Electronic Supplementary Information (ESI) for

Translating MOF chemistry into supramolecular chemistry: soluble coordination nanofibers showing efficient photon upconversion

Masanori Hosoyamada,[a] Nobuhiro Yanai,*[a,b] Keisuke Okumura,[a] Takayuki Uchihashi,[c] and Nobuo Kimizuka*[a]

[a]Department of Chemistry and Biochemistry, Graduate School of Engineering, Center for Molecular Systems (CMS), Kyushu University, 744 Moto-oka, Nishi-ku, Fukuoka 819-0395, Japan.

[b]PRESTO, JST, Honcho 4-1-8, Kawaguchi, Saitama 332-0012, Japan.

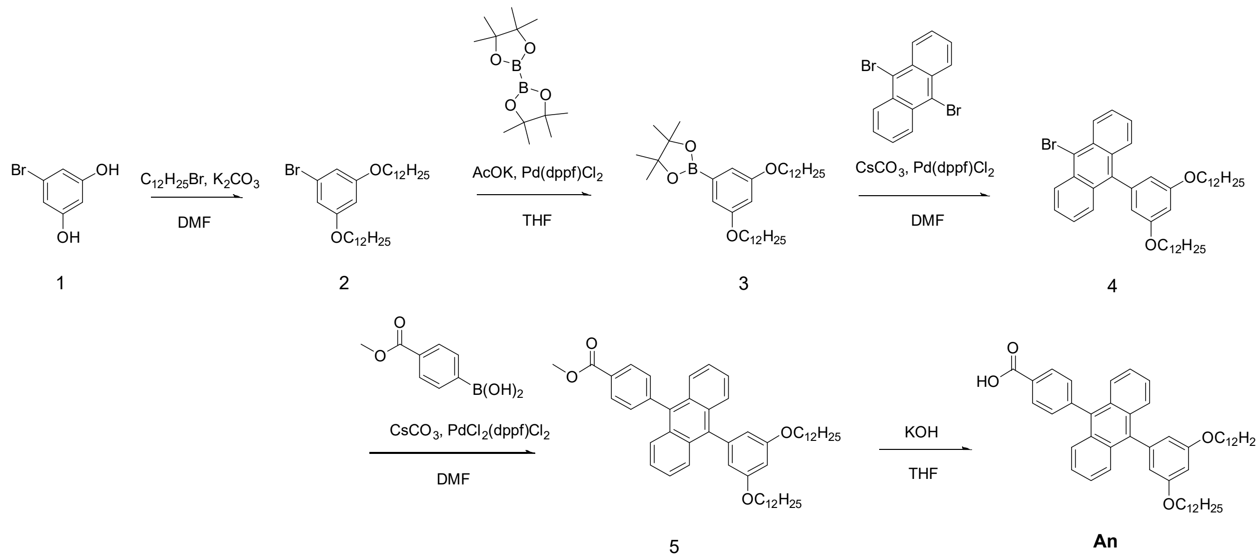
[c]Department of Physics, Nagoya University, Furo-cho, Chikusa-ku, Nagoya, 464-8602, Japan

E-mail: yanai@mail.cstm.kyushu-u.ac.jp; n-kimi@mail.cstm.kyushu-u.ac.jp.

1. Experimental Section

Materials. All reagents and solvents for synthesis were used as received without further purification.

Scheme S1. Synthetic routes of **An**



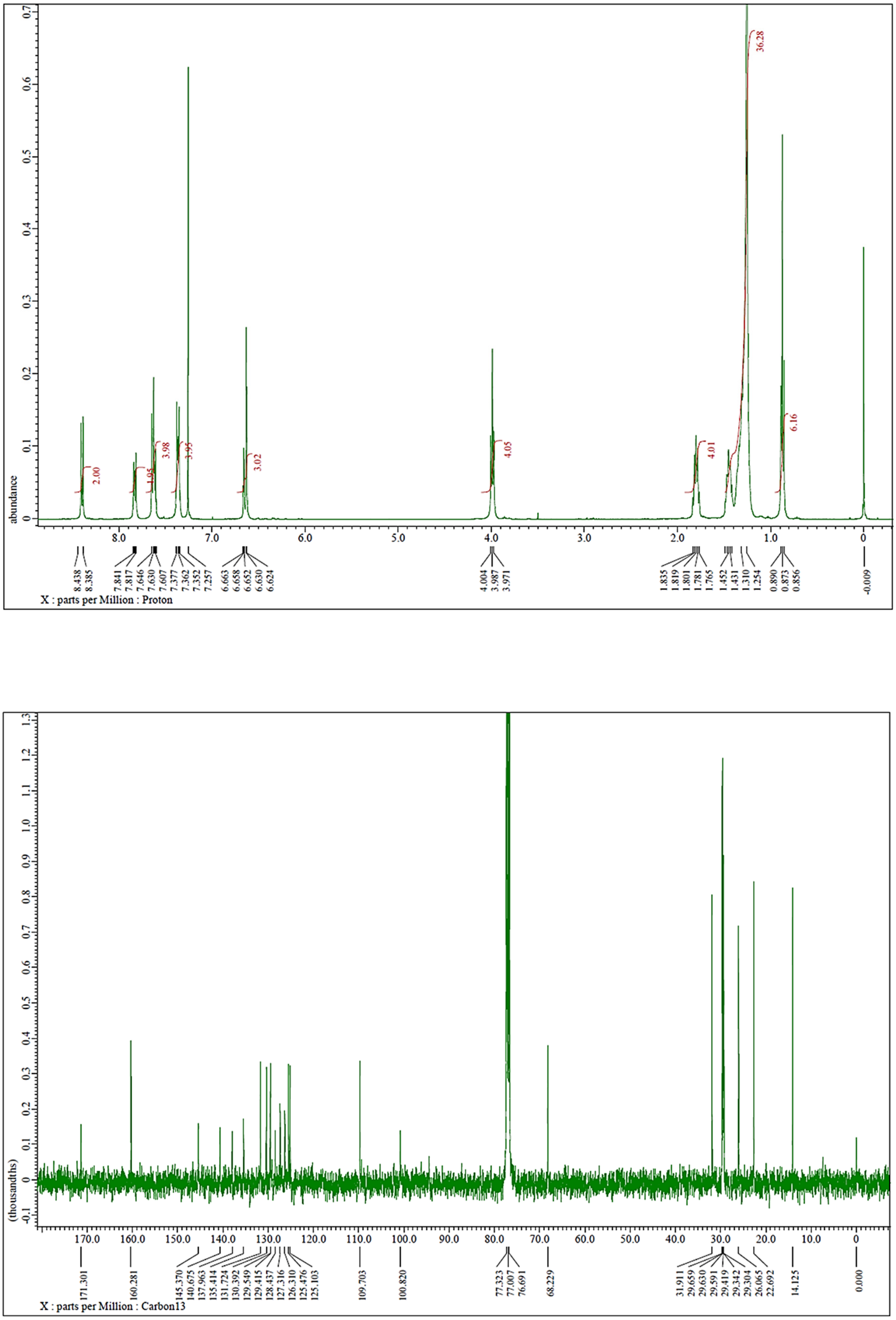
Synthesis of 1-bromo-3,5-bis(dodecyloxy)benzene (2). To a solution of 5-bromoresorcinol (1.0 g, 5.3 mmol) and potassium carbonate (2.8 g, 21.2 mmol) in 15 mL of N,N-dimethylformamide (DMF), 1-bromododecane (2.9 g, 11.6 mmol) was added. The reaction mixture was stirred for 5 h at 80 ºC. The mixture was added to 100 mL of H_2O and washed with hexane (3 x 50 mL). The organic phase was dried over sodium sulfate and evaporated under reduced pressure. The resulting crude product was purified by column chromatography (SiO_2, CH_2Cl_2) to give a pale yellow liquid. Yield: 2.8 g (99%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 6.64-6.63(d, 2H), 6.37-6.36 (t, 1H), 3.91-3.87 (t, 3H), 1.77-1.72 (m, 4H), 1.44-1.26 (m, 36H), 0.90-0.86 (t, 6H).

