Electronic Supplementary Information (ESI)

"Clickable" Pillar[5]arenes

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Experimental Section

Materials. All solvents and reagents were used as supplied.

Measurements. The ^{1}H NMR spectra were recorded at 500 MHz and ^{13}C NMR spectra were recorded at 125 MHz with a JEOL- ECA500 spectrometers.

10OH-Pillar and **2c** were synthesized according to the previous paper.[1,2]

1. Under a nitrogen atmosphere **10OH-Pillar** (1.30 g, 2.13 mmol) was dissolved in DMF (30 mL) and THF (30 mL). Sodium hydride (1.60 g, 67.7 mmol) was added and the reaction mixture was stirred. Then, excess of propargyl bromide (5.10 g, 42.6 mmol) was added and the reaction mixture was heated at 60 ^{o}C for 48h. After removal of the solvent, the resulting solid was dissolved in $CHCl_3$ and water. The organic layer was dried over anhydrous Na_2SO_4. After filtration, solvents were evaporated to give a solid. Column chromatography (silica gel; acetone : chloroform = 1 : 1) afforded a white solid (**1**, 1.39 g, 1.40 mmol, Yield: 66%). ^{1}H NMR ($CDCl_3$, 500 MHz, ppm): δ 6.86 (s, 10H, phenyl protons), 4.53, (s, 20H, methylene protons at adjacent to O atoms), 3.81 (s, 10H, protons from methylene bridge), 2.27 (s, 10H, protons from C≡H). ^{13}C NMR ($CDCl_3$, 125 MHz, ppm): δ 149.3, 128.8, 115.4 (C of phenyl), 79.2, 74.8 (C of acethylene), 56.5 (C of methylene adjacent to O atom), 29.7 (C of methylene bridge). Anal. Calcd for C65H50O10*0.10DMF C, 78.56; H, 5.12; N 0.14. Found: C, 78.87; H, 5.43; N, 0.35. LRFABMS: *m/z* calcd for C105H151O10 $[M]^{+}$: 990, found 990.

3a. Under a nitrogen atmosphere **1** (0.0350 g, 0.0350 mmol) and **2a** (0.0466 g, 0.367 mmol) were dissolved in DMF (1 mL). Ascorbic acid (6.19 mg, 0.0350 mmol) and $CuSO_4$ $5H_2O$ (04.37 mg, 0.0175 mmol) were added and the reaction mixture was stirred. The reaction mixture was heated at 60 ^{o}C for 24h. After removal of the solvent, water was added. The precipitate was isolated by filtration, and washing with water. The resulting solid was dissolved in acetone. The solution was poured into diethyl ether and the resulting precipitate was collected by filtration. (**3a**, 0.0500 g, 0.0221 mmol, Yield: 63%). ^{1}H NMR (DMSO-d_6, 500 MHz, 110 ^{o}C, ppm): δ 8.01 (s, 10H, protons from triazole), 6.91 (s, 10H, phenyl protons), 4.86 (br, 20H, methylene protons adjacent to O atom), 3.65 (s, 10H, protons from methylene bridge), 1.65, 1.12, 0.79 (m, 110H, protons from hexyl groups). ^{13}C NMR (DMSO-d_6, 125 MHz, 25 ^{o}C, ppm): δ 149.9, 143.8, 128.6, 123.3, 115.1 (C of phenyl and triazole groups), 61.4 (C of methylene adjacent to O

atoms), 50.3 (C of methylene adjacent to triazole groups), 31.1, 31.0, 30.2, 26.1, 22.4, 14.0 (C of methylene bridge and hexyl groups). HRESIMS: *m/z* calcd for C125H180N30O10Na $[M + Na]^+$: 2284.43984, found 2284.43977.

