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Amorphous Porphyrin Glasses Exhibit Near-Infrared Excimer Luminescence

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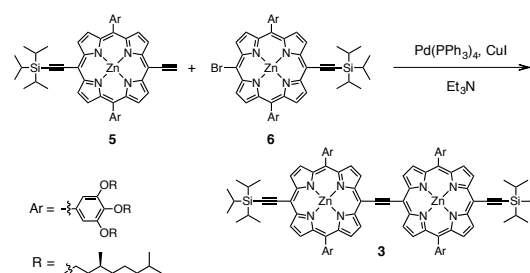
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1. General Method:

NMR spectra were recorded on Bruker AV-300. Matrix-assisted laser-dissociation ionization time-of-flight (MALDI-TOF) mass spectra were recorded on mass spectrometer (Bruker, Autoflex Speed). UV/vis absorption spectra were recorded on a spectrophotometer (Shimadzu, UV-1800) equipped with a Peltier thermoelectric temperature controlling unit (Shimadzu, TCC-240A). Fluorescence spectra in toluene solution were recorded on a fluorescence spectrophotometer (JASCO, FP-8300ST equipped with WRE-362) and corrected for spectral sensitivity. The T_g was observed under nitrogen stream by differential scanning calorimeter (Shimadzu, DSC-60Plus). Resonance Raman spectra were performed by microscopic spectroscopic Raman spectrometer (HORIBA, LabRAM ARAMIS) by using 532 nm excitation wavelength (Nd:YVO₄ laser), wherein the NIR luminescence did not overlap with Raman shift.

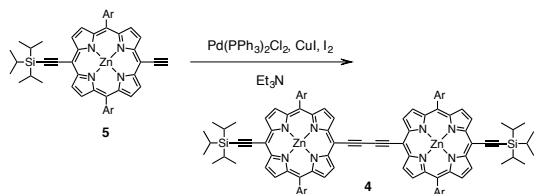
2. Synthesis of Porphyrin Glasses: Synthesis of porphyrin **1** and **2** was reported elsewhere.^{S1} Porphyrin dimer **3** and **4** were newly synthesized, where the synthetic procedures of the precursor porphyrin **5** and **6** were described in our previous report.^{S1}

2.1. Synthesis of porphyrin dimer 3: A solution of porphyrin **5** (14 mg, 8.2 μ mol) and **6** (85 mg, 50 μ mol) in Et₃N (6 mL) was deaerated by freeze-pump-thaw cycles and then purged argon. The solution was stirred in the presence of Pd(PPh₃)₄ (1.3 mg, 1.1 μ mol) and CuI



(0.7 mg, 3.7 μ mol) at 50 °C for 18 h. The mixture was diluted by toluene (30 mL), and washed with water. The residue was passed through silica gel column chromatography with toluene as the eluent, followed by size-exclusion chromatography (Bio-Rad Laboratories, BioBeads[®] S-X1) with toluene/pyridine (20/1, v/v). The porphyrin dimer **3** was obtained brownish green substance (24 mg, 7.4 μ mol) in 90% yield. ¹H NMR (300 MHz, CDCl₃): δ 10.38 (d, J = 4.2 Hz, 4H; porphyrin- β), 9.78 (d, J = 4.5 Hz, 4H; porphyrin- β), 9.23 (d, J = 4.2 Hz, 4H; porphyrin- β), 9.07 (d, J = 4.5 Hz, 4H; porphyrin- β), 7.47 (s, 8H; *meso*-Ar), 4.4–4.1 (m, 24H; ArOCH₂-), 2.2–0.8 (m, 270H); ¹³C NMR (75 MHz, CDCl₃): δ 152.8, 152.7, 151.2, 150.4, 150.3, 137.1, 131.3, 123.3, 114.0, 72.0, 67.7, 39.5, 39.2, 37.7, 37.4, 36.5, 29.9, 29.7, 28.1, 27.9, 24.9, 24.7, 22.8, 22.71, 22.66, 22.55, 19.8, 19.7, 19.1. MALDI-TOF MS (dithranol): m/z calc for C₂₀₈H₃₁₈N₈O₁₂Si₂Zn₂: 3304.26; found 3304.76 [M]⁺. λ_{max} /nm ($\epsilon/\mu\text{M}^{-1}\text{cm}^{-1}$ in toluene): 426 (0.15), 489 (0.31), 574 (0.02), and 720 (0.08).

