion exchange (6,7). The bandgap also depends on QD size due to the quantum confinement effect (8); as QD size decreases, confinement increases,

leading to a larger bandgap. These CsPbBr₃-QDs are easy to prepare by hot injection method by using cheap starting materials such as PbBr₂ and Cs₂CO₃ (9). Colloidal CsPbX₃ QDs, first explored by Protescu et al. (9), have demonstrated promising optoelectronic properties for various applications (10, 11). Their advantages include a tunable bandgap (405–700 nm), wide excitation, narrow-band emission (FWHM = 12–42 nm), high color gamut (up to 140% NTSC), defect tolerance, and minimal self-absorption. The goal of this initial part of the project was to synthesise a wide array of possible catalyst materials and test them as photocatalysts for the photodimerization of isoprene under visible light.

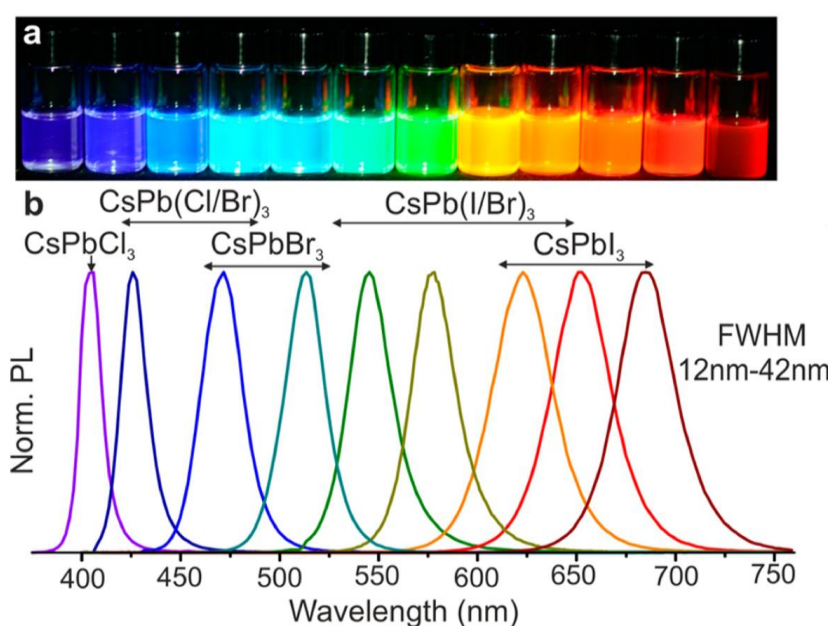
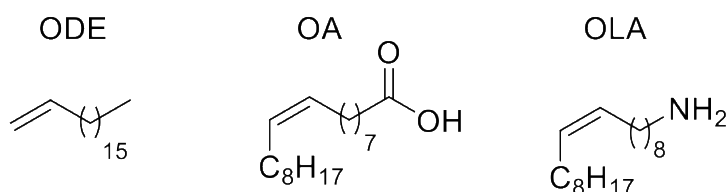
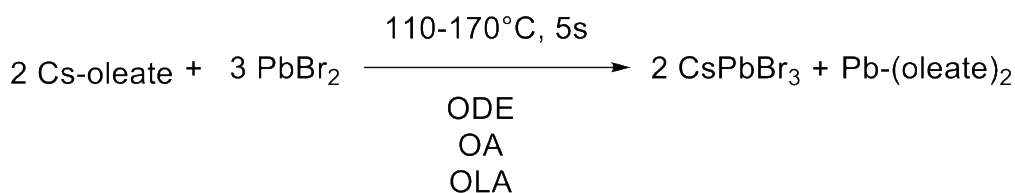


Figure 1: Size and composition dependence of colloidal lead halide perovskite CsPbX₃ QDs. (a) Colloidal solutions in toluene under UV lamp ($\lambda=365$ nm); (b) representative photoluminescence (PL) spectra ($\lambda_{exc}=400$ nm, except 350 nm for CsPbCl₃ sample). Ref. (9)