3b. Under a nitrogen atmosphere **1** (0.250 g, 0.252 mmol) and **2b** (0.349 g, 2.62 mmol) were dissolved in DMF (7 mL). Ascorbic acid (44.2 mg, 0.252 mmol) and $CuSO_4\,5H_2O$ (31.2 mg, 0.125 mmol) were added and the reaction mixture was stirred. The reaction mixture was heated at 60 ^oC for 24h. After removal of the solvent, water was added. The precipitate was isolated by filtration, and washing with water. The resulting solid was dissolved in acetone. The solution was poured into diethyl ether and the resulting precipitate was collected by filtration. (**3b**, 0.114 g, 0.0491 mmol, Yield: 20%). ^1H NMR (DMSO-d_6, 500 MHz, 25 ^oC, ppm): δ 8.30 (br, 10H, protons from triazole), 7.21 (br, 50H, phenyl protons), 6.89 (br, 10H, phenyl protons), 5.51 (br, 20H, methylene protons adjacent to triazole groups), 4.97, 4.66 (br, 20H, methylene protons adjacent to O atom), 3.58 (br, 10H, protons from methylene bridge). ^{13}C NMR (DMSO-d_6, 125 MHz, 25 ^oC, ppm): δ 149.7, 144.3, 136.7, 129.5, 129.0, 128.7, 125.4, 115.4 (C of phenyl and triazole groups), 62.3 (C of methylene adjacent to O atoms), 53.8 (C of methylene adjacent to triazole groups), 29.5, (C of methylene bridge). HRESIMS: *m/z* calcd for C135H120N30O10Na $[M + Na]^+$: 2343.97014, found 2343.97048.

3c. Under a nitrogen atmosphere **1** (0.250 g, 0.252 mmol) and **2c** (0.674 g, 2.62 mmol) were dissolved in DMF (7 mL). Ascorbic acid (44.2 mg, 0.252 mmol) and $CuSO_4\,5H_2O$ (31.2 mg, 0.125 mmol) were added and the reaction mixture was stirred. The reaction mixture was heated at 60 ^oC for 36h. After removal of the solvent, water was added. The precipitate was isolated by filtration, and washing with water. The resulting solid was dissolved in chloroform. Column chromatography (silica gel; chloroform : methanol = 9 : 1) afforded a solid (**3c**, 80.7 mg, 0.0227 mmol, Yield: 9%). ^1H NMR (DMSO-d_6, 500 MHz, 25 ^oC, ppm): δ 7.20-8.70 (br, 100H, protons from pyrene and triazole groups), 6.89 (br, 10H, phenyl protons), 5.95 (br, 20H, methylene protons adjacent to triazole groups), 4.95, 4.66 (br, 20H, methylene protons adjacent to O atom), 3.53 (br, 10H, protons from methylene bridge). ^{13}C NMR (DMSO-d_6, 125 MHz, 25 ^oC, ppm): δ 148.0, 142.6, 129.7, 129.6, 129.0, 127.7, 127.3, 127.2, 127.1, 126.5, 126.0, 125.2, 124.5, 124.3, 123.7, 122.8, 122.6, 121.4, 113.7 (C of pyrene, benzene and triazole groups), 60.6 (C of methylene adjacent to O atoms), 49.8 (C of methylene adjacent to triazole group), 29.4, (C of methylene bridge). Anal. C235H160N30O10*0.80$CHCl_3$ C, 77.39; H, 4.43; N 11.48. Found: C, 77.71; H, 4.64; N, 11.18. MALDITOFMS: *m/z* calcd for

$C_{235}H_{160}N_{30}O_{10}Na$ $[M + Na]^+$: 3584, found 3584.

