Electronic Supplementary Information

Through-Space π-Delocalized Pillar[5]arene

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Experimental

Materials. All solvents and reagents were used as supplied.

Measurements. The ^{1}H NMR spectra were recorded at 270 and 400 MHz and ^{13}C NMR spectra were recorded at 67.5 and 100 MHz with a JEOL-JNM EX270 and 400 spectrometers, respectively. The FT-IR spectra were obtained using a JASCO FT-IR460 plus infrared spectrometer. Gel permeation chromatography (GPC) analysis was carried out on Shodex GPC LF804 by using THF as an eluent at 25 ^{o}C at the flow rate of 1 mL min^{-1} after calibration with the standard polystyrene samples. Recyclable preparative high-pressure liquid chromatography (HPLC) was carried out on a Japan Analytical Industry LC-9204 (Shodex K-2002 column) instrument using $CHCl_3$ as an eluent. Fluorescence spectra were recorded on a Hitachi F-2500 fluorescence spectrometer. UV-Vis absorption spectra were recorded with a JASCO V-630. For fluorescence and UV-Vis measurements, one centimeter quartz cuvets were used. Relative quantum yields were determined by using 1-methylnaphthalene in cyclohexane (Φ_{fl} = 0.250 at excitation at 290 nm) and quinine sulfate in aqueous 0.10 M H2SO4 solution (Φ_{fl} = 0.546 at excitation at 365 nm) as a standard.

Pillar[5]arene was prepared according to the literature.[1]

Triflate Moieties Modified Pillar[5]arene (DTfPillar[5]arene). To a solution of Pillar[5]arene (1.00 g, 1.64 mmol) in pyridine (20 mL), trifluoromethanesulfonic anhydride (4.2 mL, 24.6 mmol) was added at 0 ^{o}C under nitrogen atmosphere. Then, the mixture was stirred at room temperature for 48 h. The solution was poured into water and the precipitate was collected by filtration. Column chromatography (silica gel,

toluene) afforded a whitish yellow solid (**DTfPillar[5]arene**, 0.95 g, 0.49 mmol, yield: 30.0%). R_f = 0.80 (silica gel, toluene 100%). ^{1}H NMR (acetone-d_6, 270 MHz, ppm) δ 7.52 (s, 10H, phenyl), 4.37 (s, 10H, methylene). ^{13}C NMR ($CDCl_3$, 67.5 MHz, ppm) δ 147.4, 133.1, 125.5 (phenyl), 120.2, 116.9 (triflate group), 31.1 (methylene bridge). Anal. Calcd for C45H20F30O30S10*2/3C5H5N: C, 29.26; H, 1.19; N, 0.47. Found: C, 29.09; H, 1.38; N, 0.63. FAB mass *m*/*z* = 1931 (M^+). GPC (THF, polystyrene standards): M_n = 1,800, M_w/M_n = 1.02.

Phenylethynyl Moieties Modified Pillar[5]arene (DPhEPillar[5]arene). To a solution of DTfPillar[5]arene (0.100 g, 0.051 mmol) in DMF (5 mL), ethynylbenzene (0.085 mL, 0.78 mmol), triethylamine (1 mL) and $PdCl_2(PPh)_2$ (0.18 g, 0.025 mmol) were added under nitrogen atmosphere. The mixture was stirred at 90 ^{o}C for 3 h. The solution was poured into water and the precipitate was collected by filtration. The resulting yellow residue was dissolved in $CHCl_3$ and was purified by a recycling preparative HPLC using $CHCl_3$ as an eluent. (**DPhEPillar[5]arene**, 38.7 mg, 0.028 mmol, yield: 52.4%). R_f = 0.35 (silica gel, toluene/hexane = 50%/50%). ^{1}H NMR ($CDCl_3$, 400 MHz, ppm): δ 7.80-6.20 (br, 60H, phenyl), 4.20-3.60 (br, 10H, methylene). ^{13}C NMR ($CDCl_3$, 100 MHz, ppm): δ 133.5, 131.5, 128.2 (phenyl), 86.5 (ethynyl) 29.7 (methylene bridge). FAB mass *m*/*z* = 1451 (M^+). GPC (THF, polystyrene standards): M_n = 1,200, M_w/M_n = 1.04.