2.2. Synthesis of porphyrin dimer 4:



A solution of porphyrin **5** (19 mg, 12 μmol), $\text{Pd}(\text{PPh}_3)_2\text{Cl}_2$ (1.3 mg, 1.9 μmol), CuI (1.1 mg, 5.8 μmol) and I_2 (45 mg, 5.8 μmol) in Et_3N (6 mL) was stirred at room temperature for 13 h. The mixture was diluted with toluene. The solution was successively washed with saturated aqueous $\text{Na}_2\text{S}_2\text{O}_3$ and brine. The organic layer was separated and purified by silica gel column chromatography with toluene. The product was eliminated from size-exclusion chromatography (BioBeads[®] S-X1) with toluene/pyridine (5/1, v/v). The porphyrin dimer **4** was obtained brownish green substance (10 mg, 3.1 μmol) in 54% yield. ^1H NMR (300 MHz, CDCl_3): δ 9.97 (d, $J = 4.5$ Hz, 4H; porphyrin- β), 9.77 (d, $J = 4.5$ Hz, 4H; porphyrin- β), 9.15 (d, $J = 4.5$ Hz, 4H; porphyrin- β), 9.06 (d, $J = 4.5$ Hz, 4H; porphyrin- β), 7.44 (s, 8H; meso-Ar), 4.4–4.1 (m, 24H; ArOCH_2 -), 2.2–0.8 (m, 270H); ^{13}C NMR (75 MHz, CDCl_3): δ 153.2, 152.5, 151.0, 150.5, 150.1, 137.7,

137.0, 133.4, 133.0, 131.4, 131.0, 123.3, 114.1, 102.6, 100.1, 99.0, 87.7, 82.6, 71.9, 67.6, 39.5, 39.2, 37.7, 37.5, 37.4, 36.4, 29.9, 28.1, 27.9, 24.9, 24.7, 22.8, 22.72, 22.69, 22.6, 19.8, 19.6, 19.1, 11.9. MALDI-TOF MS (dithranol): m/z calc for $\text{C}_{210}\text{H}_{118}\text{N}_8\text{O}_{12}\text{Si}_2\text{Zn}_2$: 3328.26; found 3328.67 $[\text{M}]^+$. $\lambda_{\text{max}}/\text{nm}$ ($\epsilon/\mu\text{M}^{-1}\text{cm}^{-1}$ in toluene): 459 (0.23), 492 (0.12), 578 (0.01), 657 (0.04). and 709 (0.05).

3. Film Preparation: Quartz and silicon substrates were washed with acetone and isopropyl alcohol prior to use. Porphyrin films were prepared by a typical spin-cast method; approximately 0.6 mM toluene solution was placed on the substrate rotating at the spinning speed of 500 rpm at 30 sec followed by 1000 rpm at 60 sec. Porphyrin-doped polymer films were prepared using PMMA ($M_n = 23000$ and $M_w = 90000$) as an inert matrix. The porphyrin was premixed with 5 wt% PMMA toluene solution to adjust the doped concentrations of porphyrins to be 1 wt% and 10 wt% against PMMA. The porphyrin doped-PMMA solution was spin-casted onto a quartz glass under the same conditions for preparation of the neat porphyrin films.