Synthesis of 2-(3,5-bis(dodecyloxy)phenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3). To a solution of **2** (2.8 g, 5.3 mmol), bis(pinacolate)diboron (2.0 g, 8.0 mmol) and potassium acetate (1.6 g, 15.9 mmol) in 20 mL of THF, Pd(dppf)Cl_2 (0.21 g, 0.27 mmol) was added. The reaction mixture was refluxed for 5 h under N_2 atmosphere. The mixture was added to 100 mL of H_2O and washed with $CHCl_3$ (3 x 100 mL). The organic phase was dried over sodium sulfate and evaporated under reduced pressure. The resulting crude product was purified by column chromatography (SiO_2, CH_2Cl_2:hexane = 2:3) to give a pale yellow liquid. Yield: 1.6 g (51%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 6.93-6.92(d, 2H), 6.56-6.55 (t, 1H), 3.96-3.93 (t, 3H), 1.80-1.75 (m, 4H), 1.44-1.27 (m, 48H), 0.90-0.86 (t, 6H).

Synthesis of 9-(3,5-bis(dodecyloxy)phenyl)-10-bromoanthracene (4). To a suspension of **3** (1.6 g, 2.7 mmol), dibromoanthracene (2.7 g, 8.1 mmol), cesium carbonate (2.7 g, 8.3 mmol) in 10 mL of DMF, Pd(dppf)Cl_2 (70 mg, 0.08 mmol) was added. The reaction mixture was stirred for 10 h at 100 ºC under N_2 atmosphere. The mixture was added to 100 mL of H_2O and washed with $CHCl_3$ (3 x 100 mL). The organic phase was dried over sodium sulfate and evaporated under reduced pressure. The resulting crude product was purified by column chromatography (SiO_2, CH_2Cl_2:hexane = 1:10) to give a yellow liquid. Yield: 1.2 g (61%). ^1H NMR (300 MHz, $CDCl_3$): δ 8.62-8.57 (d, 2H), 7.77-7.74 (d, 2H), 7.61-7.55 (m, 2H), 7.41-7.35 (m, 2H), 6.63-6.62(t, 1H), 6.54-6.53 (d, 2H), 3.98-3.93 (t, 3H), 1.82-1.73 (m, 4H), 1.45-1.25 (m, 36H), 0.89-0.85 (t, 6H).

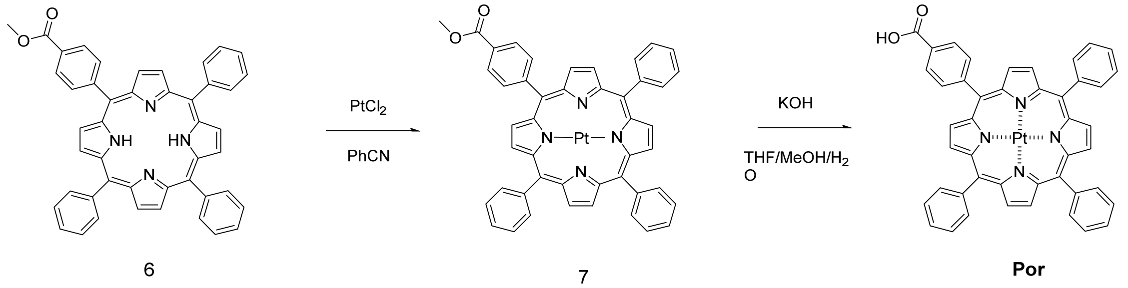
Synthesis of methyl 4-(10-(3,5-bis(dodecyloxy)phenyl)anthracen-9-yl)benzoate (5). To a solution of **4** (1.1 g, 1.7 mmol), 4-(Methoxycarbonyl)phenylboronic Acid (0.59 g, 3.3 mmol), cesium carbonate (1.6 g, 4.7 mmol) in 10 mL of DMF, Pd(dppf)Cl_2 (40 mg, 0.05 mmol) was added. The reaction mixture was stirred for 10 h at 100 ºC under N_2 atmosphere. The mixture was added to 100 mL of H_2O and washed with $CHCl_3$ (3 x 100 mL). The organic phase was dried over sodium sulfate and evaporated under reduced pressure. The resulting crude product was purified by column chromatography (SiO_2, CH_2Cl_2:hexane = 1:1) to give a yellow liquid. Yield: 1.1 g (91%). ^1H NMR (300 MHz, $CDCl_3$): δ 8.30-8.27 (d, 2H), 7.82-7.79 (m, 2H), 7.61-7.56 (m, 4H), 7.36-7.32 (m, 4H), 6.66-6.65 (t, 1H), 6.62-6.61 (d, 2H), 4.02 (s, 3H), 4.00-3.96 (t, 3H), 1.84-1.75 (m, 4H), 1.46-1.22 (m, 36H), 0.89-0.85 (t, 6H).

