

Supporting Information

Synthesis of Insulated Molecular Wire by Click Polymerization

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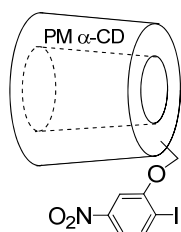
General

6-*O*-monotosyl permethylated α -cyclodextrin (**4**) was prepared by the reported procedure.¹ Other reagents were purchased from commercial sources and used without further purification. Matrix assisted laser desorption/ionization time-of-flight (MALDI-TOF) mass spectra was obtained with α -cyano-4-hydroxycinnamic acid as a matrix and NaTFA as a cationization reagent on a SHIMADZU KRATOS TOF MASS spectrometer AXIMA-CFR Plus. ¹H NMR for 400 MHz and ¹³C NMR for 100 MHz spectra were recorded by a JEOL ECX-400P spectrometer. The ¹H NMR chemical shifts are reported relative to tetramethylsilane (TMS, 0.00 ppm). The ¹³C NMR chemical shifts are reported relative to CDCl₃ (77.0 ppm). EI-MS were recorded on a Shimadzu GCMS-QP5050A with a direct inlet. High-resolution mass spectra (ESI-HRMS) were obtained with a JEOL SX-102A spectrometer. Elemental analysis was carried out at the Center for Organic Elemental Microanalysis, Graduate School of Pharmaceutical Science, Kyoto University. GC analysis was carried out using a Shimadzu GC-17A equipped with an integrator (C-R8A) with a capillary column (CBP-5, 0.25 mm i.d. \times 25 m). The HPLC separation was performed on a Japan Analytical Industry Co. Ltd. LC-9204 recycling preparative HPLC equipped with JAIGEL-1H and -2H columns or LC-908 recycling preparative HPLC equipped with JAIGEL-2.5H and -3H columns using CHCl₃ as the eluent. Analytical size-exclusion chromatography (SEC) was carried out on a GL-Science GL-7400 HPLC System equipped with a GL-7410 HPLC pump, a GL-7400 UV detector, and GL-7454 RI detector through a column set consisting of Shodex KF-801, -802, -802.5, -803, -804 using THF as the eluent at a flow rate of 0.6 mL min⁻¹. Average molecular weights and the polydisperse index (PDI) of polyrotaxanes were estimated with polystyrene standards as calibration standards. The absolute quantum yields were determined using a calibrated integrating sphere system (HAMAMATSU Quantaaurus-QY).

1. Synthesis of π -conjugated guest-linked PMCD (**1**)

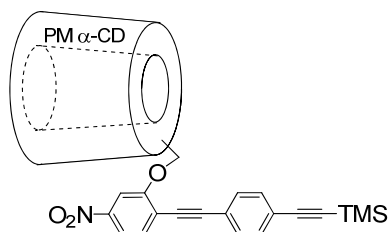
Permethylated α -cyclodextrin derivatives (**5-7**) were prepared by the similar method as our previously reported procedures.²

Synthesis of **5**.



2-Iodo-5-nitrophenol (3.0 g, 11.0 mmol), 6-*O*-monotosyl α -cyclodextrin permethylate **4** (10.0 g, 7.32 mmol), and dry K_2CO_3 (2.10 g, 14.6 mmol) were placed in a round-bottom flask and dried at 100 °C *in vacuo*. The mixture was dissolved in DMF (60 mL) and stirred at 85 °C overnight. The mixture was diluted with EtOAc and washed with saturated aqueous NaHCO_3 and brine. The organic layer was separated and dried over Na_2SO_4 . The solvent was removed *in vacuo*, and the residue was purified by column chromatography on silica gel with EtOAc-EtOH (9:1) as eluent to give **5** (10.5 g, orange solid, 98%); ^1H NMR (400 MHz, CDCl_3 , 23.7 °C): δ (ppm) = 7.65 (d, J = 8.4 Hz, 1H, ArH), 7.36 (d, J = 8.4 Hz, 1H, ArH), 7.12 (dd, J = 2.1, 8.4 Hz, 1H, ArH), 5.12-5.00 (m, 6H, CD- H_1), 4.44-3.10 (m, 87H, CD-H, OCH_3); ^{13}C NMR (100 MHz, CDCl_3 , 23.7 °C): δ (ppm) = 158.84, 138.74, 138.6-138.5 (several peaks overlapped), 113.57, 113.50, 104.46, 104.46, 100.6-99.7 (several peaks overlapped), 82.8-82.0 (several peaks overlapped), 79.42, 71.4-71.2 (several peaks overlapped), 70.45, 69.72, 61.87, 59.2-59.0 (several peaks overlapped), 58.79, 58.72, 57.9-57.8 (several peaks overlapped).