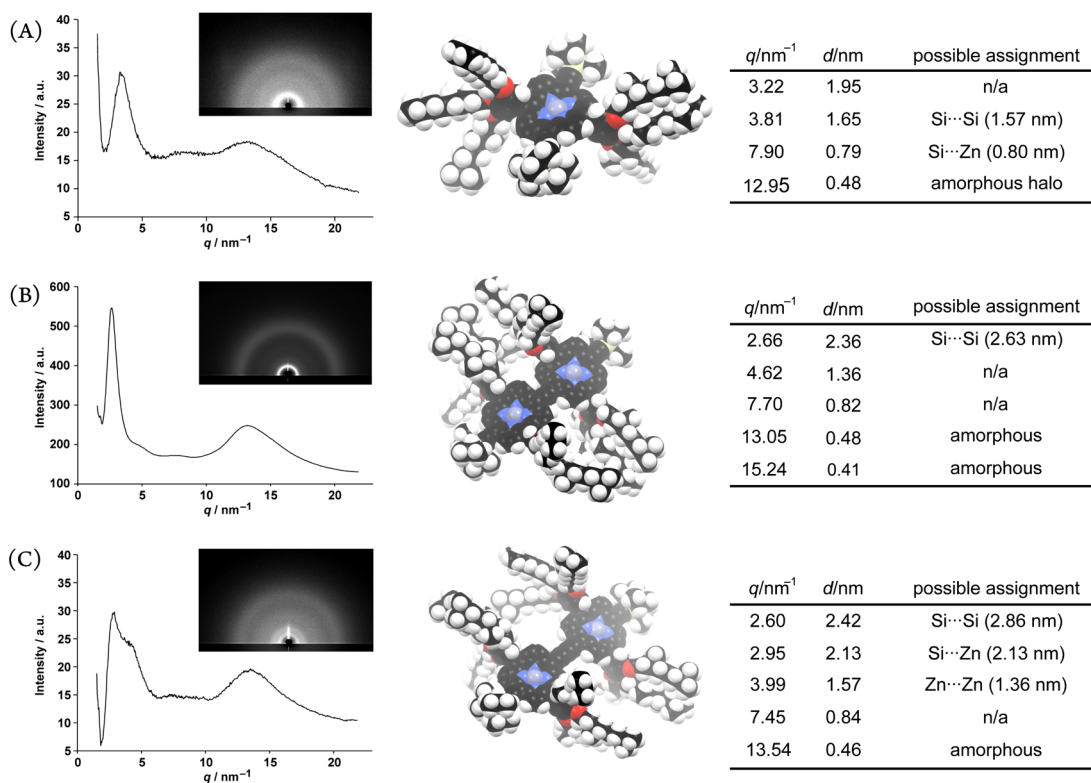


Figure S1. GIXS patterns (inset) and one-dimensional profiles of **2** (A), **3** (B), **4** (C) on a silicon wafer observed with a synchrotron X-ray with 0.11° of the incident angle obtained from integrated radial azimuthal angles. Tables summarize the deconvoluted peaks of the GIXS profiles, which were assigned based on the geometry-optimized models produced using the MM+ force field (the HyperChem Ver. 8.0 software).

4. Micro-beam Grazing-Incident X-ray Scattering (GIXS) Measurements:

GIXS was measured for spin-cast films of porphyrin on a silicon wafer utilizing synchrotron radiation at the BL45XU beamline in SPring-8 (RIKEN SPring-8 Centre Hyogo, Japan). The X-ray micro-beam of 1 Å in wavelength (approximately 6 μm in diameter) was directly irradiated on the films at incident angle of 0.11°, and X-ray scattering from the films (irradiated area was approximately 0.01 mm²) was detected with the combination of an image intensifier and a CMOS camera (Hamamatsu Photonics K. K.) or a PILATUS 300K-W (Dectris Ltd.) at 330 mm of the sample-to-detector distance. When a sample is irradiated by the incident X-rays at a grazing angle lower than the critical angle of total reflection of the sample, total reflection of the incident X-rays occurs and only evanescent X-rays permeate the sample. The critical angle of total reflection of the Si substrate surface is ca. 0.14°. Therefore, the incident beam reaches the substrate and its total reflection also occurs at the substrate surface.

5. NIR Emission Measurements: The NIR steady-state photoluminescence spectrum was measured using a Fluorolog 3ps NIR spectroscopy system (HORIBA, Kyoto, Japan) and corrected for the response of the detector system. The following measurement conditions were employed: excitation wavelength 350 nm, step 1

nm, int. time 0.1 s, slit Ex/Em 5 nm/6 nm. Emission lifetimes (τ) of spin-cast film were measured by nano-LEDs (N-355, response time ≤ 1.2 ns HORIBA, Kyoto, Japan) and a photomultiplier (R5108, response time ≤ 1.1 ns, Hamamatsu photonics, Hamamatsu, Japan). Emission lifetimes were determined from the slope of logarithmic plots of the decay profiles. The absolute quantum measurements were performed by QE-5000 (Otsuka Electronics Co., Osaka, Japan) using an integrated sphere equipped with an excitation laser (450 nm). Opaque drop-cast films were tentatively employed to improve the ratio of incident and emitted light intensity to determine the Φ values.