4. Quantum dot synthesis



The CsPbBr₃ QDs were synthesized using a modified hot-injection method (9), ensuring high size control, which is crucial for their optoelectronic properties. First, a Cs-oleate precursor solution was prepared by mixing Cs₂CO₃ (131 mg, 0.398 mmol), oleic acid (0.4 mL), and 1-octadecene (6.4 mL) in a 25 mL Schlenk tube, vacuum-drying at 120°C for 1 h, and heating under an Ar atmosphere until gas formation ceased. Separately, PbBr₂ (488 mg, 1.30 mmol), OA (3.5 mL), oleylamine (3.5 mL), and ODE (35 mL) were vacuum-dried under the same conditions and heated under Ar at different temperatures ranges from 110-170°C to tune QD size. The Cs-oleate solution was heated to the desired temperature, and 4.2 mL (0.49 mmol) was quickly injected into the PbBr₂ solution, stirred for 5 sec, and immediately cooled in an ice-water bath. The resulting yellow-greenish crude solution was warmed to room temperature, followed by centrifugation at 1100 rcf (3500 rpm, 11 cm) for 10 min to remove larger aggregates and unreacted salts. The supernatant was transferred to a pre-weighed centrifuge tube, and acetone (ODE:Acetone = 1:1 by volume) was added as an anti-solvent to induce precipitation. The mixture was centrifuged at 6440 rcf (8000 rpm, 9 cm) for 5 min, and the QD precipitate was collected, weighed, and redispersed in dry pentane.

5. Quantum dots characterization

To confirm the successful synthesis of CsPbBr₃ QDs, various characterization techniques were used. The QDs were synthesized using a hot injection method, allowing control over their size and bandgap energy by adjusting the synthesis temperature and duration. To analyze their optical properties, QDs were synthesized at three different temperatures,

and their absorption and photoluminescence (PL) were measured. UV-Vis absorption spectroscopy confirmed that absorption occurred between 400–500 nm (Figure 2), aligning with reported values. Among the samples, the QDs with absorption near 400 nm exhibited a greenish yellow color, indicating a shift toward the visible spectrum. PL measurements showed that the QDs emitted light between 425–550 nm when excited at 385 nm (Figure 2). As the synthesis temperature increased, both absorption and PL peaks shifted to longer wavelengths (redshift), indicating a decrease in bandgap energy due to the quantum confinement effect. The adiabatic triplet energy of isoprene was calculated at the (U)B3LYP/6-311+G(d,p) level to be 2.57 eV for the s-trans isomer and 2.19 eV for the s-cis isomer, corresponding to wavelengths of 482 nm and 565 nm, respectively. These values matched well with the emissions of CsPbBr₃-QDs and were consistent with a previous report (9). These results confirm that CsPbBr₃-QDs absorb and emit within the visible light range, suggesting their potential for isoprene photodimerization. However, further investigation is needed to assess their full suitability for this application.

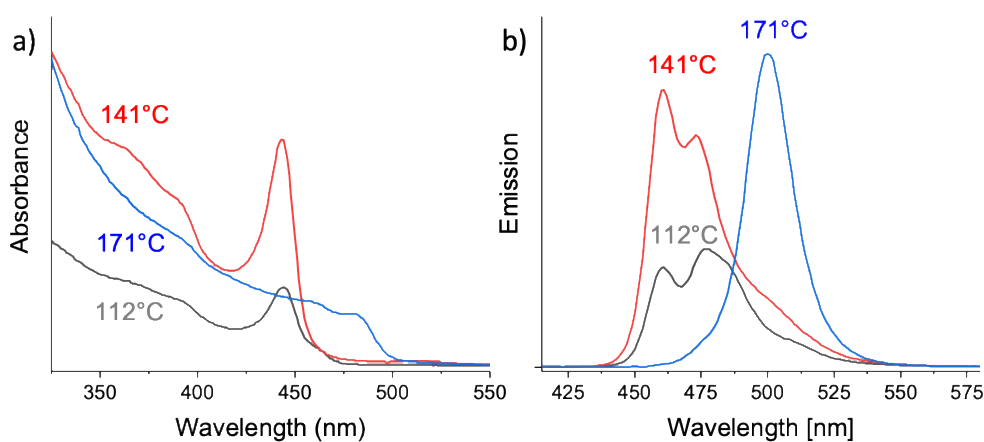


Figure 2: Colloidal CsPbBr₃-QDs. (a) Absorption spectra. (b) PL spectra at room temperature (RT).