Synthesis of An. 5 (1.1 g, 1.5 mmol) and potassium hydroxide (0.6 g, 15 mmol) was added to 15 mL of THF and 2 mL of H_2O. The reaction mixture was refluxed for 8h. After neutralization with 4N HCl, the mixture was added to 100 mL of H_2O and washed with $CHCl_3$ (3 x 100 mL). The organic phase was dried over sodium sulfate and evaporated under reduced pressure. The resulting crude product was purified by column chromatography (SiO_2, $CHCl_3$) and by precipitation (MeOH) to give pale yellow solids. Yield: 0.50 g (41%). ^1H NMR (400 MHz, $CDCl_3$, TMS): δ 8.44-8.39 (d, 2H), 7.65-7.82 (m, 2H), 7.65-7.60 (m, 4H), 7.39-7.34 (m, 4H), 6.66-6.65 (t, 1H), 6.63-6.62 (d, 2H), 4.00-3.97 (t, 3H), 1.84-1.77 (m, 4H), 1.49-1.25 (m, 36H), 0.89-0.86 (t, 6H) ^{13}C NMR (101 MHz, $CDCl_3$, TMS): δ 171.30, 160.28, 145.37, 140.67, 137.96, 135.41, 131.72, 130.39, 129.55, 129.41, 128.44, 127.32, 126.31, 125.48, 125.10, 109.70, 100.82, 68.23, 31.91, 29.66, 29.63, 29.59, 29.42, 29.34, 29.30, 26.07, 22.69, 14.12. MS (MALDI): m/z = 742.2 (M^+) Elemental Analysis (%) Calculated for $C_{51}H_{66}O_4$: C, 82.43; H, 8.95. Found: C, 82.43; H, 8.99.



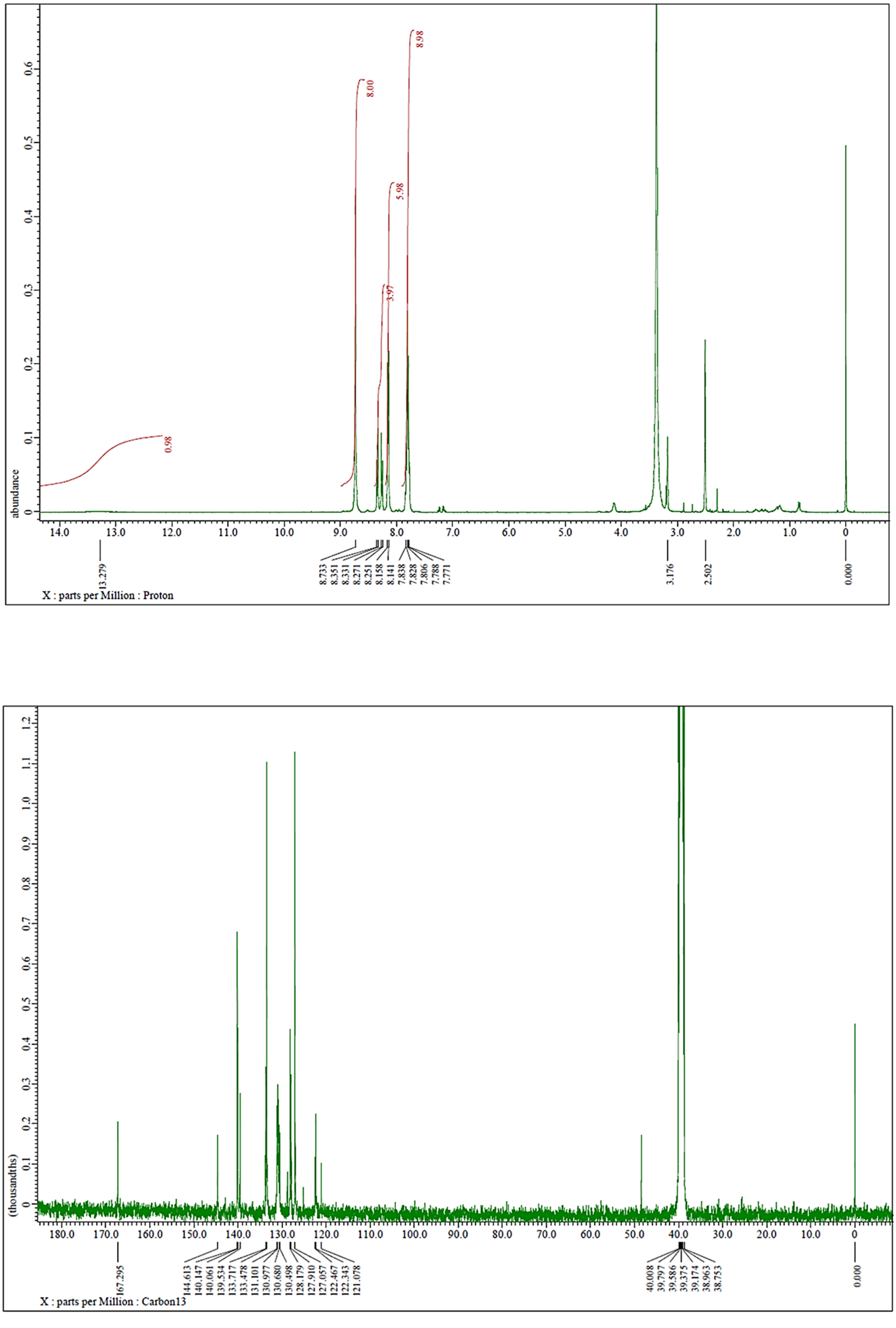
^1H NMR (top) and ^{13}C NMR (bottom) spectra ($CDCl_3$, TMS) of **An**.