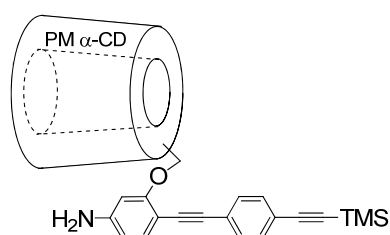
Synthesis of **6**.



To a solution of **5** (8.1 g, 5.55 mmol) in NH^iPr_2 (40 mL) was added $\text{Pd}(\text{PPh}_3)_2\text{Cl}_2$ (156 mg, 0.22 mmol), CuI (10.5 mg, 0.055 mmol), and 1-ethynyl-4-(trimethylsilylethynyl)benzene (1.20 g, 6.1 mmol) under nitrogen. After stirring for 10 h at 50 °C, the mixture was filtered through a Celite pad and concentrated, followed by a chromatographic purification on silica gel with EtOAc-EtOH (9:1) as eluent to give **6**

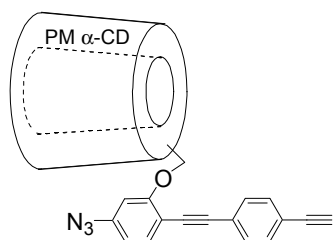
(4.64 g, orange solid, 95%). MALDI-TOF MS: (m/z) 1551 ($[M+Na]^+$, $C_{72}H_{109}NO_{32}SiNa$, calcd. 1551); 1H NMR (400 MHz, $CDCl_3$, 23.2 °C): δ (ppm) = 7.96 (d, J = 8.4 Hz, 1H, ArH), 7.64 (d, J = 2.4 Hz, 1H, ArH), 7.61 (dd, J = 2.4, 8.4 Hz, 1H, ArH), 7.28-7.23 (m, 2H, ArH), 7.20-7.16 (m, 2H, ArH), 5.17-5.00 (m, 6H, CD-H₁), 4.60-3.04 (m, 87H, CD-H, OCH₃), -0.06 (s, 9H, (CH₃)₃Si); ^{13}C NMR (100 MHz, $CDCl_3$, 23.2 °C): δ (ppm) = 160.12, 139.74, 133.25, 131.86, 131.34, 123.70, 122.40, 110.73, 108.42, 105.85, 104.21, 100.47, 100.09, 99.54, 96.08, 92.93, 88.12, 82.6-82.0 (several peaks overlapped), 81.55, 81.37, 81.12, 71.7-71.3 (several peaks overlapped), 70.74, 67.64, 62.0-61.6 (several peaks overlapped), 59.3-59.1 (several peaks overlapped), 58.77, 58.33, 58.0-57.9 (several peaks overlapped), 57.31, 0.00.

Synthesis of 7.