^{1}H NMR Spectrum of 1

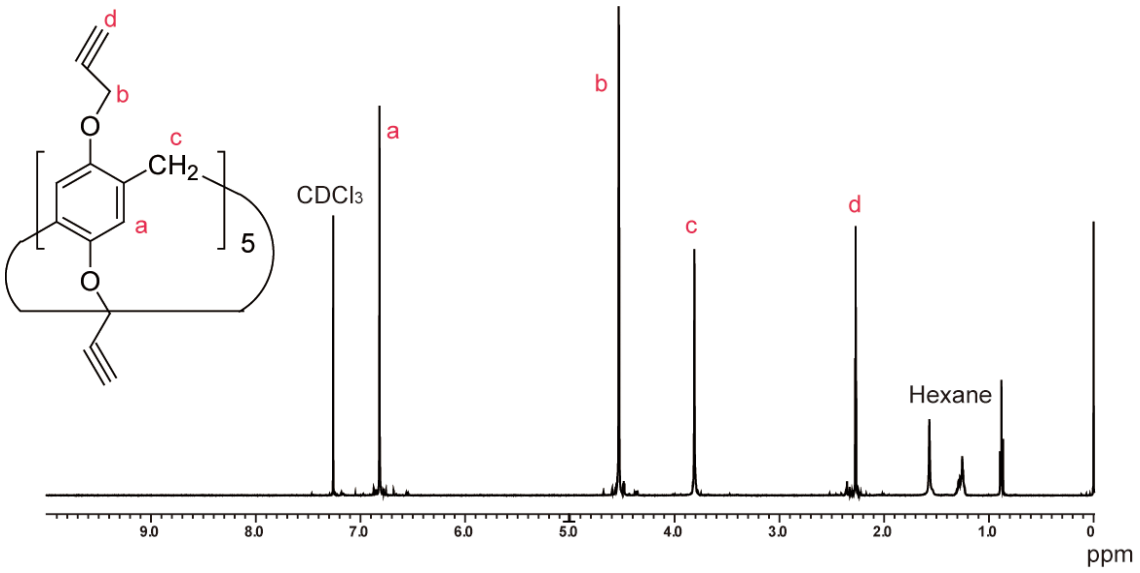

Figure 1S. ^{1}H NMR spectrum of **1** in $CDCl_3$ at 25 ^oC.

^{13}C NMR Spectrum of 1

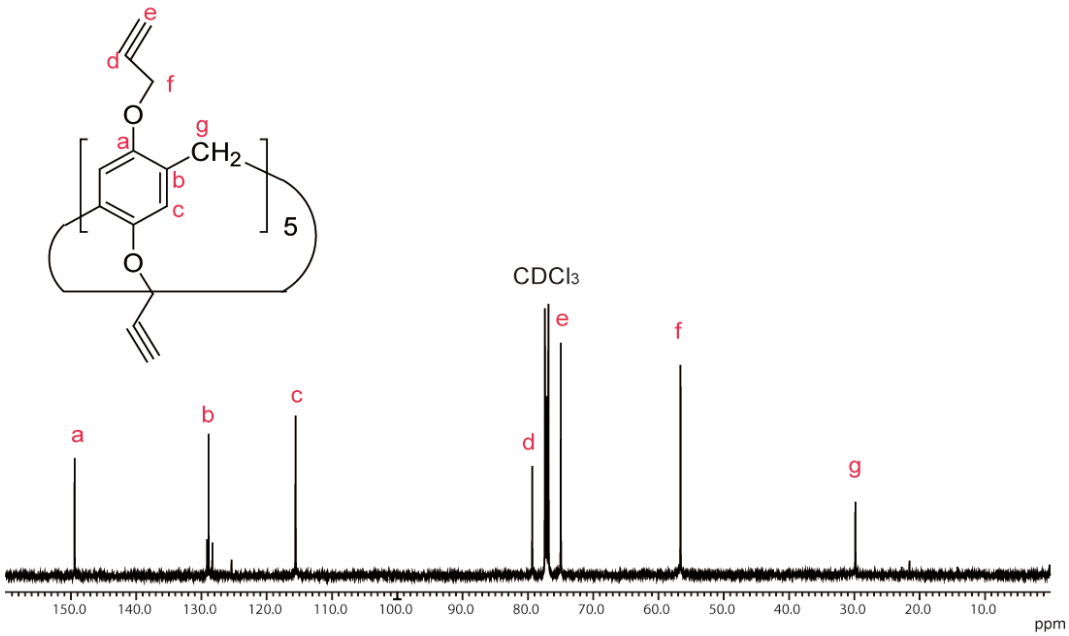

Figure 2S. ^{13}C NMR spectrum of **1** in $CDCl_3$ at 25 ^{o}C.