Scheme S2. Synthetic routes of **Por.**



Synthesis of [5-(4-Methoxycarbonylpheny)-10,15,20-triphenylporphyrinato]-Pt(II) (7). A solution of 5-(4-Methoxycarbonylpheny)-10,15,20-triphenylporphyrin (106.1 mg, 0.15 mmol) and platinum(II) chloride (83.5 mg, 0.31 mmol) in 10mL of benzonitrile was stirred for 3h at 220 ºC by using a microwave reactor (Biotage Initiator 2.5). The reaction mixture was diluted with CH_2Cl_2 and evaporated under reduced pressure. The resulting crude product was purified by column chromatography (SiO_2, CH_2Cl_2: hexane = 3:2) to give red powders. Yield: 83.2 mg (63%). ^1H NMR (300 MHz, $CDCl_3$): δ 8.79-8.73 (m, 6H), 8.69-8.68 (d, 2H), 8.43-8.41 (d, 2H), 8.26-8.23 (d, 2H), 8.16-8.13 (m, 6H), 7.77-7.70 (m, 9H), 4.1 (s, 3H).

Synthesis of Por. A solution of **7** (75.0 mg, 0.085 mmol) and potassium hydroxide (73.8 mg, 1.3 mmol) in 9 mL of THF/MeOH/H_2O (1:1:1) was refluxed for 2h. After neutralization with 4N HCl, the mixture was added to 20 mL of H_2O and washed with $CHCl_3$ (3 x 20 mL). The organic phase was dried over sodium sulfate and evaporated under reduced pressure. The resulting crude product was purified by column chromatography (SiO_2, $CHCl_3$: MeOH = 20:1) to give red powders. Yield: 70.7 mg (96 %) ^1H NMR (400 MHz, DMSO-d_6, TMS): (s, 1H), 8.73 (s, 8H), 8.35-8.25(dd, 4H), 8.16-8.14 (d, 6H), 7.84-7.77 (m, 9H) ^{13}C-NMR (101 MHz, DMSO- d_6, TMS) δ 167.30, 144.61, 140.15, 140.06, 139.53, 133.72, 133.48, 131.10, 130.98, 130.68, 130.50, 128.18, 127.91, 127.06, 122.47, 122.34, 121.08 MS (MALDI): m/z = 850.7 (M^+) Elemental Analysis (%) Calculated for $C_{45}H_{28}N_4O_2Pt$: C, 63.45; H, 3.31; N, 6.58. Found: C, 63.56; H, 3.41; N, 6.48.



^{1}H NMR (top) and ^{13}C NMR (bottom) spectra (DMSO-d_6, TMS) of **Por**.

Synthesis of Al-**An.** To a solution of **An** (100.0 mg, 135 μmol) and $Al(NO_3)_3 \cdot 9H_2O$ (16.8 mg, 45 μmol) in 4 mL of DMF, trimethylamine (13.7 mg, 135 μmol) in 1 mL of DMF was added. The reaction mixture was stirred for 3 h at 100 ºC by using the microwave reactor. After cooling to room temperature, the precipitates were collected by filtration and washed with DMF and methanol. The resulting pale yellow powder was dried for 5h at 100 ºC under vacuum. Yield: 61 mg (92 %) based on the Al salt.
Elemental Analysis (%) Calculated for [Al(**An**)$_2$(OH)]: C, 80.17; H, 8.64; N, 0. Found: C, 80.10; H, 8.68; N, 0.03.

Synthesis of Al-**An**-**Por.** A reaction similar to the synthesis of Al-**An** was performed in the presence of different concentration of **Por**. We have also conducted the similar synthetic procedure without **An**, but there were no precipitates containing **Por**. This result rules out the contamination of our product with Al-**Por** complexes.

Characterizations.

^{1}H NMR (300 MHz) spectra were measured on a Bruker DRX-spectrometer using TMS as the internal standard. ^{1}H NMR (400 MHz) and ^{13}C NMR (101 MHz) spectra were measured on a JEOL JNM-ECZ400 using TMS as the internal standard. IR measurements were conducted on a SHIMADZU FT-IR-8400S. Elemental analysis was conducted at the Elemental Analysis Center, Kyushu University. X-ray powder diffraction (XRPD) analysis was conducted on a BRUKER D2 PHASER with a Cu Kα source (λ= 1.5418 Å) Absorption spectra were recorded on a JASCO V-670 spectrophotometer. Fluorescence spectra were measured by using a PerkinElmer LS 55 fluorescence spectrometer. The samples were excited with an incidence angle of 45° to the quartz cell surface and the fluorescence was detected along the normal. The upconverted luminescence spectra were recorded on an Otsuka Electronics MCPD-7000 instrument with the excitation source using an external, adjustable 532 nm or 515 nm semiconductor laser. Time-resolved photoluminescence lifetime measurements were carried out by using a time-correlated single photon counting lifetime spectroscopy system, HAMAMATSU Quantaurus-Tau C11367-02 (for fluorescence lifetime)/C11567-01(for delayed luminescence lifetime).