We confirmed the reproducibility of the photophysical properties of porphyrin glasses. However, the intensity ratio of monomeric and excimer emission of **4** slightly altered depending on the samples, although the emission peak positions unchanged. In the present experiments, the optical densities of **4** and other spin-cast films were sufficiently low enough to ensure that the incident and emitted light to pass through the samples. Then, we consider that the efficiency of energy transfer to an energy sink is a key step key to produce the NIR-luminescent excimer, and thus the photophysical properties are susceptible to the heterogeneity of the porphyrin glass. At this moment, it is difficult to assign the NIR luminescence to photoexcited singlet or triplet, which is under active investigations.

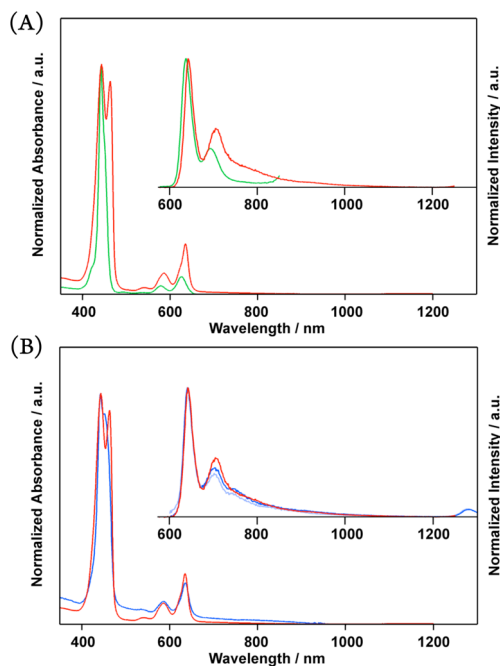


Figure S2. (A) Normalized absorption and emission spectra of **2** in toluene (green) and neat spin-cast film (red). Emission obtained by excitation at 442 nm for toluene solution and 450 nm for neat film. (B) Normalized absorption and emission spectra of neat **2** (red) and **2**-doped PMMA (10 wt%, blue, and 1 wt% pale blue) in spin-cast film on a quartz substrate. Emission obtained by excitation at 450 nm.

References

[S1] Morisue, M.; Hoshino, Y.; Shimizu, K.; Shimizu, M.; Kuroda, Y. *Chem. Sci.* **2015**, *6*, 6199–6206.

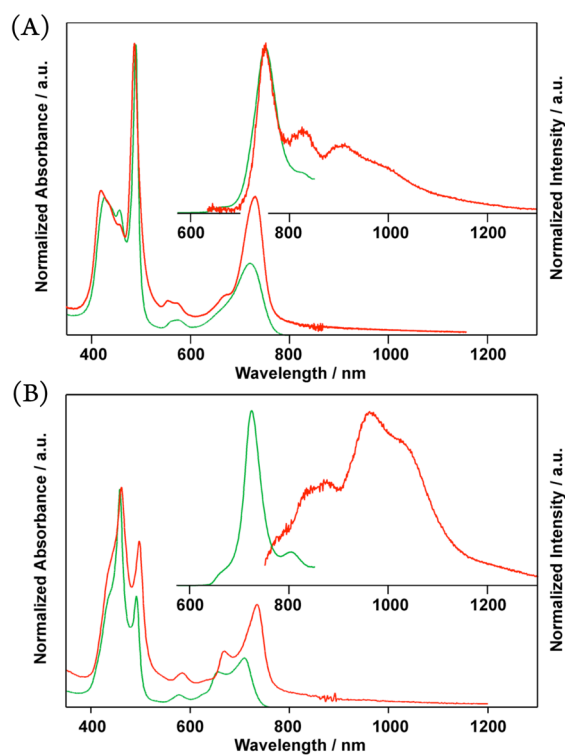


Figure S3. (A) Normalized electronic absorption and emission spectra of **3** in toluene (green) and neat spin-cast film (red). Emission obtained by excitation at 456 nm for toluene solution and 450 nm for neat film. (B) Normalized electronic absorption and emission spectra of **4** in toluene (green) and neat spin-cast film (red). Emission obtained by excitation at 450 nm for toluene solution, 500 nm for neat film.

