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Supporting Information for

Visible-to-UV photon upconversion in air-saturated water by multicomponent co-assembly

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Materials.

All reagents and solvents for synthesis were used as received without further purification otherwise noted. 4-bromophenol, 1,4-phenylenediboronic acid, tetrakis (triphenylphosphine) palladium(0), and trimethylamine (ca. 25% in ethanol) were purchased from TCI, sodium hydride (60% oil dispersion) and Na₂SO₄ was purchased form Wako, and potassium carbonate was purchased from KISHIDA.

All reagents and solvents for measurement were used as received without further purification. Bis[2-(4,6-difluorophenyl)pyridinato-C2,N](picolinato)iridium(III) (FIrpic) was purchased from Sigma-Aldrich. Sodium decanoate (Dec) was purchased from TCI Analytical grade methanol was purchased from Wako Pure Chemical and deionized water was generated by Direct-Q UV (Merck Millipore). For sample preparation of TTA-UC measurements, all the solids (A1, FIrpic and Dec) were first dissolved in methanol. After evaporating methanol, deionized water was added, and the aqueous dispersions were generated via ultrasonication and heating. The deaeration of the aqueous dispersion was conducted by repeated freeze-pump-thaw cycles.

Characterizations.

¹H NMR (400 MHz) spectra were measured on a JEOL JNM-ECZ 400 using TMS as the internal standard. Elemental analysis was conducted by using Yanaco CHN Corder MT-5 at the Elemental Analysis Center, Kyushu University. UV-vis absorption spectra were recorded on JASCO V-670 and V-770 spectrophotometers. Luminescence spectra were measured by using an FP-8300 fluorescence spectrometer. The absolute fluorescence quantum yield was measured in an integrating sphere using a Hamamatsu Photonics absolute quantum yield measurement system. Dynamic light scattering (DLS) and zeta potential measurements were carried out by using a Malvern Nano-ZS ZEN3600. Scanning electron microscopy (SEM) images were measured by using a HITACHI FE-SEM SU9000. The aqueous dispersion of A1-FIrpic-Dec ([A1] = 10 mM [FIrpic] = 100 μ M [Dec] = 80 mM) was cast on a TEM grid and dried in air.

TTA-UC measurements.

For TTA-UC emission measurements, a diode laser (445 nm, 75 mW, RGB Photonics) was used as the excitation laser source. The laser power was controlled by combining a software (Ltune) and a variable neutral density filter and measured using a PD300-UV photodiode sensor (OPHIR Photonics). The laser beam was focused on the sample using a lens. The diameter of the laser beam ($1/e^2$) was measured at the sample position using a CCD beam profiler (SP620, OPHIR Photonics). The typical laser size was 3.93×10^{-4} cm². The emitted light was collimated by an achromatic lens, the excitation light was removed using short pass filters (425 nm and 400 nm), and the emitted light was again focused by an achromatic lens to an optical fiber connected to a multichannel detector (MCPD-9800, Otsuka Electronics). UC Photoluminescence decays of A1 were measured using a UNISOKU TSP- 2000 system. The TTA-UC efficiency (100% is set as a maximum) was measured by using an absolute quantum yield measurement system specially built by Hamamatsu Photonics. The sample was held in an integrating sphere and excited by the laser excitation source (445 nm, 75 mW, RGB Photonics). The scattered excitation light was removed using a 420 nm short-pass filter and emitted light was monitored with a multichannel detector. The spectrometer was calibrated including the integration sphere and short-pass filter by Hamamatsu Photonics.

Scheme S1. Synthesis of Acceptor (A1)



Synthesis of 1

A dispersion of 4-bromophenol (519 mg, 3.0 mmol), 1,4-phenylenediboronic acid (166 mg, 1.0 mmol), potassium carbonate (829 mg, 6.0 mmol), and tetrakis (triphenylphosphine) palladium(0) (60 mg, 0.052 mmol) in 5.0 ml methanol was heated by microwave at 80 °C for 12 h. The resulting dispersion was washed several times with ethyl acetate and water, dried over anhydrous Na₂SO₄. The solvent was removed under reduced pressure, and the product was purified by silica gel column chromatography (Hexane/THF = 1/1). The product was purified by recrystallization in acetonitrile to give colorless crystals of **1**. (yield: 46 %).

