Supplementary Information

Emission Amplification by Sumanene Nanocrystals in an Onigiri-Type Organic–Organic Assembly

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Supporting information

General remark

UV-visible absorption spectra were recorded on a JASCO V-670 spectrometer. Fluorescence spectra were recorded on a JASCO FP6500 spectrometer. ^{1}H and ^{13}C NMR were measured on JEOL JNM-LA500. $CDCl_3$ was used as a solvent and the residual solvent peak was used as an internal standard (^{1}H NMR: 7.26 ppm, ^{13}C NMR: 77.0 ppm). Gel permeation chromatography (GPC) was performed on JAIGEL 1H and 2H using a JAI Recycling Preparative HPLC LC-908W. Transmission electron microscopy (TEM) images were obtained using a JEOL JEM-2100F microscope. Scanning electron microscopy (SEM) images were obtained using a JEOL JSM-6700F microscope. Powder X-ray diffraction (XRD) patterns were recorded on a Rigaku RINT Ultima Ⅲ with CuKα X-ray source and a reflection free sample holder.

Materials

Sumanene (**1**) was synthesized by the reported method.[1] Sumanenetrione (**2**) was synthesized by following the preparation of trimethylsumanenetrione from trimethylsumanene.[2]

To a solution of **1** (1.2 mg, 4.9 μmol) in DMF (5 ml) at -60 °C under argon atmosphere was added a solution of $NaN(SiMe_3)_2$ (1.4 M in THF, 30 μl, 42 μmol). After stirring for 2 h, the solution was bubbled with oxygen gas for 15 min at -60 °C. The reaction was quenched by pouring the reaction mixture into silica gel cooled by liquid nitrogen. The silica gel was filtered and washed by ethyl acetate to give a crude product. The crude products of four batches were combined, and purified by GPC to give **2** (1.3 mg, 4.2 μmol, 21% yield) as an orange solid. The spectral data were identical to those reported.[3]

2: ^{1}H NMR ($CDCl_3$, 500 MHz) δ: 7.40 (s, 6H) ppm. ^{13}C NMR ($CDCl_3$, 125 MHz) δ: 188.2, 149.7, 143.6, 126.6 ppm.

Experimental details

Fabrication of nanocrystalline dispersions.

1. Fabrication of **RS1**.

A THF (5 ml) solution of **1** (1.2 mg, 4.9 μmol) was prepared, and 100 μl of the solution was injected rapidly into vigorous stirred water (10 ml) using a microsyringe at room temperature. Stirrings were continued for 5 seconds after injection, and colorless and clear dispersion was formed.

2. Fabrication of **RS2**.

A THF (5 ml) solution of **2** (1.5 mg, 4.9 μmol) was prepared, and 100 μl of the solution was injected rapidly into vigorous stirred water (10 ml) using a microsyringe at room temperature. Stirrings were continued for 5 seconds after injection, and colorless and clear dispersion was formed.

3. Fabrication of $\mathbf{RS2_{SDS}}$.

A THF (5 ml) solution of **2** (1.5 mg, 4.9 μmol) and an aqueous solution (50 ml) of sodium dodecylsulfate (15 mg, 52 μmol) were prepared, and 100 μl of the THF solution of **2** was injected rapidly into the vigorous stirred SDS aqueous solution (10 ml) using a microsyringe at room temperature. Stirrings were continued for 5 seconds after injection, and colorless and clear dispersion was formed.

4. Fabrication of **AS1-2**.

A THF (5 ml) solution of **1** (1.2 mg, 4.9 μmol) and a THF (5 ml) solution of **2** (1.5 mg, 4.9 μmol) were prepared. 100 μl of the solution of **1** was injected rapidly into vigorous stirred water (10 ml) using a microsyringe at room temperature, and stirrings were continued for 5 seconds after injection. 100 μl of the solution of **2** was injected into that stirred aqueous sample by using a microsyringe, successively. Stirrings were continued for 30 seconds after injection, and colorless and clear dispersion was formed.

5. Fabrication of **AS2-1**.

A THF (5 ml) solution of **1** (1.2 mg, 4.9 μmol) and a THF (5 ml) solution of **2** (1.5 mg, 4.9 μmol) were prepared. 100 μl of the solution of **2** was injected rapidly into vigorous stirred water (10 ml) using a microsyringe at room temperature, and stirrings were continued for 5 seconds after injection. 100 μl of the solution of **1** was injected into that stirred aqueous sample by using a microsyringe, successively. Stirrings were continued for 30 seconds after injection, and colorless and clear dispersion was formed.