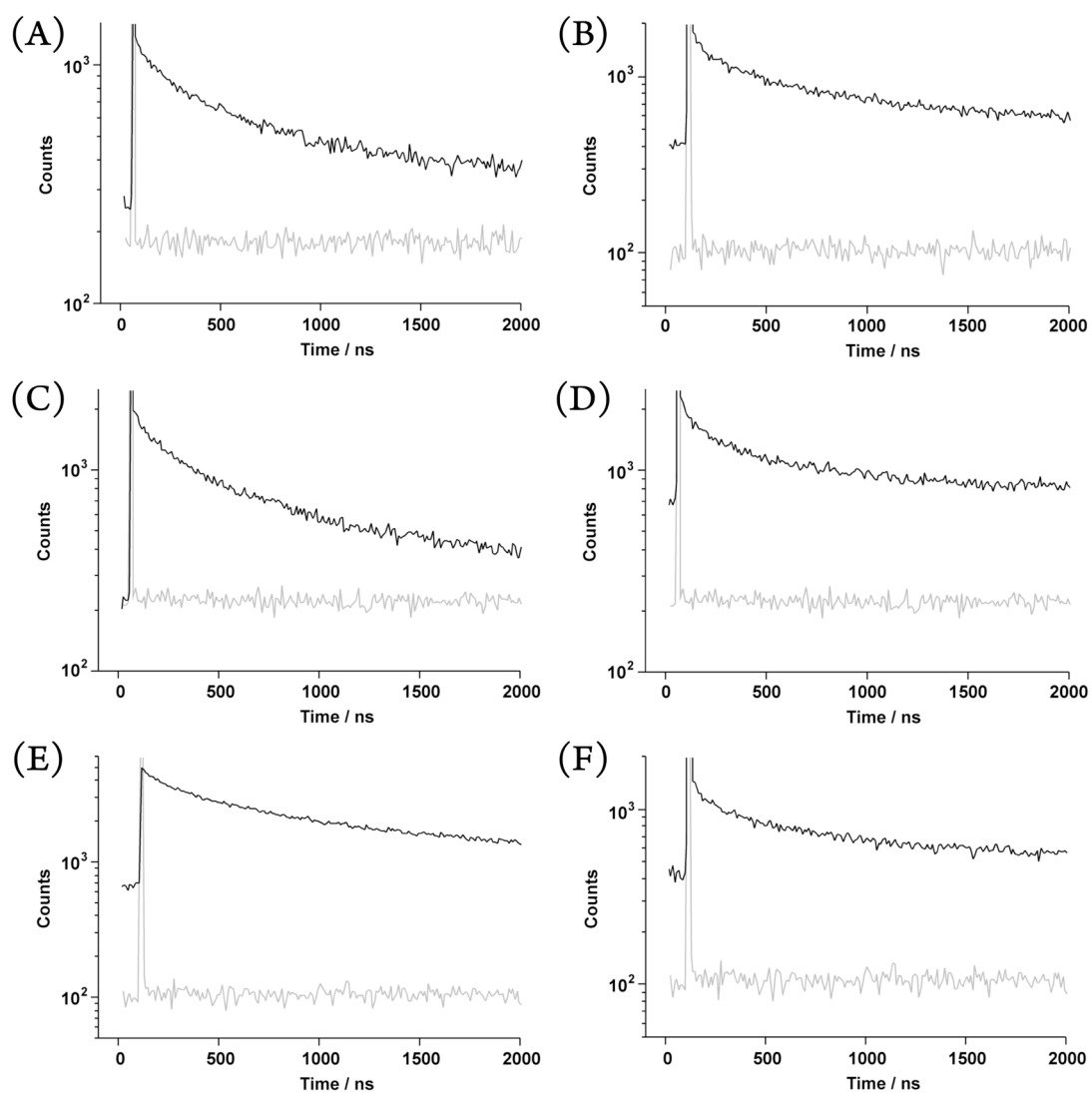


Figure S4. Emission decay profiles of porphyrin glasses; **2** at 770 nm (A) and 970 nm (B) (excitation wavelength = 450 nm), **3** at 770 nm (C) and 970 nm (D) (excitation wavelength = 500 nm), and **4** at 770 nm (E) and 970 nm (F) (excitation wavelength = 500 nm).