^{1}H NMR Spectra of 3a

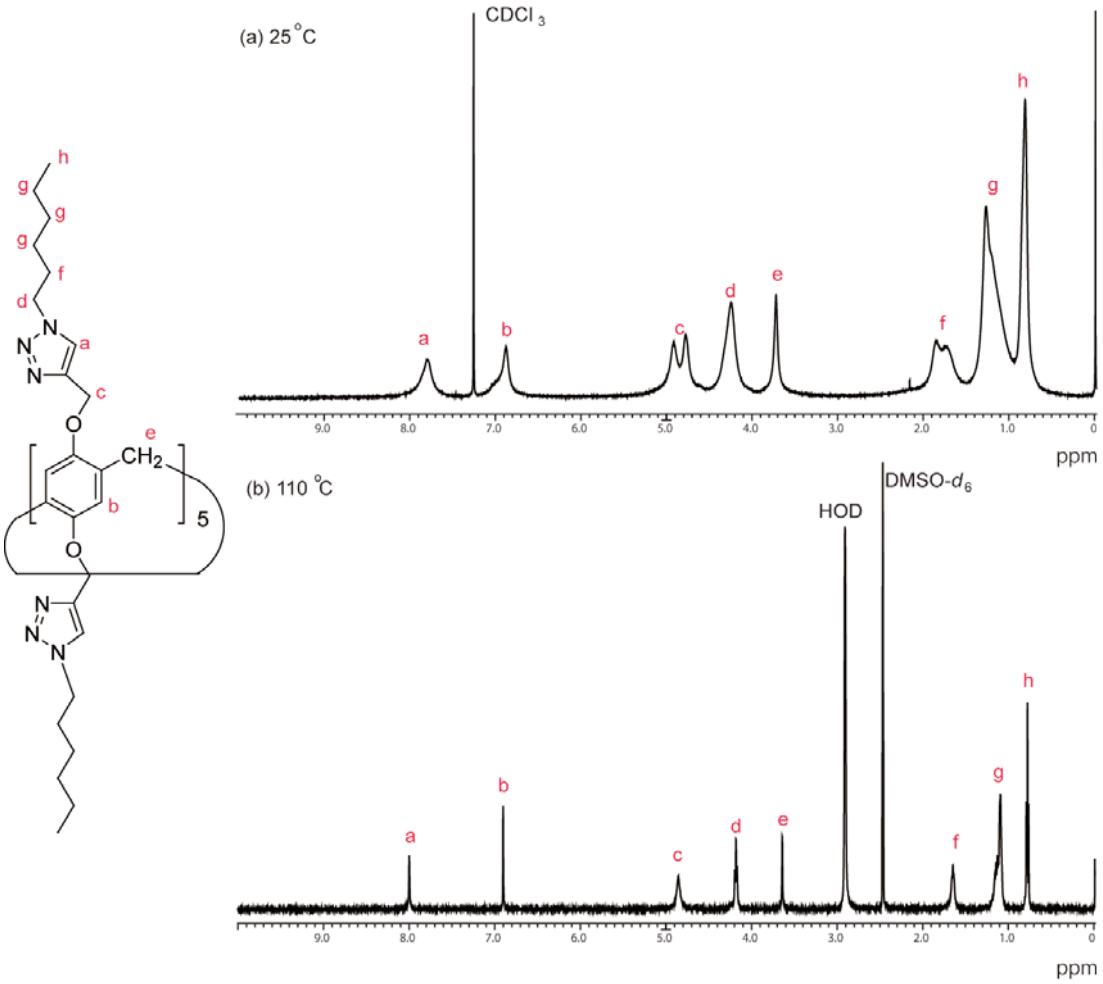

Figure 3S. ^{1}H NMR spectra of **3a** in (a) $CDCl_3$ at 25 ^{o}C and (b) DMSO-d_6 at 110 ^{o}C.