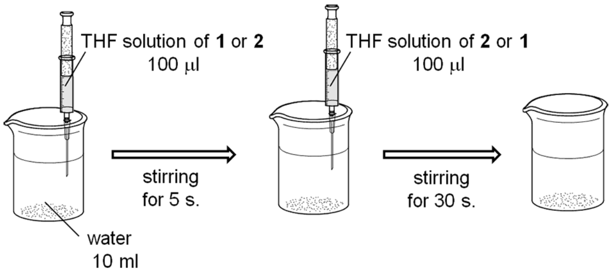

Figure S1. A schematic illustration of the stepwise reprecipitation method**.**

Scanning electron microscopy (SEM)

Samples for SEM observation were prepared as follows: the nanocrystalline aqueous dispersions (**RS1**, **RS2**, $\mathbf{RS2_{SDS}}$, **AS1-2**, and **AS2-1**) were filtered on milipore filters (OMNIPORE membrane filter with pore size of 0.1 μm) and dried *in vacuo*. Filtered nanocrystalline powders were transferred on carbon seal for observation. SEM images were observed at 5.0 kV. Figure S1 shows a SEM image of $\mathbf{RS2_{SDS}}$.

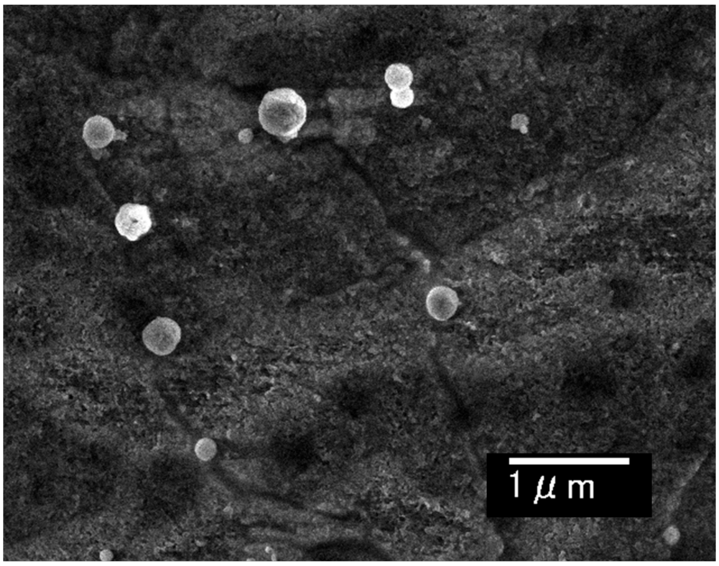

Figure S2. A SEM image of **RS2**$_{\mathbf{SDS}}$.

Transmission electron microscopy (TEM)

Samples for TEM observation were prepared as follows: 2-3 droplets of the nanocrystalline aqueous dispersions (**RS1**, **RS2**, **AS1-2**, and **AS2-1**) were dropped onto grids (200-mesh Cu, Nisshin EM) and dried under atmospheric pressure and *in vacuo*. TEM images were observed at 200 kV.

Powder X-ray diffraction (XRD)

Samples for powder XRD of bulk crystals of **1** and **2** were prepared by grinding the recrystallized crystals. Samples for powder XRD of **RS1**, **RS2**, and **AS2-1** were prepared as follows: 500 ml of the aqueous dispersions of **RS1** and **RS2** were filtered on milipore filters (OMNIPORE membrane filter with pore size of 0.1 μm). The powders were gathered on a reflection free sample holder. Figure S2-S5 show XRD patterns of bulk crystals and **RS1** and **RS2**.

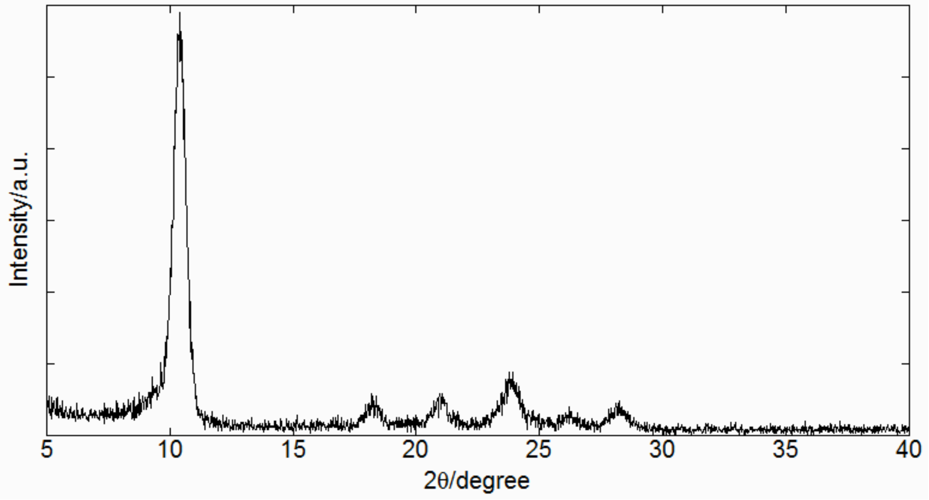

Figure S3. A powder XRD pattern of bulk crystals of **1**.