HS-AFM observation.

HS-AFM observations were performed using a laboratory-built instrument. As an operation mode of AFM, we used an amplitude-modulation mode. For the fast imaging, we used a specially designed small cantilever with a spring constant of ~0.2 N/m and a resonant frequency of ~800 kHz in liquid (BL-AC7DS-KU4, Olympus, Tokyo, Japan). The free oscillation amplitude of the cantilever for the amplitude modulation imaging was ~2 nm and the set-point amplitude for the feedback control was approximately 80% of the free amplitude. As a sharp probe to gain a high-quality image, an amorphous carbon pillar which was deposited on the original blunt tip by electron beam deposition was used.

A highly oriented pyrolytic graphite (HOPG) was chosen as a solid substrate for the HS-AFM imaging of Al-**An** because its hydroponic surface was suitable for the Al-**An** nanofibers stably adsorbing. A droplet (~ 3 μl) of methylcyclohexane including Al-**An** was deposited on the freshly cleaved HOPG substrate. Within a minute after the deposition, the substrate was washed by a methylcyclohexane solution while being careful so as not to dry the surface. After that the sample stage was immersed into the observation pool filled with methylcyclohexane solution and the HS-AFM imaging was carried out at room temperature (23 ~ 25 °C)

Determination of TTA-UC efficiency.

The upconverted luminescence efficiency Φ_{UC}' in deaerated toluene was determined relative to a standard, Rhodamine B in ethanol (10 μM), according to Eq. 1.

$$\Phi_{UC}' = 2\Phi_{std}\left(\frac{A_{std}}{A_{UC}}\right)\left(\frac{I_{UC}}{I_{std}}\right)\left(\frac{\eta_{UC}}{\eta_{std}}\right) \qquad (1)$$

where Φ, A, I and η represent the quantum yield, absorbance at 515 nm, integrated photoluminescence spectral profile and refractive index of the medium. For the estimation of Rhodamine B, photon counts between 550 nm to 750 nm were used for the estimation of Φ_{std} and I_{std}, and the absolute fluorescence quaumtum yield was Φ_{std} = 59.1%. The reflective indexes of toluene and ethanol are 1.49 and 1.36 at 293 K. Note that the theoretical maximum of Φ_{UC}' is standardized to be 1 (100%). For the precise estimation of quantum efficiency, we used 515 nm laser as an excitation source because **Por** shows a larger absorption at 515 nm than at 532 nm.

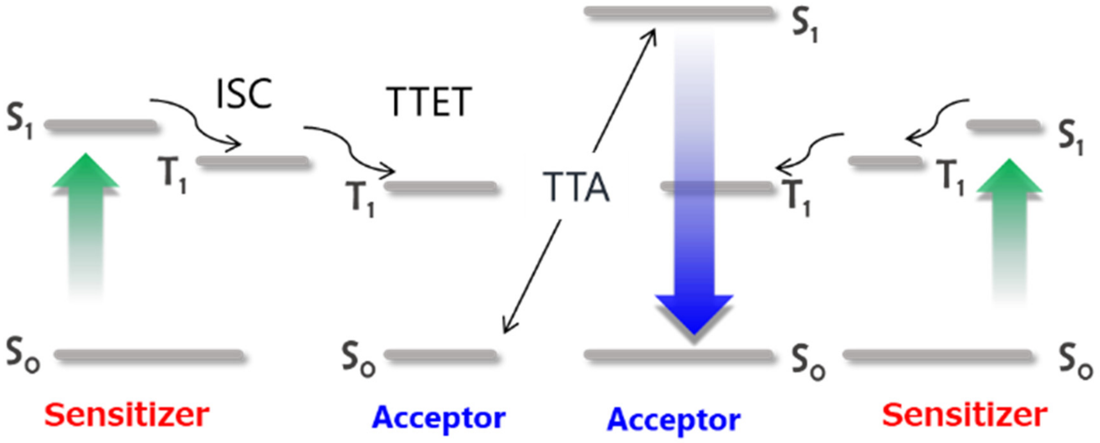


Fig. S1 Energy diagram of the TTA-UC process. The TTA-UC utilizes a pair of sensitizer with high intersystem crossing (ISC) efficiency and acceptor (emitter) with a high fluorescence quantum yield. Green and blue arrows indicate the absorption and emission processes, respectively. TTET: triplet-triplet energy transfer, TTA: triplet-triplet annihilation.