^{13}C NMR Spectrum of 3a

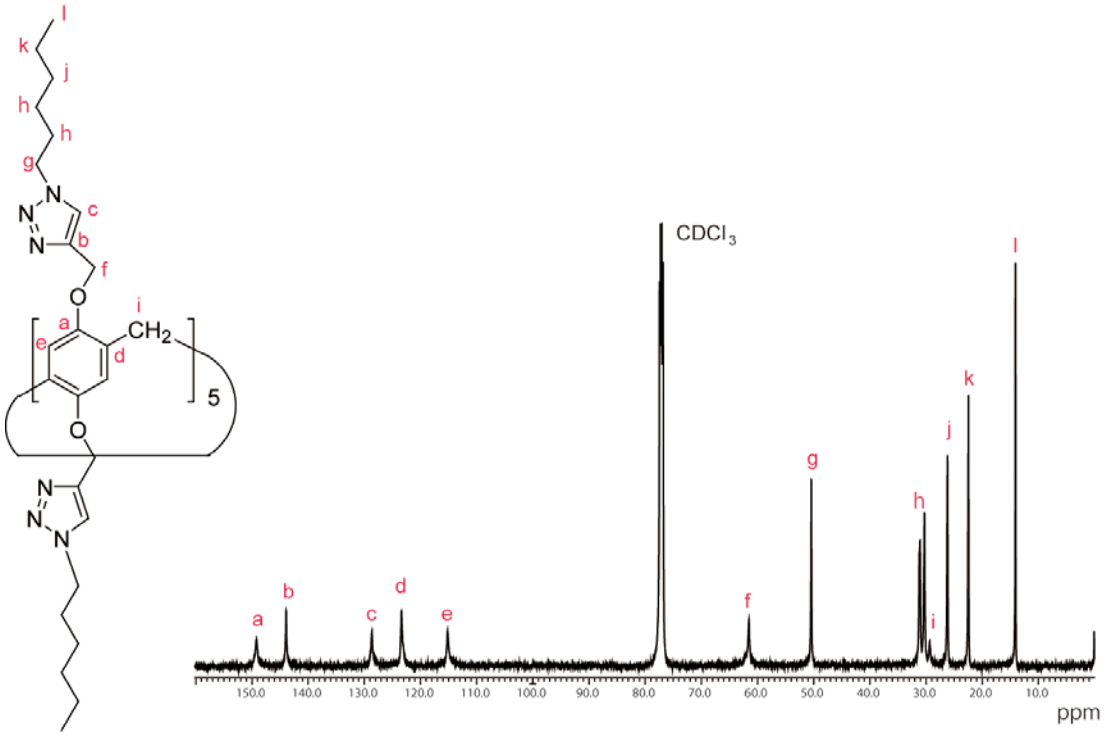

Figure 4S. ^{13}C NMR spectrum of **3a** in DMSO-d_6 at 25 ^{o}C.

^{1}H NMR Spectrum of 3b

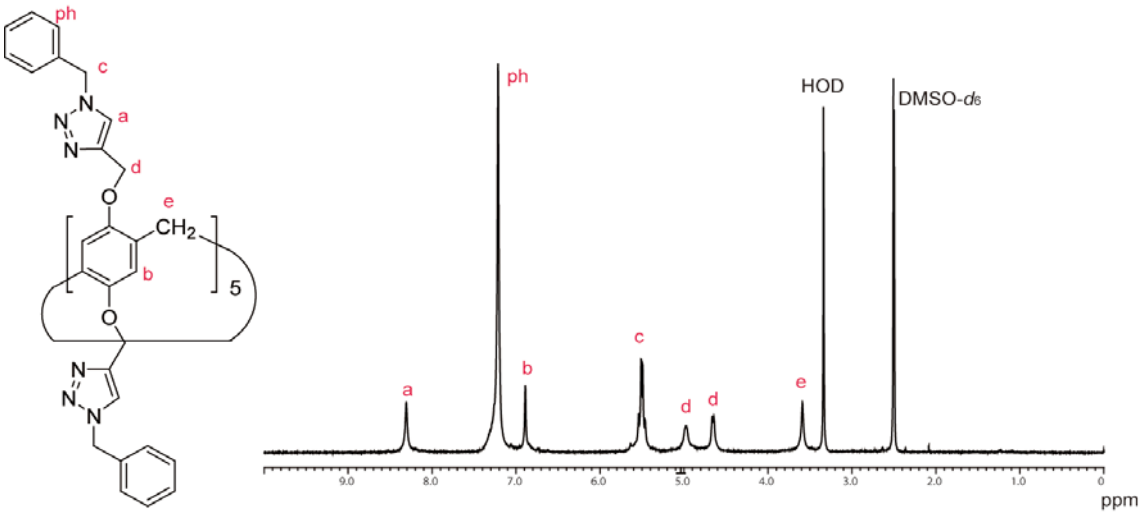

Figure 5S. ^{1}H NMR spectrum of **3b** in DMSO-d_6 at 25 ^{o}C.