6. Catalytic tests

6.1. Photodimerization of isoprene – Reaction setup

The reaction mixture was prepared by combining the QD solution with inhibitor-free, degassed isoprene. The solution was purged with argon and

sonicated for 1 min to remove residual oxygen. The samples were then illuminated using 410 nm monochromatic light in the Rayonet reactor, 400–500 nm LEDs ($\lambda_{\text{max}} = 460$ nm), and natural sunlight. The resulting dimers were isolated by filtration, dissolved in pentane, and analyzed by GC-MS and ^1H NMR in chloroform-D.

6.1.1. Isoprene dimer formation under visible LEDs

The photocatalytic performance of the synthesized QDs for isoprene photodimerization was evaluated under visible-light conditions. Initial tests under monochromatic 410 nm light in the Rayonet reactor showed no dimer formation, indicating that this wavelength was not effective for the reaction. When exposed to 400–500 nm LEDs with a peak wavelength of 460 nm, only trace amounts of dimers were detected (Figure 3). This limited dimerization could be attributed to the presence of capping ligands on the QDs, which may have caused steric hindrance, restricting isoprene access to the QD surface. To improve dimerization efficiency, further optimization was conducted using light with a maximum wavelength of 460 nm.

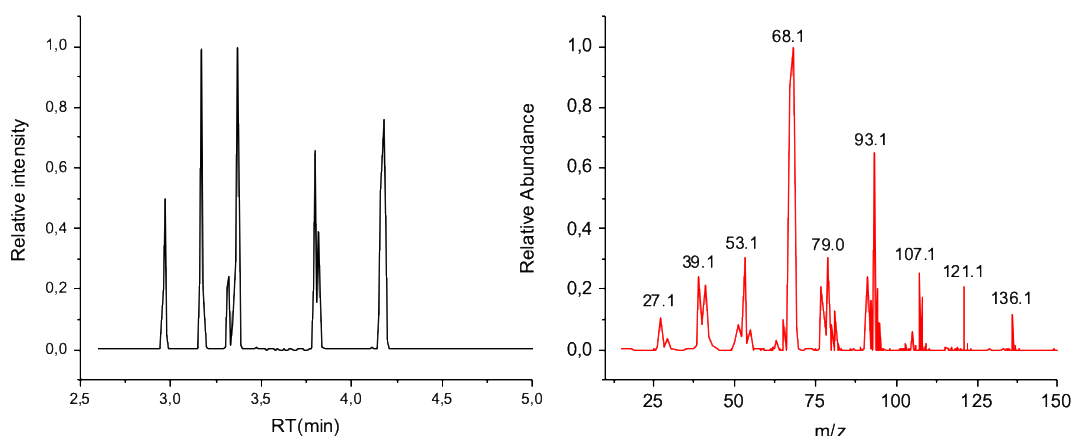


Figure 3: The chromatograms (left) and mass spectra (right) illustrate isoprene dimers formed via photosensitized dimerization using CsPbBr₃-QDs under LED light ($\lambda_{\text{max}} = 460$ nm). The dimers exhibit retention times ranging from 2.95 to 4.28 min.

6.1.2. Enhancing isoprene photodimerization using QDs and TETs

To improve isoprene photodimerization under visible light, triplet energy transmitters (TETs) were integrated with QDs. The reaction mixture was prepared by combining the triplet energy transmitter (TET) and QD solutions and sonicated for 60 min. The solvents were removed by flow-drying, yielding a QD-TET mixture. The rest of the reaction setup with isoprene followed the procedure described in Section 6.1. TETs stabilized QDs by preventing aggregation and possessed high triplet energy levels that matched well with isoprene, enabling efficient energy transfer. Their non-polar aromatic rings created a hydrophobic surface, bringing isoprene closer to the QD for enhanced interaction. This approach resulted in 85% dimer yield (Figure 4), representing a 15-fold increase, compared to QDs alone.