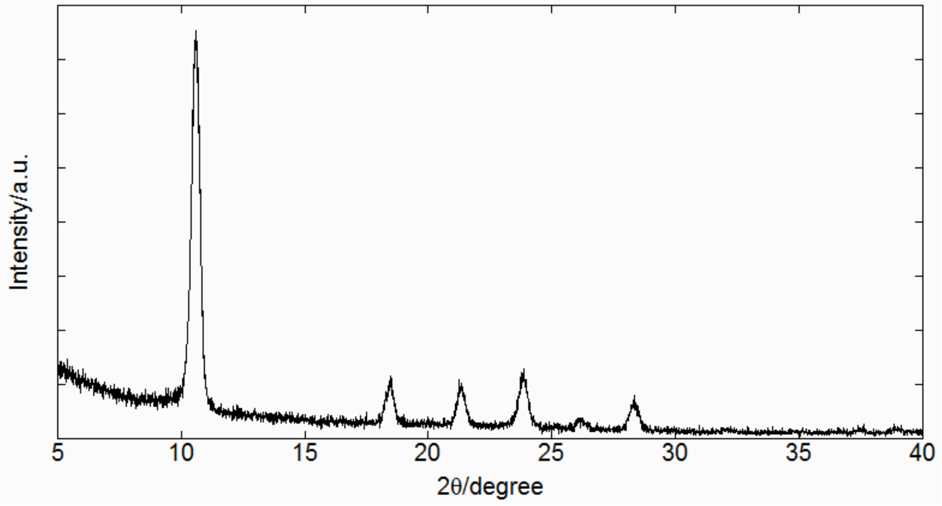

Figure S4. A powder XRD pattern of **RS1**.

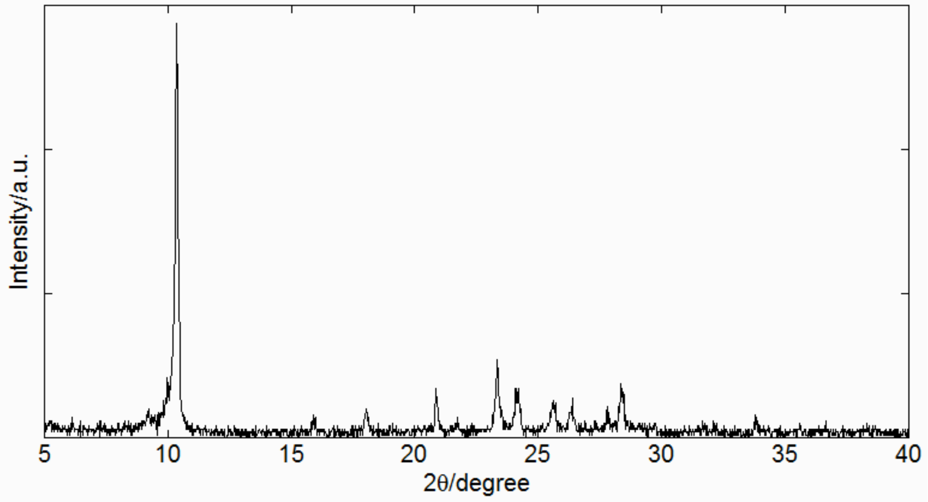

Figure S5. A powder XRD pattern of bulk crystals of **2**.