^{13}C NMR Spectrum of 3b

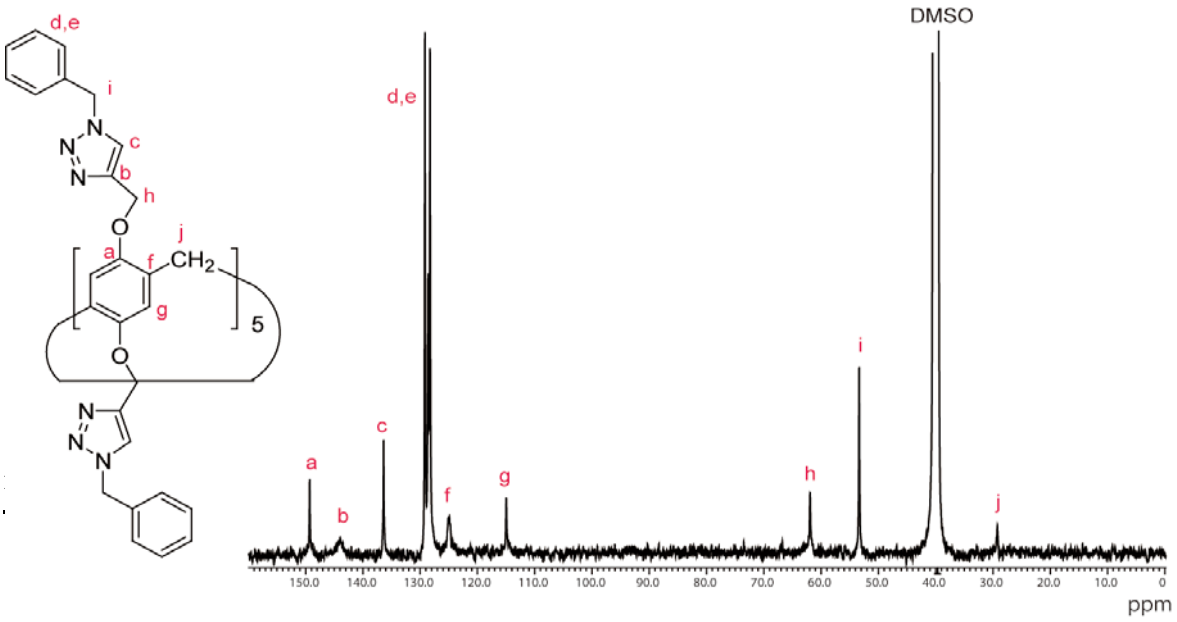

Figure 6S. ^{13}C NMR spectrum of **3b** in DMSO-d_6 at 25 ^{o}C.