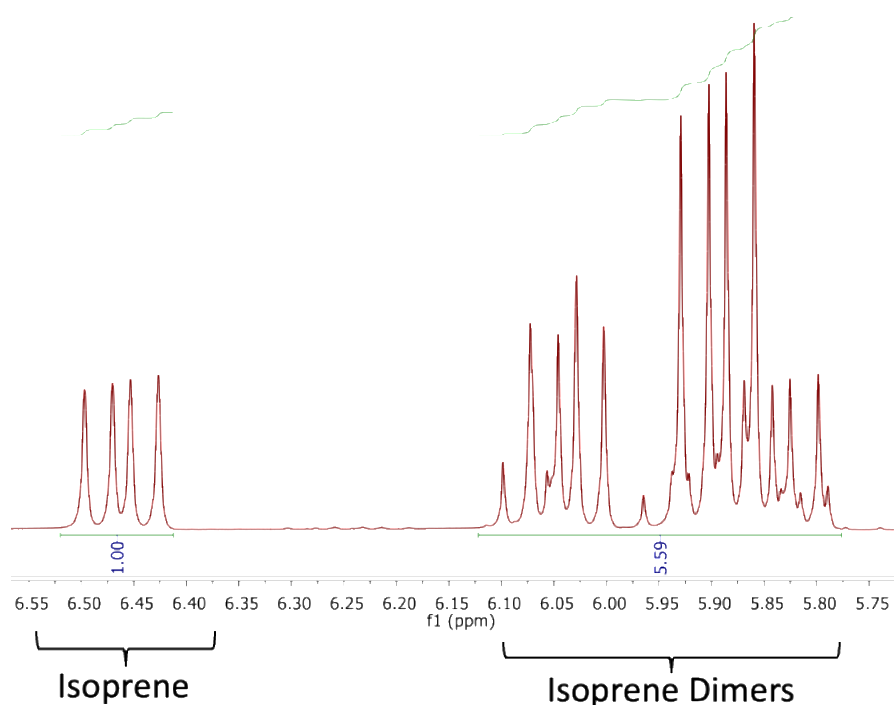


Figure 4: The partial ^1H NMR spectra of isoprene dimers (alkene chemical shift region) obtained from the photodimerization of isoprene using CsPbBr_3 QDs with TET as a photosensitizer under LED irradiation ($\lambda_{\text{max}} = 460$ nm).

6.1.3. Isoprene dimer formation under natural sunlight experiments

To test the feasibility of scaling up the reaction under natural sunlight, experiments were conducted at different locations and reaction volumes: Experiments on isoprene dimer formation using QD as a photocatalyst were conducted at three locations: RISE Processum AB, Örnsköldsvik, Sweden, August 2024; Uppsala, Sweden, September 2024; and IISER, Trivandrum, India, February 2025. A 60 mL reaction in Uppsala and a larger 1300 mL reaction at RISE, confirmed the formation of isoprene dimers under natural sunlight. However, in Sweden, poor weather and insufficient sunlight limited the reaction duration to a maximum of 6 h and also resulted in a low yield. In contrast, a 6 mL reaction at IISER, Trivandrum, India, under natural sunlight conditions with a similar duration, resulted in a significantly higher yield, 2.4 times greater than the reactions conducted in Sweden (Figure 5). These findings highlight the impact of environmental conditions on isoprene dimer formation efficiency.