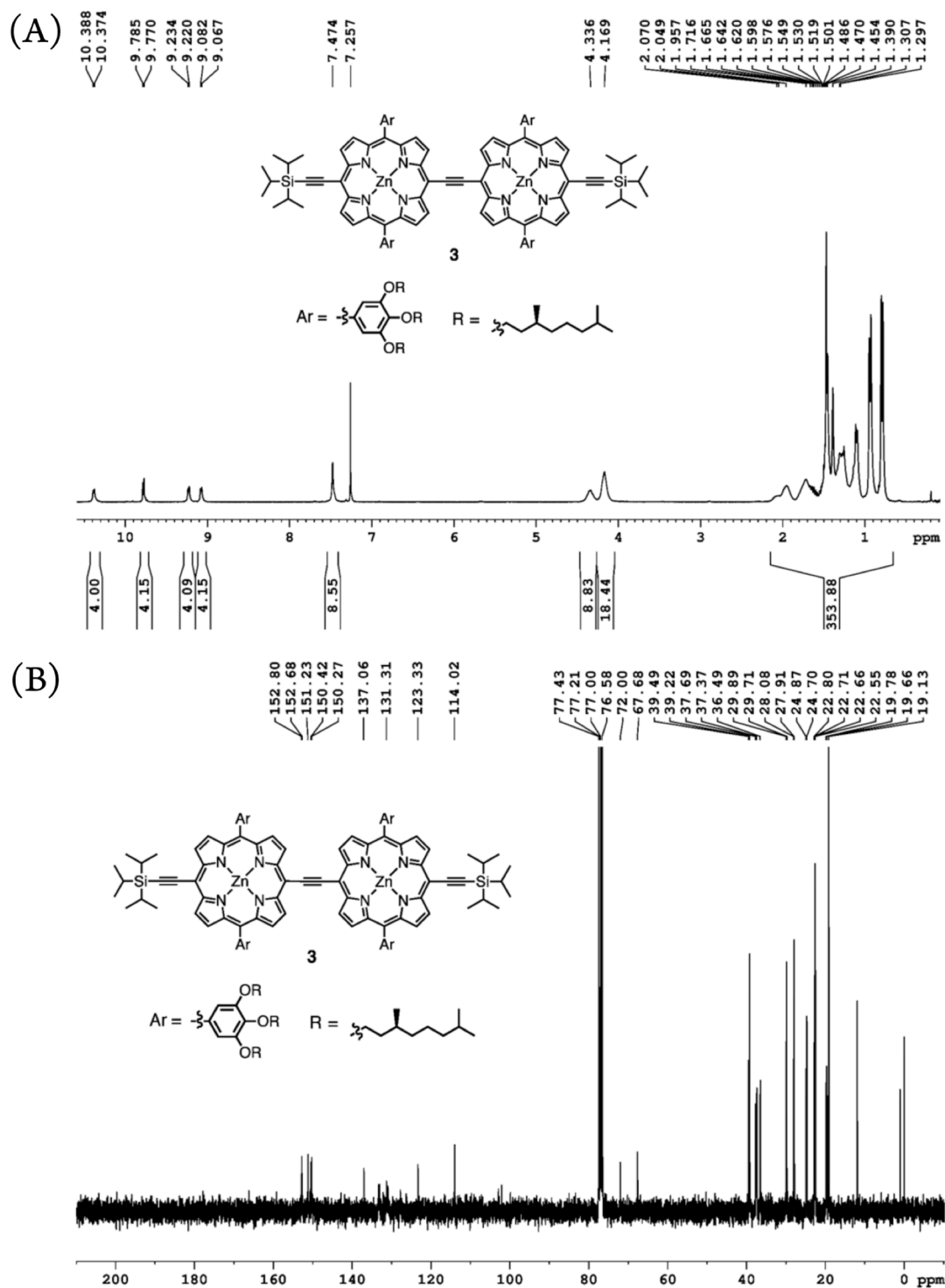


Figure S5. ^1H NMR (300 MHz, A) and ^{13}C NMR (75 MHz, B) of **3** in CDCl_3 .