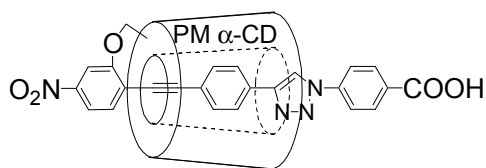
6 (2.0 g, 1.31 mmol) was added to a mixture of 0.1N HCl aq (140 mL), benzene (50 mL), and MeOH (12.5 mL), and then Fe (3.07 g, 55.0 mmol) and $FeSO_4 \cdot 7H_2O$ (947 mg, 3.41 mmol) were added with vigorous stirring, and the whole was refluxed for 3 h. The mixture was diluted with EtOAc and washed with saturated aqueous $NaHCO_3$ and brine. The organic layer was separated and dried over Na_2SO_4 . The solvent was removed *in vacuo*, and the residue was purified by column chromatography on silica gel with EtOAc-EtOH (9:1) as eluent to give **7** (1.94 g, yellow solid, 99%). MALDI-TOF MS: (m/z) 1520 ($[M+Na]^+$, $C_{72}H_{111}NO_{30}SiNa$, calcd. 1521); 1H NMR (400 MHz, $CDCl_3$, 20.2 °C): δ (ppm) = 7.44 (d, J = 8.4 Hz, 2H, ArH), 7.36 (d, J = 8.4 Hz, 2H, ArH), 7.22 (d, J = 2.4 Hz, 1H, ArH), 7.21 (d, J = 8.4 Hz, 1H, ArH), 7.15 (dd, J = 2.4, 8.4 Hz, 1H, ArH), 5.16-5.01 (m, 6H, CD-H₁), 4.58-3.02 (m, 87H, CD-H, OCH₃), -0.03 (s, 9H, (CH₃)₃Si); ^{13}C NMR (100 MHz, $CDCl_3$, 20.8 °C): δ (ppm) = 158.02, 138.64, 134.22, 130.88, 130.35, 123.86, 123.59, 112.85, 109.37, 105.84, 102.71, 101.57, 100.16, 99.75, 97.07, 93.91, 87.12, 82.5-82.2 (several peaks overlapped), 81.76, 81.55, 81.23, 71.5-71.1 (several peaks overlapped), 70.66, 67.60, 62.1-61.8 (several peaks overlapped), 59.2-59.0 (several peaks overlapped), 58.56, 58.24, 58.0-57.8 (several peaks overlapped), 57.36, -0.06.

Synthesis of **1**.



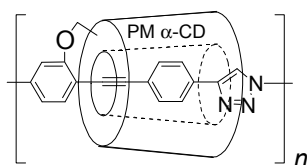
7 (100 mg, 67.1 μmol) was dissolved in CHCN_3 (5.00 mL) and cooled to 0 $^\circ\text{C}$. To the solution was added $t\text{BuNO}_2$ (69.2 mg, 671 μmol) followed by TMSN_3 (116 mg, 101 μmol). The reaction mixture was stirred at room temperature for 2 h, and then the mixture was concentrated under vacuum and crude product was purified by column chromatography on silica gel with EtOAc-EtOH (9:1) as eluent to give **7'** (102 mg, yellow solid, 100%). MALDI-TOF MS: (m/z) 1548 ($[\text{M}+\text{Na}]^+$, $\text{C}_{72}\text{H}_{109}\text{N}_3\text{O}_{30}\text{SiNa}$, calcd. 1547). To a solution of **7'** (900 mg, 0.601 mmol) in THF (1 mL) was tetrabutylammonium fluoride (1 mol/L in tetrahydrofuran) (236 mg, 0.901 mmol). After stirring for 1 h at room temperature, the mixture was diluted with EtOAc and washed with brine. The organic layer was separated and dried over Na_2SO_4 . The solvent was removed under reduced pressure and the residue was purified by column chromatography on silica gel with EtOAc-EtOH (9:1) as an eluent to give **1** (417 mg, yellow solid, 48%). MALDI-TOF MS: (m/z) 1477 ($[\text{M}+\text{Na}]^+$, $\text{C}_{69}\text{H}_{101}\text{N}_3\text{O}_{30}\text{Na}$, calcd. 1476); ^1H NMR (400MHz, CDCl_3 , 22.1 $^\circ\text{C}$): δ_{H} = 7.53 (d, J = 8.2 Hz, 2H, ArH), 7.63 (doublet-like, 3H, overlapped), 6.64 (dd, J = 1.8, 8.2 Hz, 1H, ArH), 6.57 (dd, J = 1.8, 8.2 Hz, 1H, ArH), 5.12-5.04 (m, 6H, CD- H_1), 4.98-3.01 (m, 88H, CD-H, CC-H); ^{13}C NMR (100 MHz, CDCl_3 , 21.1 $^\circ\text{C}$): δ_{C} = 160.68, 141.65, 134.43, 132.70, 132.34, 132.13, 131.74, 124.23, 121.96, 11.53, 109.01, 103.65, 100.88, 100.55, 100.51, 100.49, 100.41, 99.98, 93.69, 87.94, 83.66, 93.14, 82.9-82.4 (several peaks overlapped), 82.27, 82.06, 81.50, 81.46, 81.32, 79.16, 77.55, 72.24, 72.07, 71.9-71.4 (several peaks overlapped), 70.90, 68.01, 62.2-62.0 (several peaks overlapped), 59.56, 59.40, 59.37, 59.28, 58.62, 58.22, 58.20, 58.14, 58.12, 57.58; Anal. Calcd for $\text{C}_{69}\text{H}_{101}\text{N}_3\text{O}_{30}$: C, 57.05; H, 7.01%; Found: C, 57.17; H, 7.11%.