^{1}H NMR Spectrum of DTfPillar[5]arene

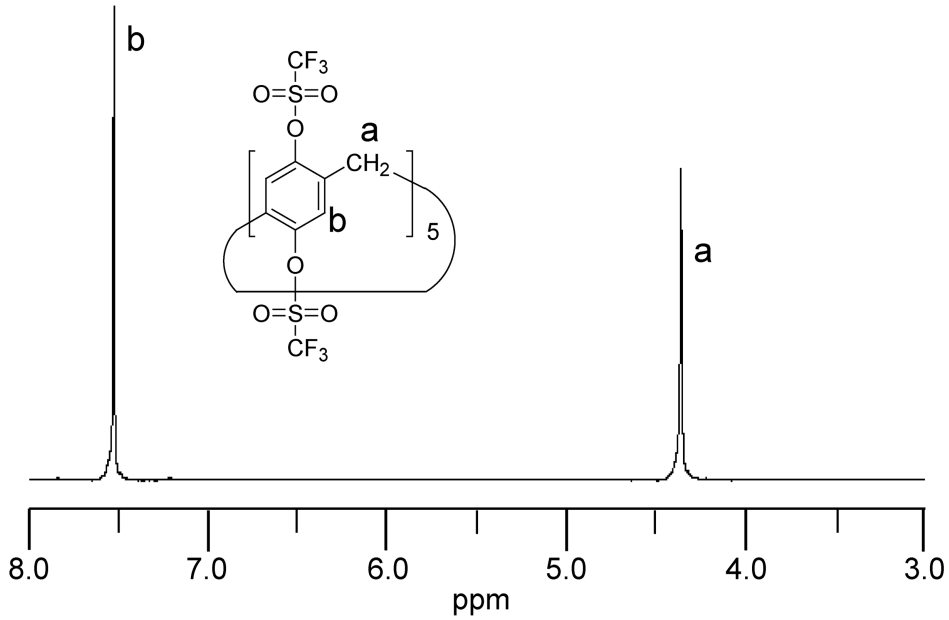

Figure 1S. ^{1}H NMR spectrum of DTfPillar[5]arene in acetone-d_6. Disappearing proton peak of hydroxyl group at 7.96 ppm from Pillar[5]arene indicated complete modification of triflate moieties.