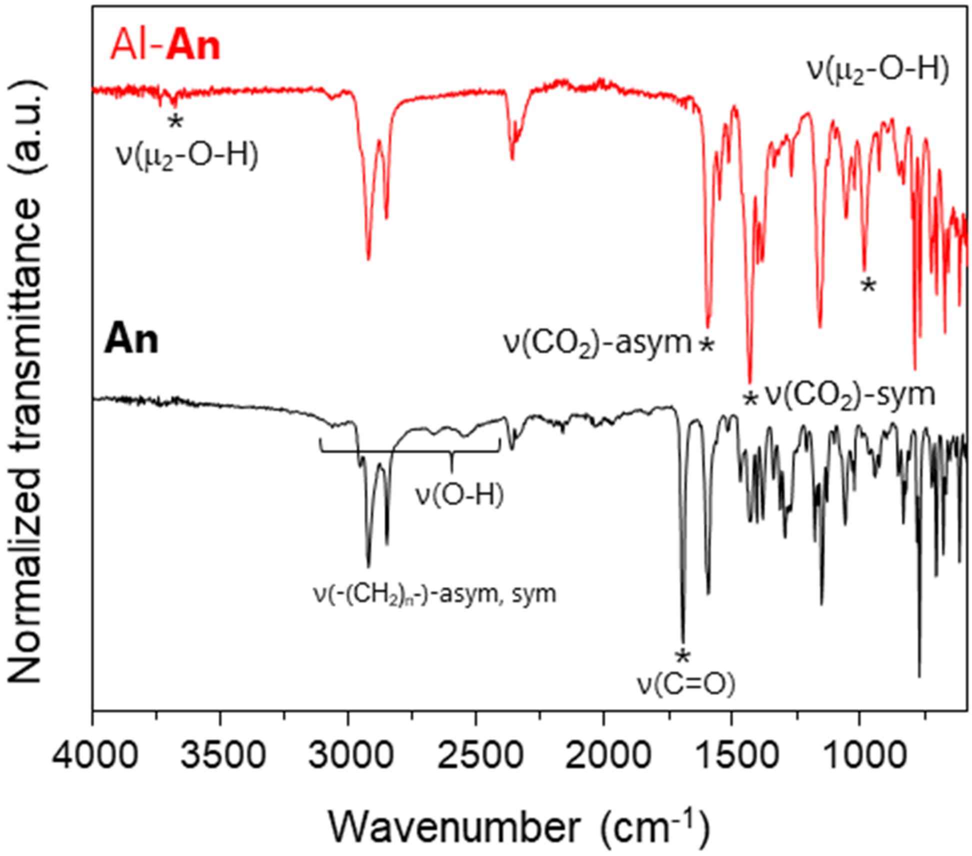


Fig. S2 FT-IR spectra of Al-**An** (red) and **An** (black).

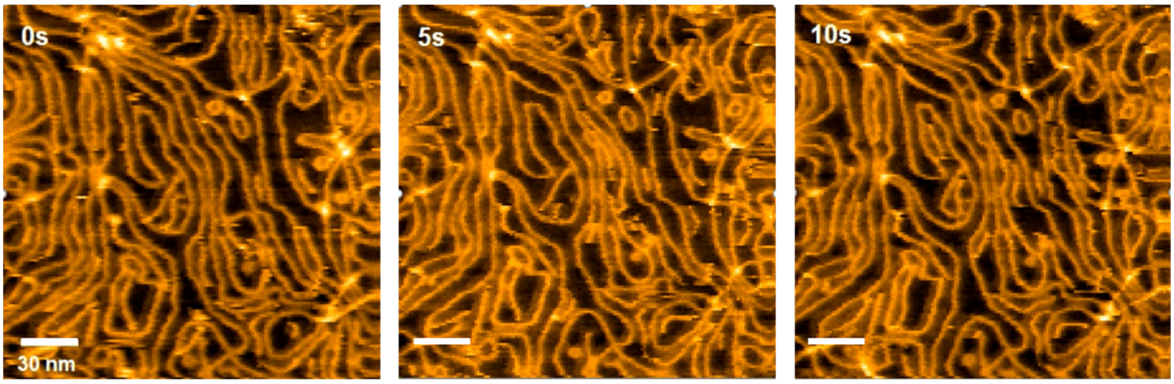


Fig. S3 HS-AFM snap shots of Al-**An** in methylcyclohenane on HOPG substrates at different times.

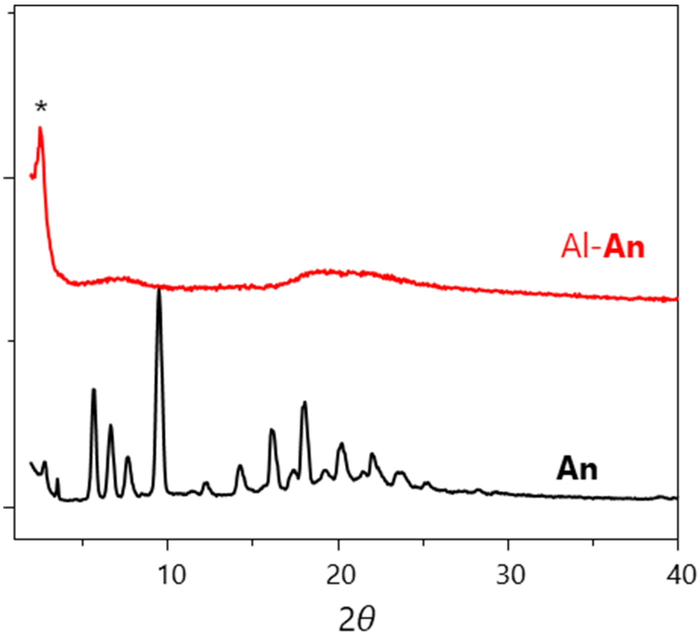


Fig. S4 XRD patterns of Al-**An** (red) and **An** (black).

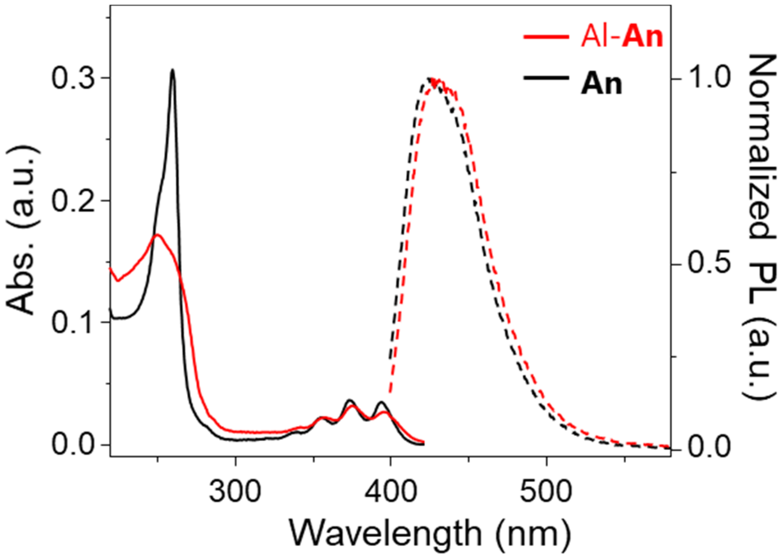


Fig. S5 UV-vis absorption spectra (solids lines) and photoluminescence (PL) spectra (dashed lines) of Al-**An** (red, 25 mM) and **An** (black, 25 μM) in methylcyclohexane.