2. Synthesis of fixed [2]rotaxane (**9**)



To a solution of **6** (300 mg, 0.186 mmol) in MeOH (7 mL), and H₂O (1.5 mL) was added K₂CO₃ (258 mg, 1.86 mmol). After stirring for 1 h at room temperature, the mixture was diluted with EtOAc and washed with brine. The organic layer was separated and dried over Na₂SO₄. The solvent was removed under reduced pressure and the residue was purified by column chromatography on silica gel with EtOAc-EtOH (9:1) as an eluent to give the corresponding desilylation product **6'** (223 mg, brilliant yellow solid, 78%). MALDI-TOF MS: (*m/z*) 1561 ([M+Na]⁺, C₆₈H₁₀₁IO₃₀Na, calcd. 1560) MALDI-TOF MS: (*m/z*) 1481 ([M+Na]⁺, C₅₉H₉₆INO₃₂Na, calcd. 1481). **6'** (200 mg, 137 μmol) was dissolved in *t*-BuOH (2.50 mL) under an argon atmosphere and degassed water (5.00 mL) was added to the solution. This suspension was stirred at 60 °C for 1 h. After cooling to ambient temperature, *p*-azidobenzoic acid (44.8 mg, 275 μmol), sodium ascorbate (10.9 mg, 27.5 μmol) and CuSO₄·5H₂O (6.86 mg, 27.5 μmol) were added to the solution. The mixture was stirred at room temperature for 10 h. The reaction mixture was extracted with CHCl₃ and the combined organic layer was washed with saturated aqueous NaCl solution and dried over anhydrous Na₂SO₄. The solvent was removed under reduced pressure and subjected to preparative SEC using CHCl₃ as eluent to give **9** (153 mg, yellow solid, 69%). MALDI-TOF MS: (*m/z*) 1642 ([M+Na]⁺, C₇₆H₁₀₆N₄O₃₄Na, calcd. 1642); ¹H NMR (400MHz, CDCl₃, 22.2 °C): δ_H = 8.30 (s, 1H, ArH), 8.25 (d, *J* = 8.2 Hz, 2H, ArH), 7.91 (d, *J* = 8.2 Hz, 2H, ArH), 7.88 (d, *J* = 8.6 Hz, 2H, ArH), 8.25 (dd, *J* = 1.8, 8.6 Hz, 1H, ArH), 7.78 (d, *J* = 1.8 Hz, 1H, ArH), 7.71 (d, *J* = 8.2 Hz, 2H, ArH), 7.60 (d, *J* = 8.2 Hz, 1H, ArH), 5.16-5.04 (m, 6H, CD-H₁), 4.86-3.01 (m, 87H, CD-H).