^{1}H NMR Spectrum of DPhEPillar[5]arene

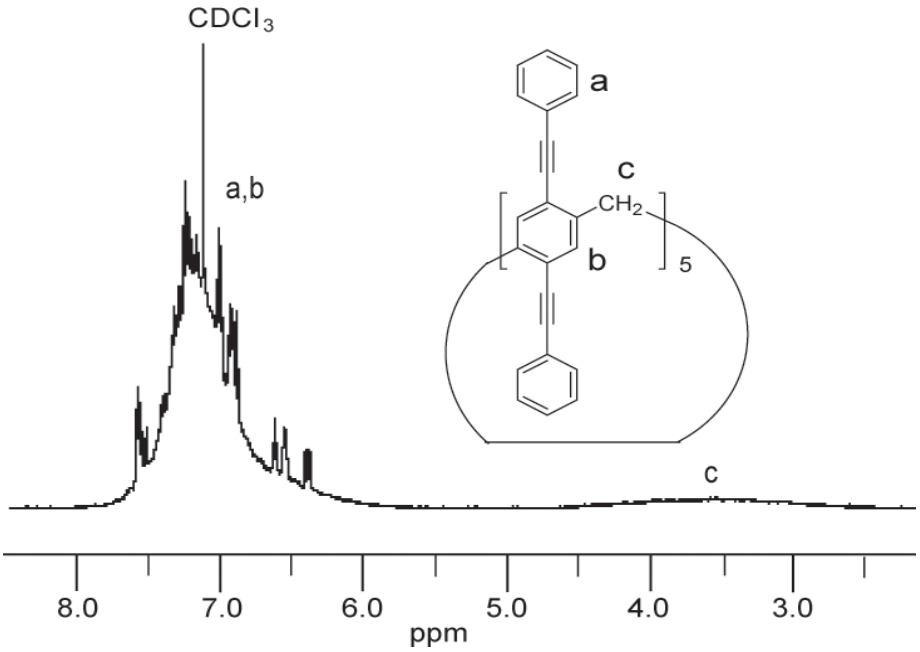

Figure 2S. ^{1}H NMR spectrum of DPhEPillar[5]arene in $CDCl_3$. Due to low conformational mobility of DPhEPillar[5]arene, peaks were broadening and splitting.

^{13}C NMR Spectrum of DTfPillar[5]arene

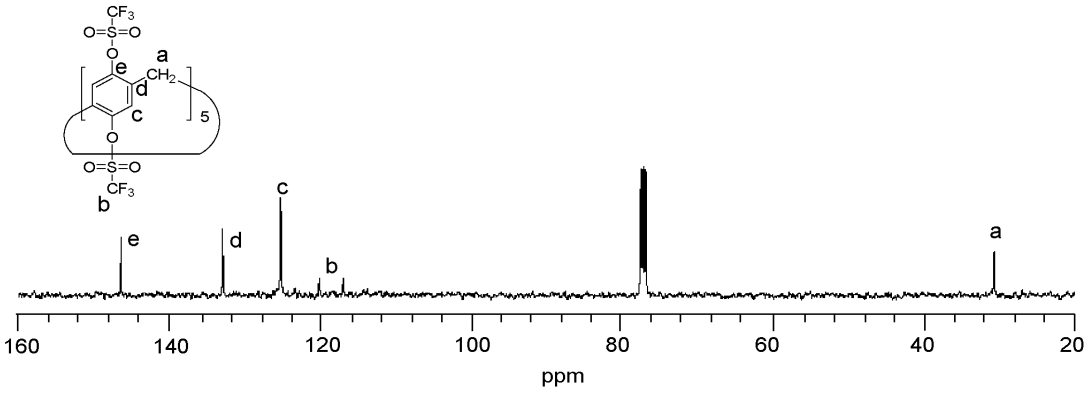

Figure 3S. ^{13}C NMR spectrum of (a) DTfPillar[5]arene in $CDCl_3$.

^{13}C NMR Spectrum of DPhEPillar[5]arene

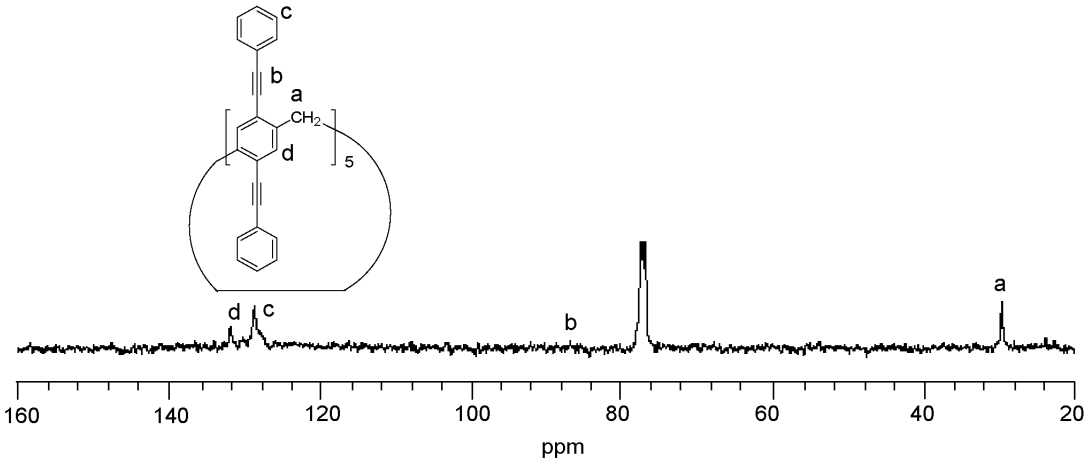

Figure 4S. ^{13}C NMR spectrum of DPhEPillar[5]arene in $CDCl_3$.