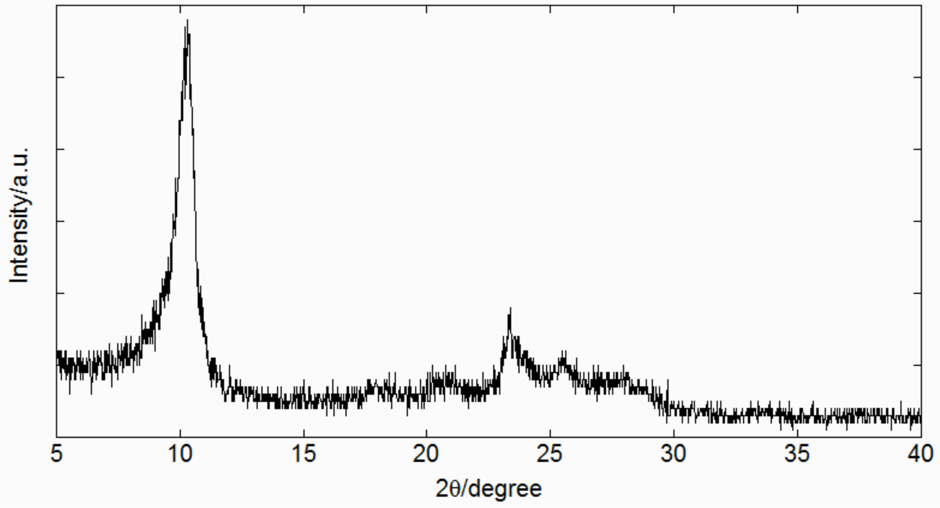

Figure S6. A powder XRD pattern of **RS2**.

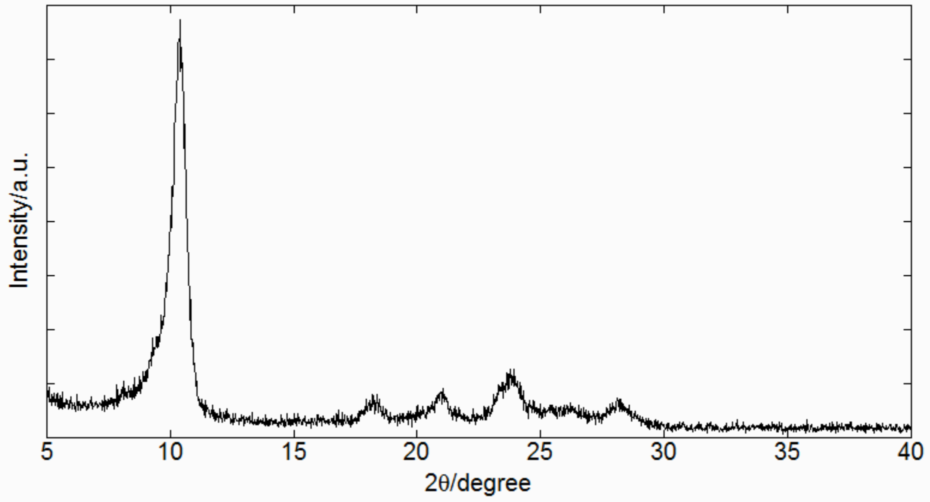

Figure S7. A powder XRD pattern of **AS2-1**.

UV-visible absorption and fluorescence spectra

Absorption and fluorescence spectra of the nanocrystalline aqueous dispersions (**RS1**, **RS2**, **RS2**$_{\mathbf{SDS}}$, **AS1-2**, and **AS2-1**) were observed by standard solution-phase spectroscopic methods.

Figure S6-S10 show absorption spectra of **RS1**, **RS2**, **RS2**$_{\mathbf{SDS}}$, **AS1-2**, and **AS2-1**.

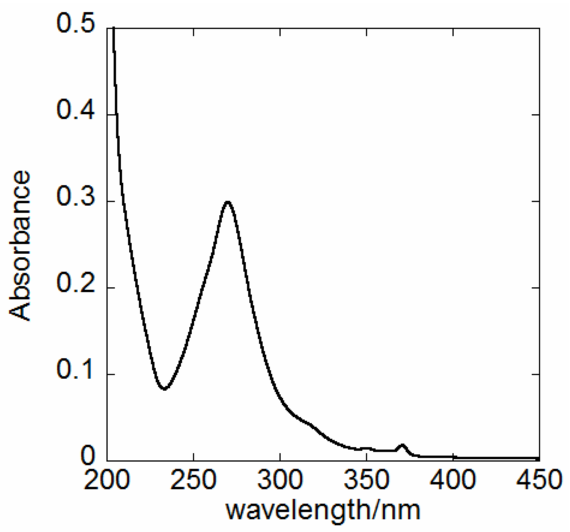

Figure S8. An UV absorption spectrum of **RS1**.