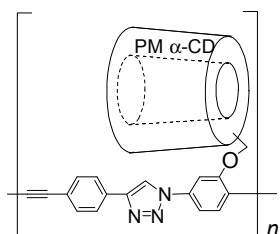
3. Synthesis of insulated molecular wire (**3**)



1 (20.0 mg, 13.8 μmol) was dissolved in *t*-BuOH (2.50 mL) under an argon atmosphere and degassed water (5.00 mL) was added to the solution. This suspension was stirred at 60 °C for 1 h. After cooling to ambient temperature, sodium ascorbate (0.546 mg, 2.76 μmol) and CuSO₄·5H₂O (0.345 mg, 1.38 μmol) were added to the solution; it was then stirred at room temperature for 10 h. The reaction mixture was

extracted with CHCl_3 and the combined organic layer was washed with saturated aqueous NaCl solution, dried over anhydrous Na_2SO_4 , and filtered to remove insoluble fractions. The solvent was removed in vacuo to yield **3** ($M_w = 1.00 \times 10^5$, PDI = 2.34, $\bar{n} = 70$) as a pale yellow solid (quant.).

4. Synthesis of uninsulated molecular wire (**3'**)



1' (200 mg, 0.13 mmol) was dissolved in NH^iPr_2 (50 mL) and THF (10 mL) under an argon atmosphere and $\text{Pd}(\text{PPh}_3)_2\text{Cl}_2$ (9.1 mg, 0.013 mmol) and CuI (0.4 mg, 2.1 μmol) were added to the solution. The mixture was stirred at 50 °C for 1 d and extracted with CHCl_3 . The combined organic layer was washed with saturated aqueous NaCl solution and dried over anhydrous Na_2SO_4 , and filtered to remove insoluble fractions. The solvent was removed in vacuo to yield **3'** ($M_w = 2.59 \times 10^4$, PDI = 2.43, $\bar{n} = 16$) as a pale yellow solid (quant.).

5. Flash-photolysis time-resolved microwave conductivity measurement (FP-TRMC)

The nanosecond laser pulses from a Nd: YAG laser (third harmonic generation, THG (355 nm) from Spectra Physics, INDY-HG, FWHM 3-5 ns) have been used as excitation sources. The photon density of the laser was set at $9.0 \times 10^{15} - 2.7 \times 10^{17}$ photons/ cm^2 . For time-resolved microwave conductivity (TRMC) measurement, the microwave frequency and power were set at ~ 9.1 GHz and 3 mW respectively, and the film of the samples (casted from 1~2 wt% CHCl_3 solutions at 0.2-0.4 μm thick) was set at the electric field maximum in the cavity. The TRMC signal picked up by a diode (rise time < 1 ns) is monitored by a digital oscilloscope (Tektronix, TDS3032B, rise time 1.4 ns). All the above experiments were carried out at room temperature. The transient photoconductivity ($\Delta\sigma$) of the samples is related to the reflected microwave power ($\Delta P_r/P_r$) and sum of the mobilities of charge carriers via:

$$\langle \Delta\sigma \rangle = \frac{1}{A} \frac{\Delta P_r}{P_r} \quad (1)$$

$$\Delta\sigma = e \sum \mu \phi N \quad (2)$$

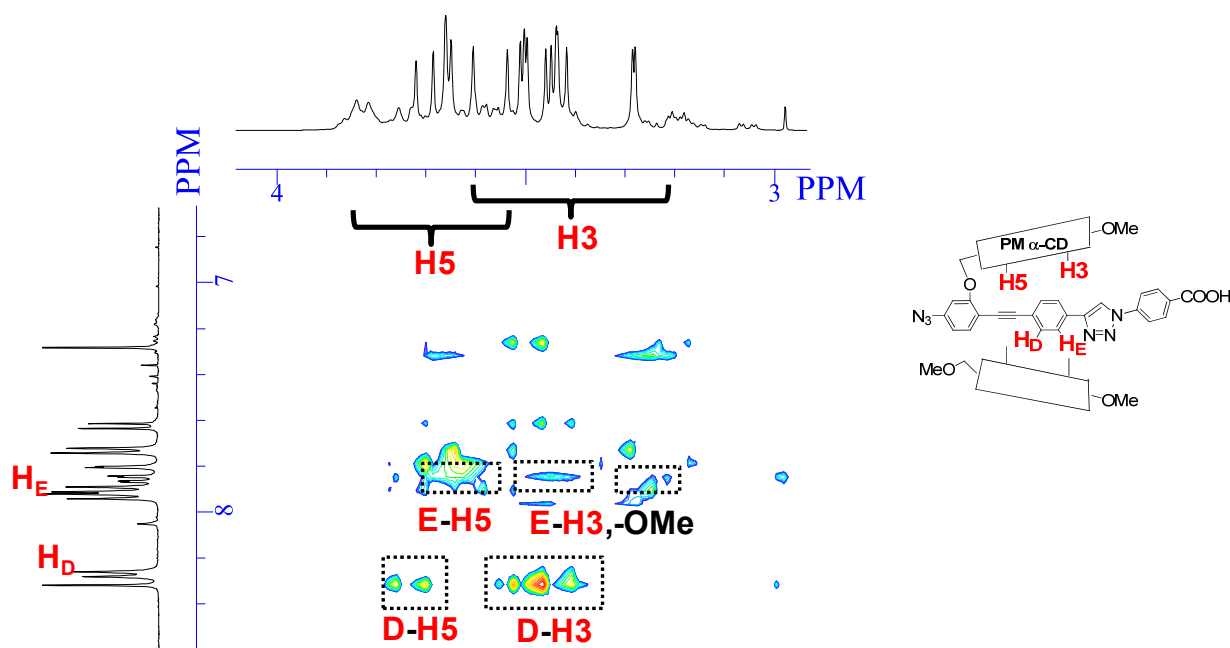
where A , e , ϕ , N , and $\sum\mu$ are a sensitivity factor, elementary charge of electron, photo carrier generation yield (quantum efficiency), the number of absorbed photons per unit volume, and sum of mobilities for negative and positive carriers respectively. The number of photons absorbed by the sample was estimated based on the power loss of an incident laser pulses averaged over 100 shots. The values of ϕ

in the polymer films were determined by transient absorption spectroscopy (TAS) and integration of transient current in direct-current time-of flight (DC-TOF) measurement. The other details of the set of apparatus were described elsewhere.³⁻⁷

Transient absorption spectroscopy measurement (TAS)

The TRMC measurement directly gives the value of $\phi\Sigma\mu$, which is the product of the quantum yield of charge carriers (ϕ) and the sum of their mobilities ($\Sigma\mu$). In-situ TAS measurement assigns the conductivity kinetics to negative or positive charge species and to determine its concentration quantitatively. The THG laser pulses from the nanosecond laser were used as excitation light sources. The incident photon densities in the present paper were set at 2.7×10^{17} photon/cm². The same films used in the TRMC measurement were irradiated with continuum white light for absorption spectroscopy perpendicularly with respect to the laser pulse. The spot size of the light probe was approximately 1 mm in diameter at the sample. After passing through the sample, the white light and/or emission was led to a grating unit (Hamamatsu, C5094) and scanned by a wide-dynamic-range streak camera (Hamamatsu, C7700). The streak image was collected via a CCD camera (Hamamatsu, C4742-98).⁸

Fig. S1 ROESY NMR of 9.



Partial 2D-ROESY NMR spectrum of **9** (600 MHz, CDCl₃) showing the correlations between aromatic protons of the π -conjugated guest and inner protons of cyclodextrins.