HPLC Trace of DPhEPillar[5]arene

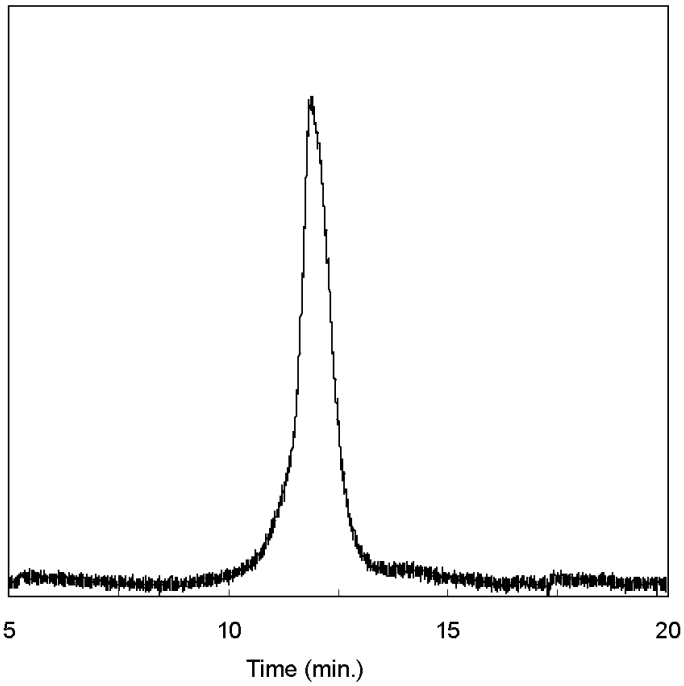

Figure 5S. HPLC trace of DPhEPillar[5]arene.