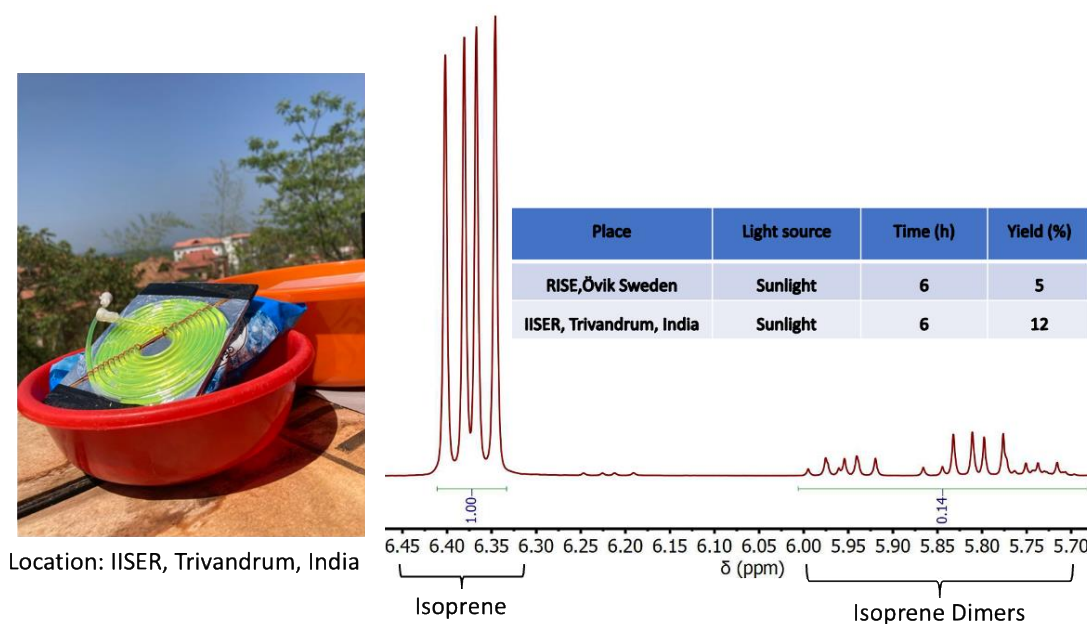


Figure 5: Flat photoreactor system used for sunlight irradiation (left). The partial ^1H NMR spectra (middle) of isoprene dimers (alkene chemical shift region) obtained from the photodimerization of isoprene using CsPbBr_3 QDs with TET as a photosensitizer under natural sunlight irradiation. The table (right) compares the formation yields under sunlight in Sweden (August 2024) and India (February 2025).

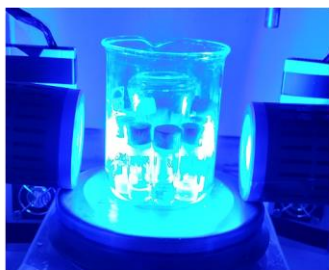
7. Conclusion

CsPbBr₃-QDs present a highly promising approach for visible-light-driven photodimerization of isoprene into jet fuel precursors. While challenges exist, particularly in terms of catalyst stability and Pb toxicity, recent advancements in stabilization strategies, Pb containment, and catalyst recycling make perovskite-based photocatalysis a strong candidate for future sustainable aviation fuel production. For further information on our results, please contact the authors.

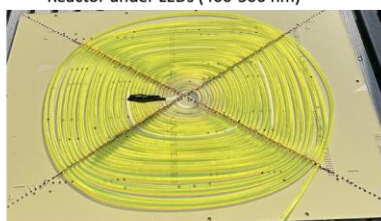
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9. Annexes



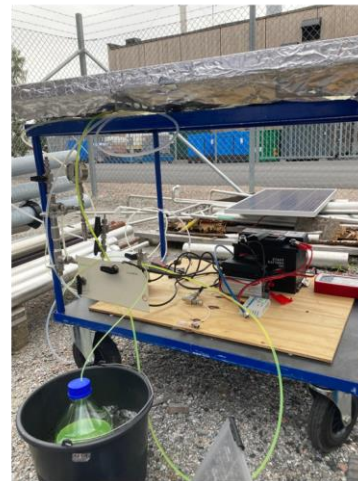
Reactor under LEDs (400-500 nm)



Reactor under Sunlight, Location: Uppsala, Sweden



Reactor under Sunlight, Location: RISE, Örnsköldsvik, Sweden



A1: Reaction setup for the photodimerization of isoprene using CsPbBr_3 QDs as a photocatalyst under LED light (top left). A 60 mL flat photoreactor system used for sunlight irradiation in Uppsala, Sweden (bottom left) in September 2024. A large-scale 1300 mL photoreactor system used for sunlight irradiation in Örnsköldsvik, Sweden (right).