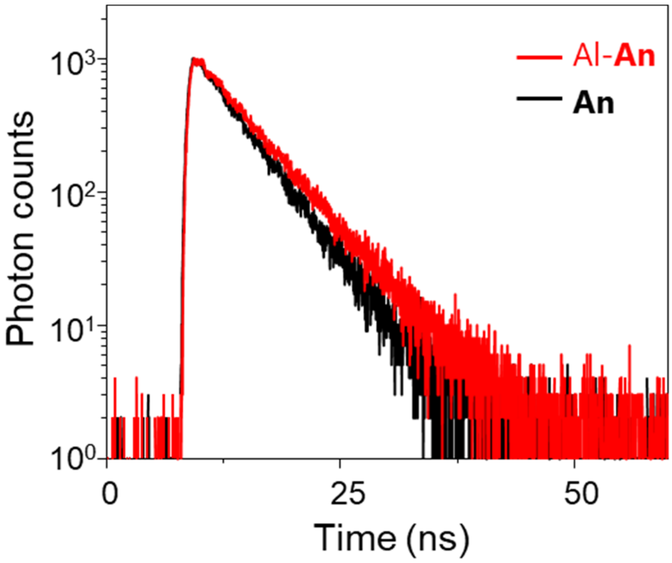


Fig. S6 Fluorescence decays at 440 nm of solutions of Al-**An** (red, 25 mM) and **An** (black, 25 mM) in methylcyclohexane under pulsed excitation at 365 nm.

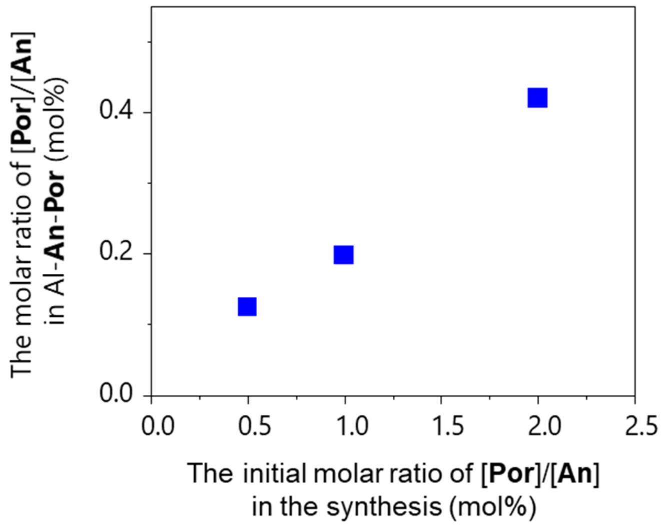


Fig. S7 The relationship between the feed molar ratio of [**Por**]/[**An**] in the synthesis and the final molar ratio of [**Por**]/[**An**] in Al-**An**-**Por**.

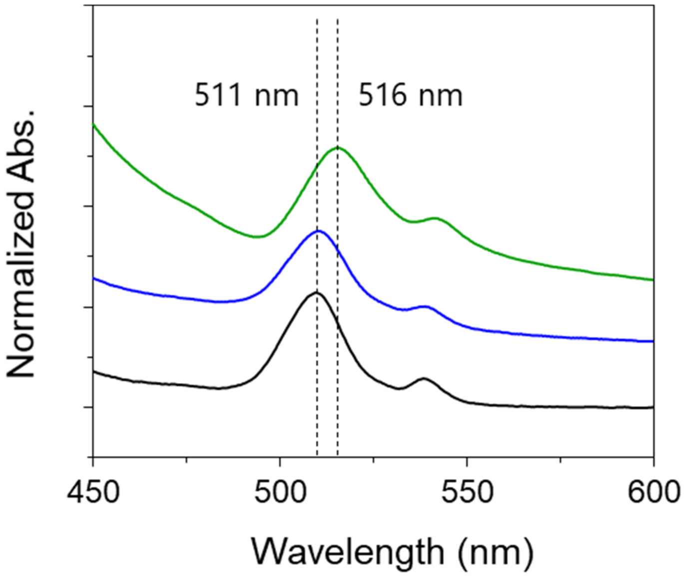


Fig. S8 UV-vis absorption spectra of toluene solutions of Al-**An**-**Por** (blue, [Al-**An**-**Por**] = 4 mM in which [**Por**] = 8 μM) and **Por** (black, [**Por**] = 10 μM), and bulk solids of **Por** (green).