Solvent-Dependence on Emission Spectra of DPhEPillar[5]arene

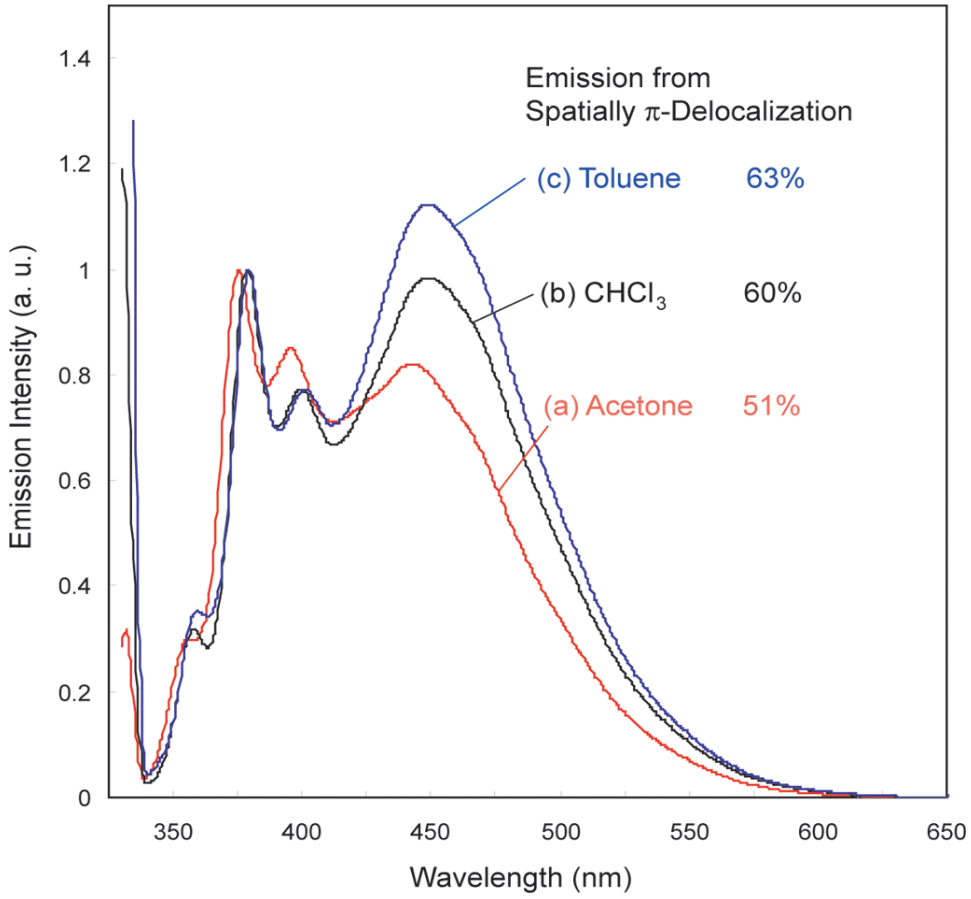

Figure 6S. Emission spectra (excited at 330 nm) of DPhEPillar[5]arene (0.010 mM) in (a) acetone, (b) $CHCl_3$ and (c) toluene. As polarity of measurement solvents was increased, the emission around 450-550 nm from spatially π-delocalized repeating units was increased. Low conformational mobility of DPhEPillar[5]arene in hydrophobic solvents should lead to the effective through-space π-delocalization within the cavity of DPhEPillar[5]arene.

Substituent Effect on Emission Spectra

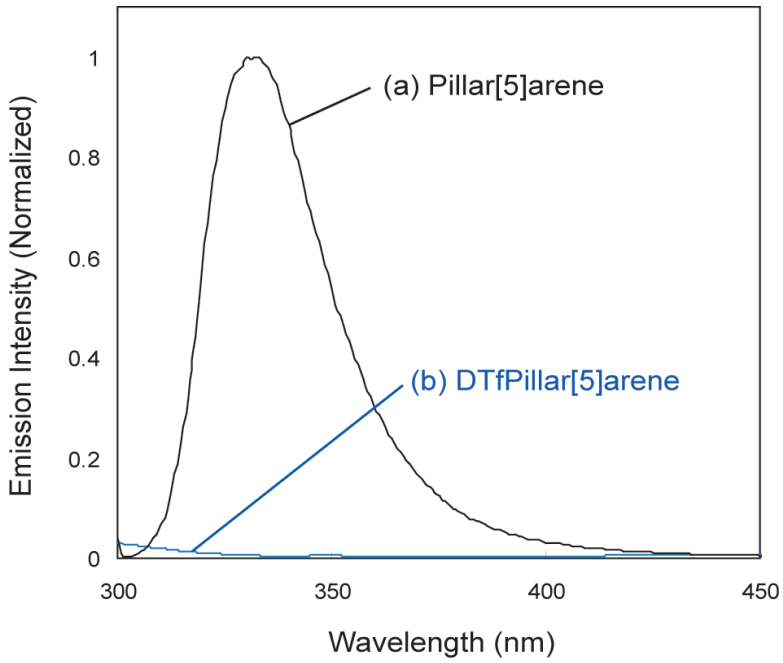

Figure 7S. Emission spectra of (a) Pillar[5]arene (0.020 mM in CH_3OH, black line) and (b) DTfPillar[5]arene (0.10 mM in $CHCl_3$, blue line) by excited at absorption maximum wavelength. Compared to Pillar[5]arene, the emission of DTfPillar[5]arene was extremely quenched. The quenching of the emission by modification of triflate groups into Pillar[5]arene is due to electron transfer from electron rich benzene rings to electron poor triflate moieties.

Reference

1) Ogoshi, T.; Kanai, S.; Fujinami, S.; Yamagishi, T.; Nakamoto, Y. *J. Am. Chem. Soc.* **2008**, *130*, 5022.