Fig. S2 Space-filling model of IMW 3.



Fig. S3 (a) Conductivity transients observed upon excitation of 355 nm at 5.9×10^{15} photons cm^{-2} in a casted film of **3** (solid) and **3'** (dashed) having a thickness of 1.5 μm , under air at 293 K. (b) Conductivity transients observed for **3** over the time range up to 1 ms. (c) Transient absorption spectra of **3** in a thin solid film was observed at 1 μs (dashed), 5 μs (dotted), 20 μs (dot-dashed), and 50 μs (solid), after excitation of 355 nm at 6.0×10^{16} photons cm^{-2} . (d) Kinetic trace of the transient optical absorption observed for **3** at 630 nm.

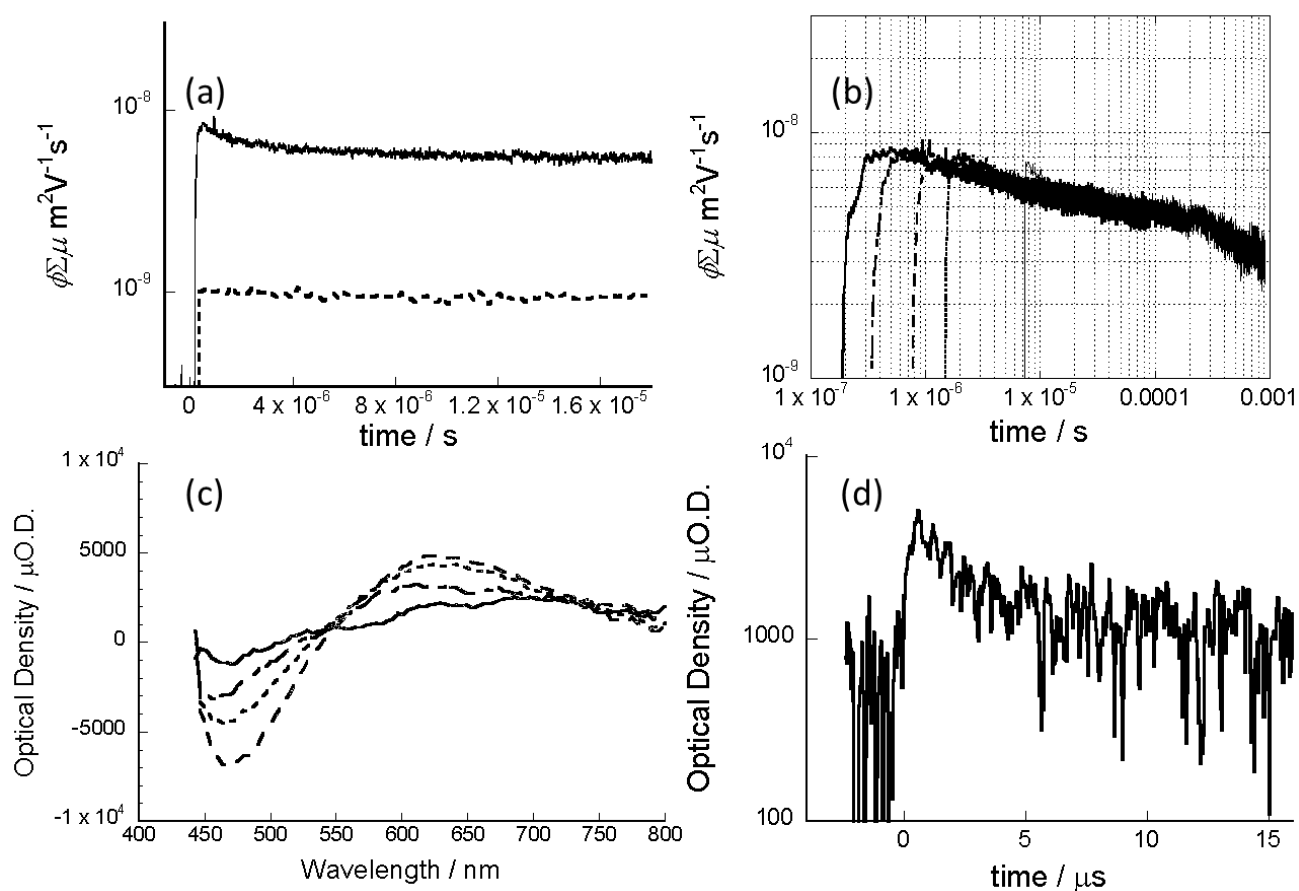
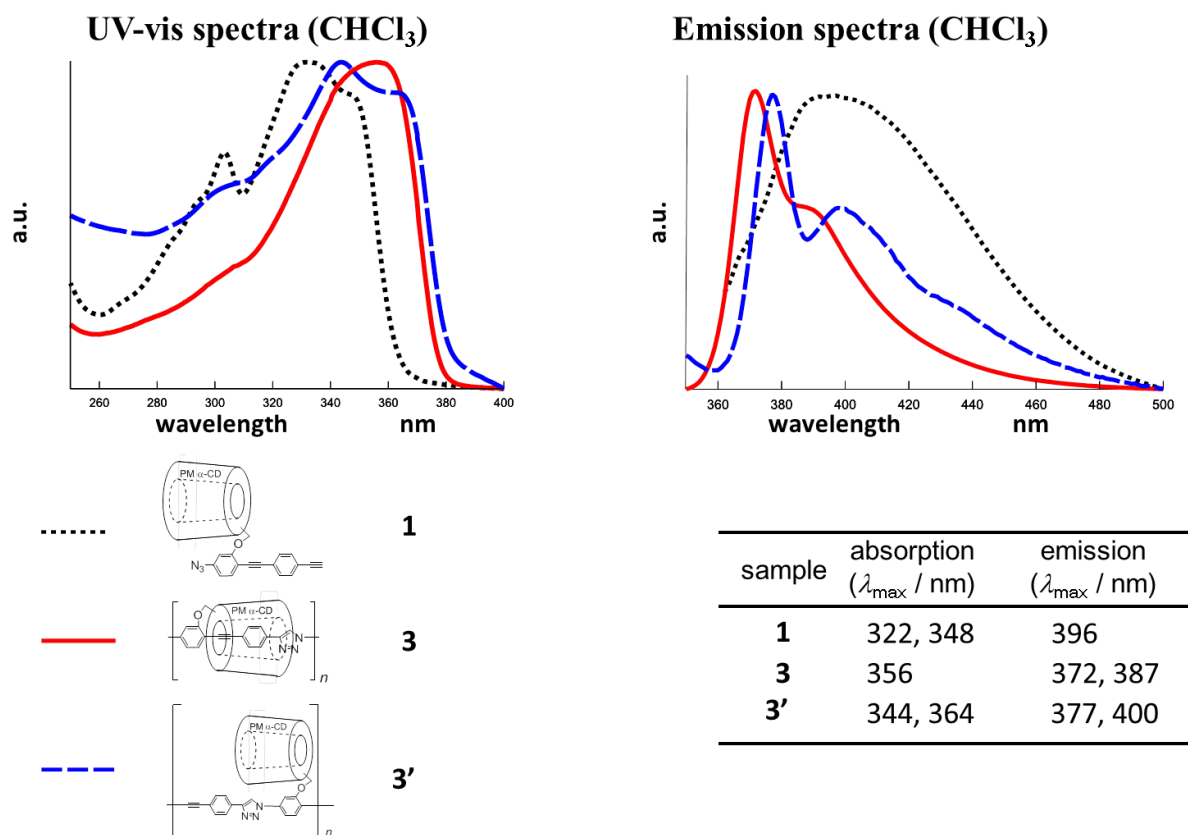


Fig. S4 UV-vis and emission spectra of **1**, **3**, and **3'**.



References

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