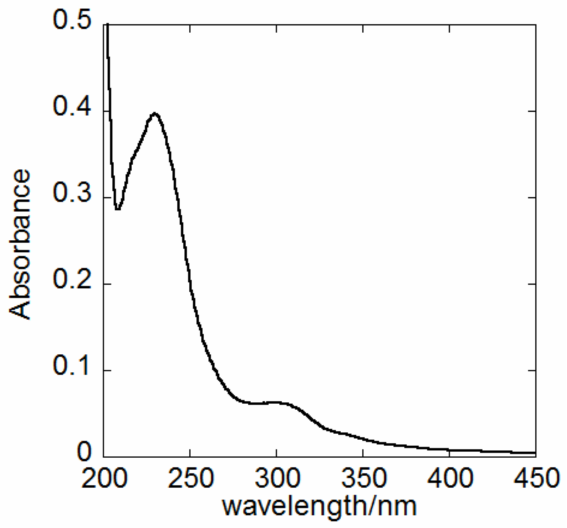

Figure S9. An UV absorption spectrum of **RS2**.

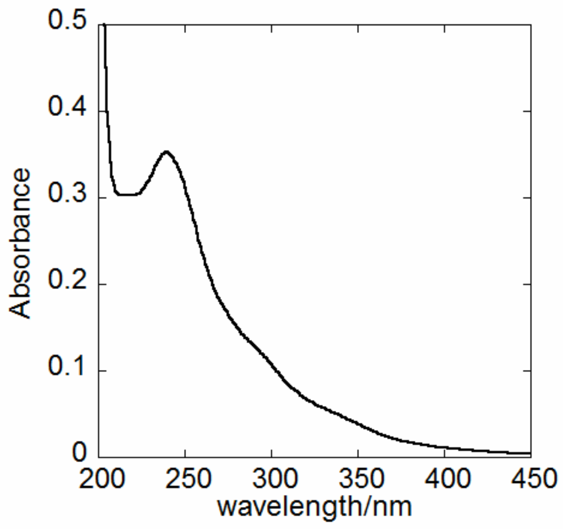

Figure S10. An UV absorption spectrum of $\mathbf{RS2_{SDS}}$.

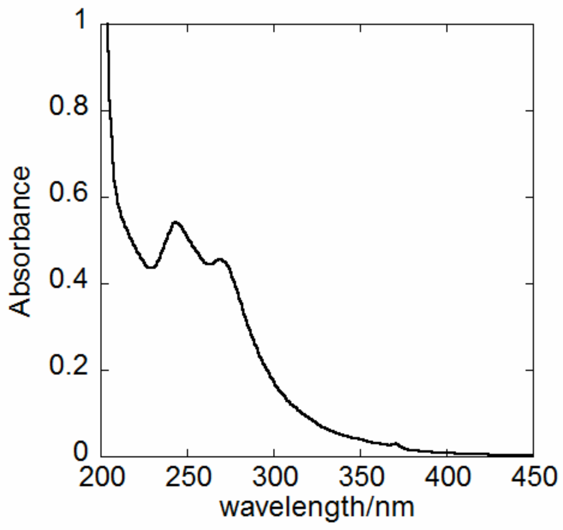

Figure S11. An UV absorption spectrum of **AS1-2**.

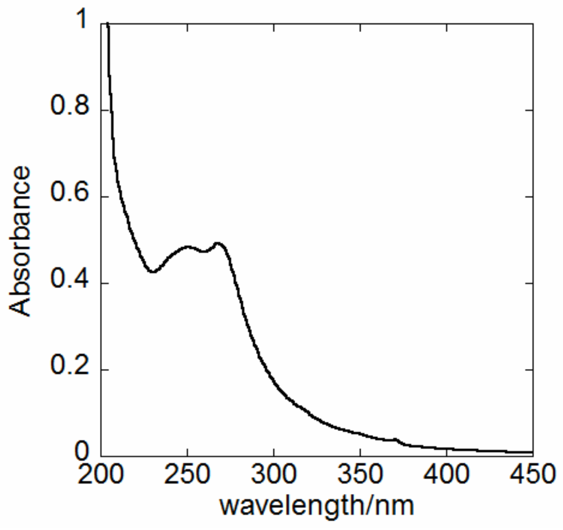

Figure S12. An UV absorption spectrum of **AS2-1**.

Reference

(1) H. Sakurai, T. Daiko, T. Hirao, *Science* 2003, **301**, 1878.

(2) R. Tsuruoka, S. Higashibayashi, T. Ishikawa, S. Toyota, H. Sakurai, *Chem. Lett.* 2010, **39**, 646–647.

(3) T. Amaya, M. Hifumi, M. Okada, Y. Shimizu, T. Moriuchi, K. Segawa, Y. Ando, T. Hirao, *J. Org. Chem.* 2011, **76**, 8049–8052.