¹H NMR (400 MHz, DMSO-d₆, TMS standard): δ (ppm) = 6.86-6.84, (d, 4H), 7.52-7.50, (d, 4H), 7.61, (s, 4H), 9.53, (s, 2H).

Synthesis of 2

1 (50 mg, 0.19 mmol) was placed in a 100 ml flask under N_2 , and 15 ml of dehydrated DMF was added. The solution was stirred at 0 °C under N_2 , and then sodium hydride (28 mg, 1.15 mmol) was

added. After 30 minutes, 1,6-dibromohexane (464 mg, 1.9 mmol) was added and stirred at 65 °C for a day. The resulting dispersion was washed several times with chloroform and water, and the organic layer was condensed by evaporation. Methanol was added into this dispersion and filtered. Resulting solid was recrystallized in toluene to obtain colorless crystal of **2** (yield: 63 %).

¹H NMR (400 MHz, CDCl₃, TMS standard): δ (ppm) = 1.93-1.81, (m, 8H), 3.45-3.42, (t, 3H), 4.03-4.00, (t, 3H), 6.99-6.96, (d, 4H), 7.57-7.54, (d, 4H), 7.60, (s, 4H).

Synthesis of A1

2 (30 mg, 0.051 mmol) was dispersed in 5 ml of trimethylamine ethanol solution. The dispersion was heated by microwave at 80 °C for 24 h. The resulting dispersion was dried by evaporation and dispersed in hot methanol. The dispersion was filtered and the filtrate was evaporated to obtain A1 (yield: 88 %).

¹H NMR (400 MHz, methanol-d₄, TMS standard): δ (ppm) = 1.42-1.35, (m, 4H), 1.57-1.49, (m, 4H), 1.80-1.71, (m, 8H), 3.03, (s, 18H), 3.97-3.94, (t, 4H), 6.91-6.89, (d, 4H), 7.49-7.47, (d, 4H), 7.52, (s, 4H).

Elemental analysis for $C_{72}H_{110}Br_4N_4O_5$: calculated (%) H 7.75 C 60.42 N 3.91 ; found (%) H 7.81 C 60.47 N 3.78.



Figure S1. An outline of the TTA-UC process.



Figure S2. (a) Concentration-dependent UV-vis absorption spectra of A1 in methanol ([A1] = 0.25-0.002 mM in methanol). (b) The absorbance of A1 at 293.5 nm at different concentrations. The fitting result is shown as a red line according to the following equation, y = Ax+B. The observed linearity supports the molecularly-dispersed state of A1 in methanol in the examined concentration range.



Figure S3. UV-vis absorption and fluorescence spectra of A1 in methanol ([A1] = 0.25 mM, $\lambda_{ex} = 241$ nm).



Figure S4. DLS profile of **A1**-Dec in water ([**A1**] = 10 mM, [Dec] = 80 mM). The average particle size was 1282±40nm.



Figure S5. SEM images of A1-FIrpic-Dec.



Figure S6. Excitation spectra of A1 in methanol (black, [A1] = 0.25 mM, $\lambda_{dt} = 360 \text{ nm}$) and A1-FIrpic-Dec in water (red, [A1] = 10 mM, $[FIrpic] = 100 \text{ }\mu\text{M}$, [Dec] = 80 mM, $\lambda_{dt} = 390 \text{ nm}$).



Figure S7. UC emission decay of A1-FIrpic-Dec at 390 nm ([A1] = 10 mM [FIrpic] = 100 μ M [Dec] = 80 mM, λ_{ex} = 445 nm). Red line is a fitting result with y = A*exp(-2(x-x_0)/\tau_T) + y_0, where τ_T is triplet lifetime and y₀ is baseline. The triplet lifetime τ_T of A1 was estimated as 24 μ s.