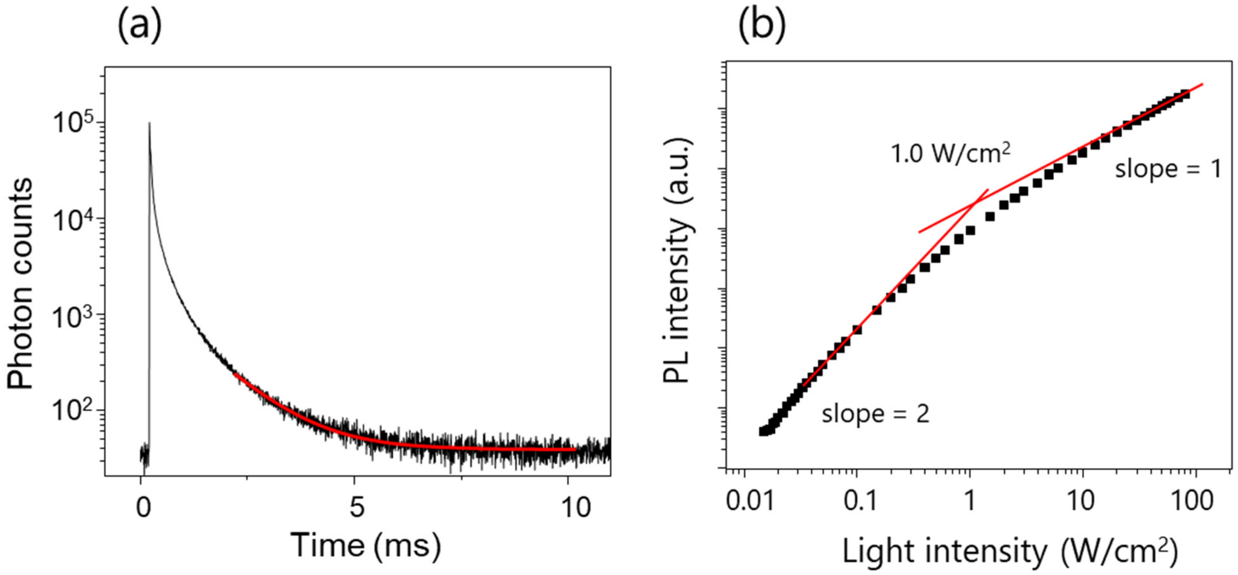


Fig. S9 (a) UC emission decays at 440 nm of Al-**An**-**Por** ([Al-**An**-**Por**] = 4 mM in which [**Por**] = 8 μM) in deaerated toluene (λ_{ex} = 531 nm). The fitting curve was obtained by using the well-known relationship of $I_{UC}(t) \propto \exp(-2t/\tau_T)$. b) Dependence of UC emission intensity at 440 nm on the excitation intensity of Al-**An**-**Por** ([Al-**An**-**Por**] = 4 mM in which [**Por**] = 8 μM) in deaerated toluene (λ_{ex} = 532 nm). The solid lines are fitting results with slopes of ca. 2 and 1 at the low and high excitation intensity regions, respectively.

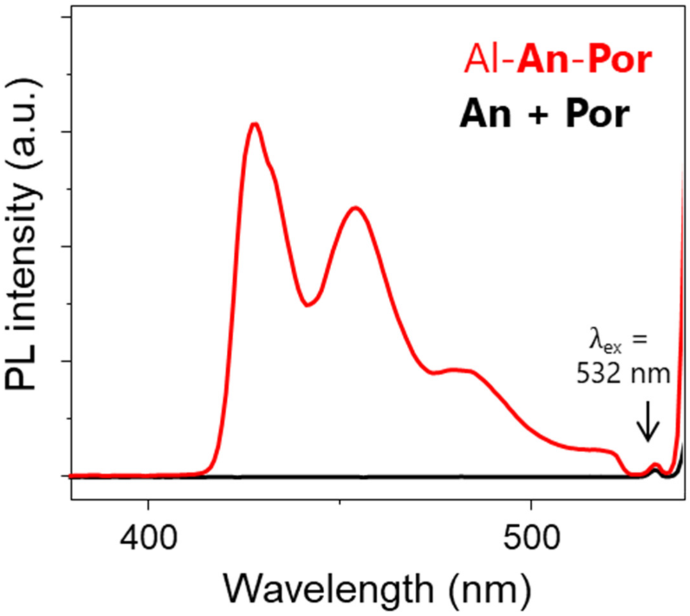


Fig. S10 Photoluminescence (PL) spectra of Al-**An**-**Por** in air-saturated toluene (red line, [Al-**An**-**Por**] = 4 mM in which [**Por**] = 8 μM) and a mixture of **An** and **Por** without Al^{3+} ions in air-saturated toluene (black line, [**An**] = 4 mM and [**Por**] = 8 μM) at 77K under 532 nm excitation (excitation intensity = 10 W cm^{-2}).

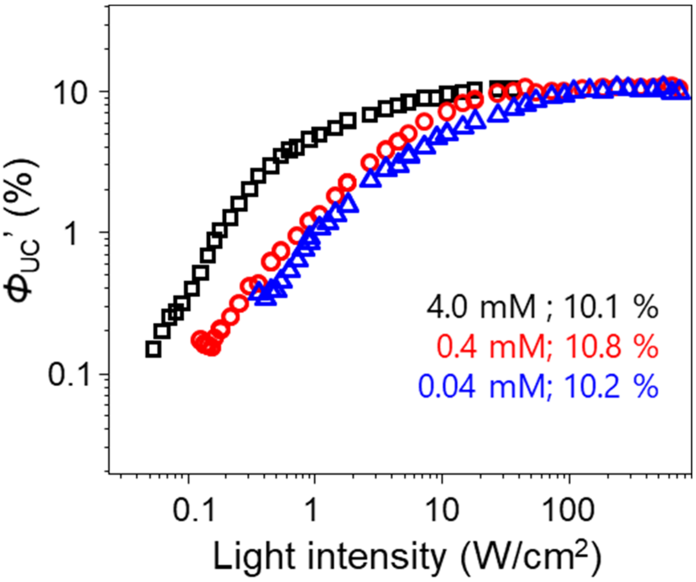


Fig. S11 UC efficiency (Φ_{UC}') of Al-**An-Por** in deaerated toluene with different concentration of [Al-**An-Por**] = 4.0 mM (black square), 0.4 mM (red circle), and 0.04 mM (blue triangle) at various excitation intensities (λ_{ex} = 515 nm).

Table S1. Fluorescence decay time constants τ_F, quantum yields Φ_F, radiative and non-radiative decay rates of excited singlet state of Al-**An** (25 μM) and **An** (25 μM) in methylcyclohexane.

	τ_F (ns)	Φ_F	k_r (×10^8 s^{-1})	k_{nr} (×10^8 s^{-1})
Al-**An**	5.1	0.66	2.0	1.01
An	4.3	0.70	2.3	0.99