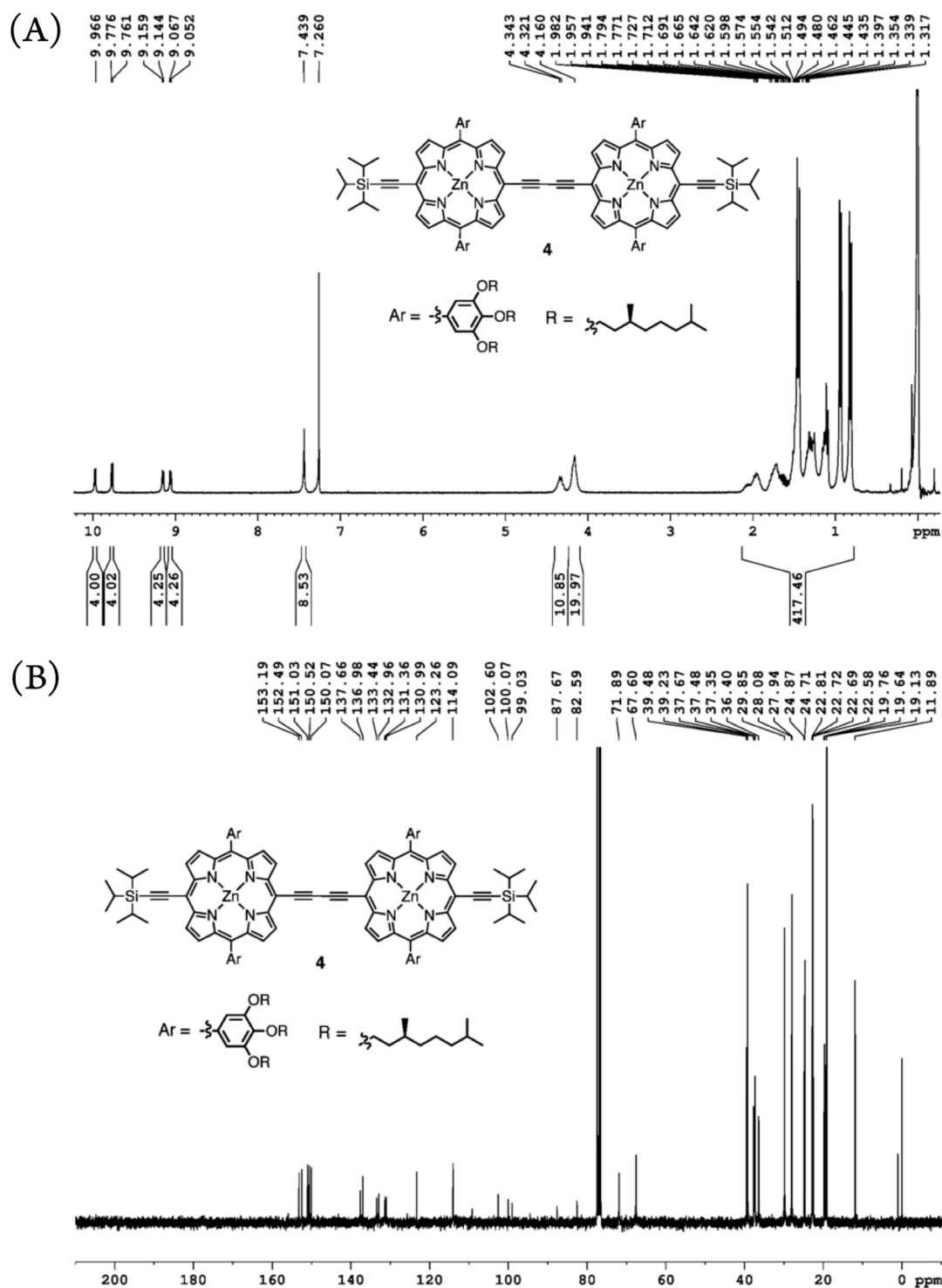


Figure S6. ^1H NMR (300 MHz, A) and ^{13}C NMR (75 MHz, B) of **4** in CDCl_3 .

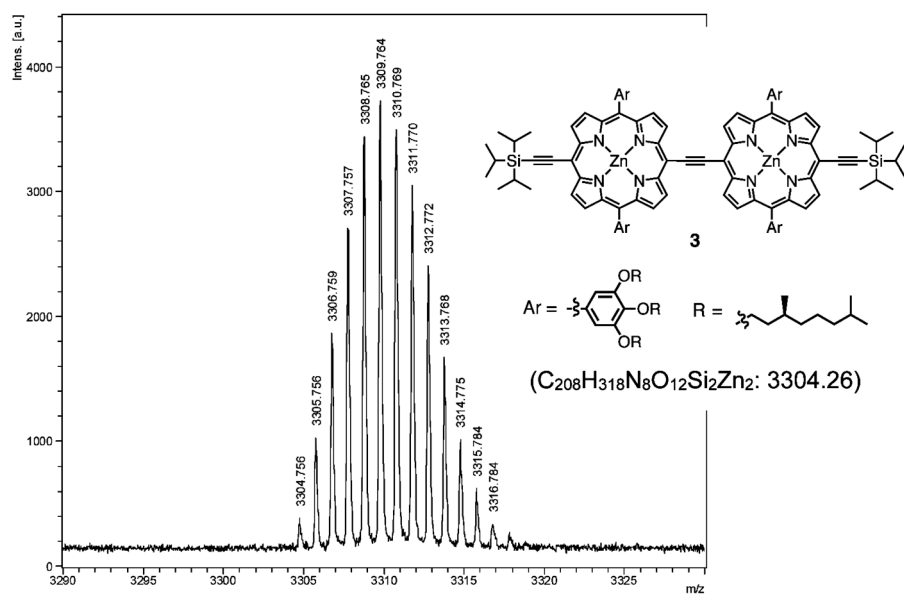


Figure S7. MALDI TOF MS spectrum of **3**.

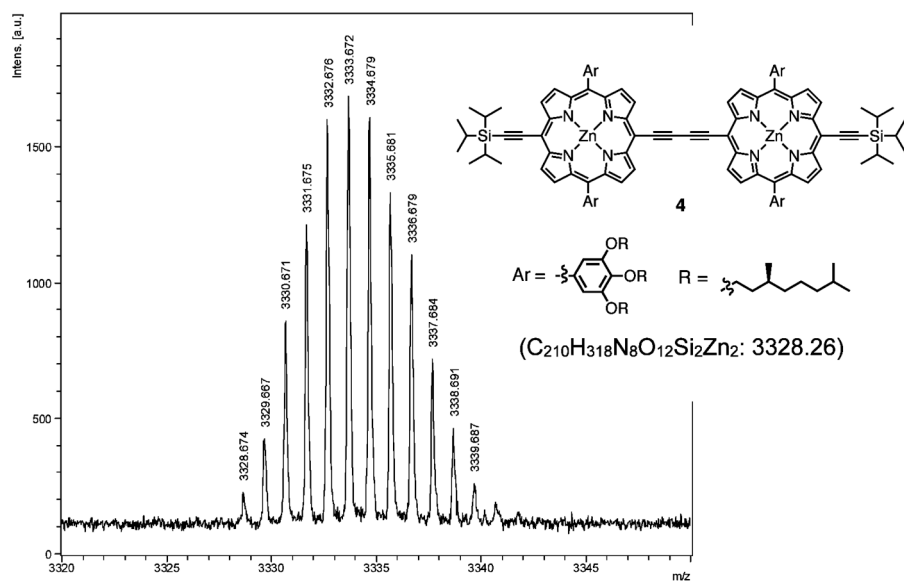


Figure S8. MALDI TOF MS spectrum of **4**.