^{1}H NMR Spectrum of 3c

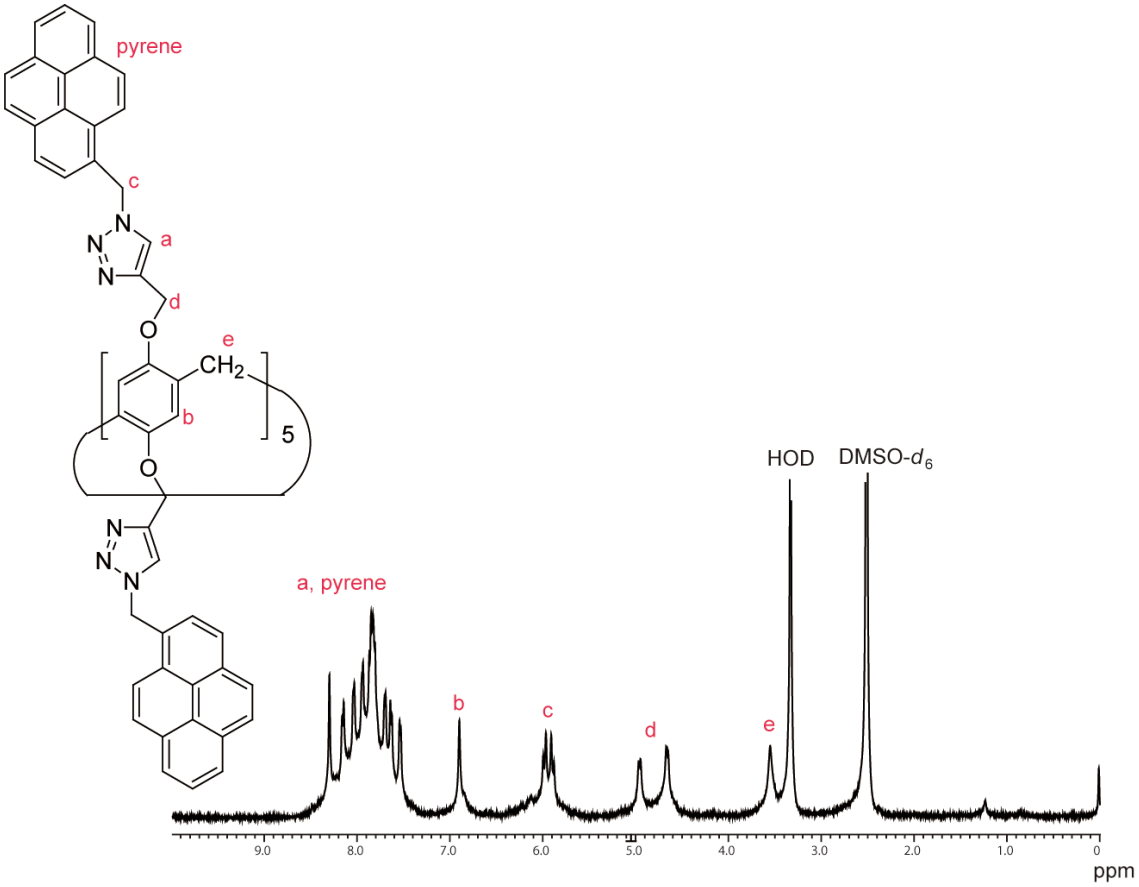

Figure 7S. ^{1}H NMR spectrum of **3c** in DMSO-d_6 at 25 ^{o}C.

^{13}C NMR Spectrum of 3c

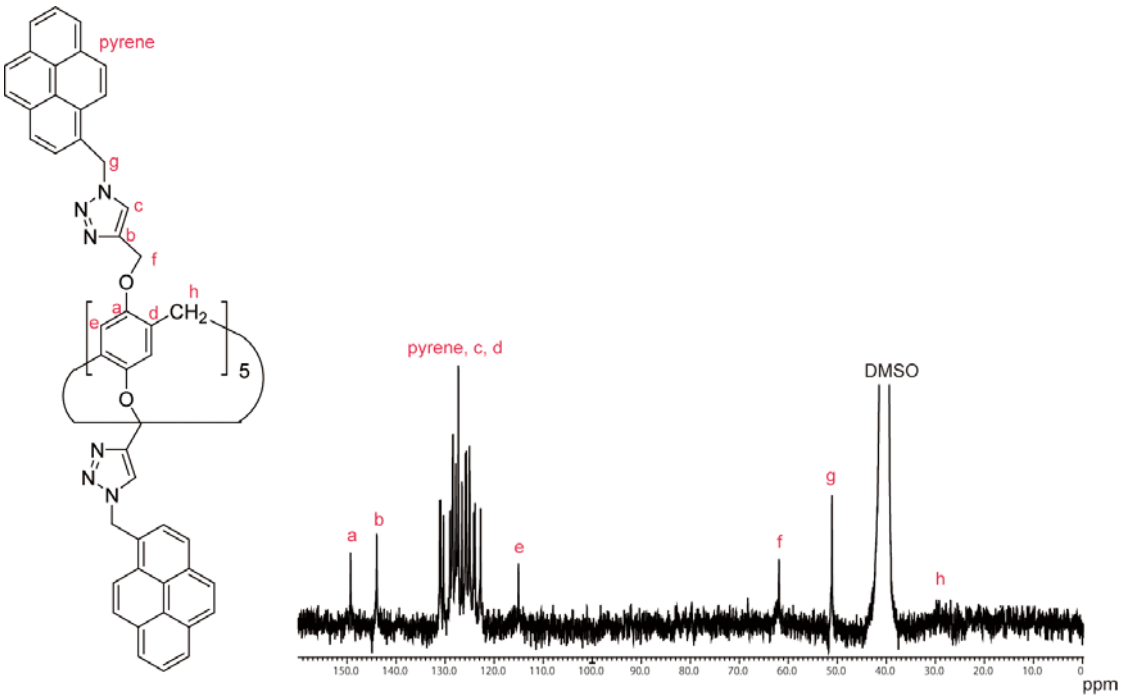

Figure 8S. ^{13}C NMR spectrum of **3c** in DMSO-d_6 at 25 ^{o}C.

Concentration-Variable Emission Spectra of 3c

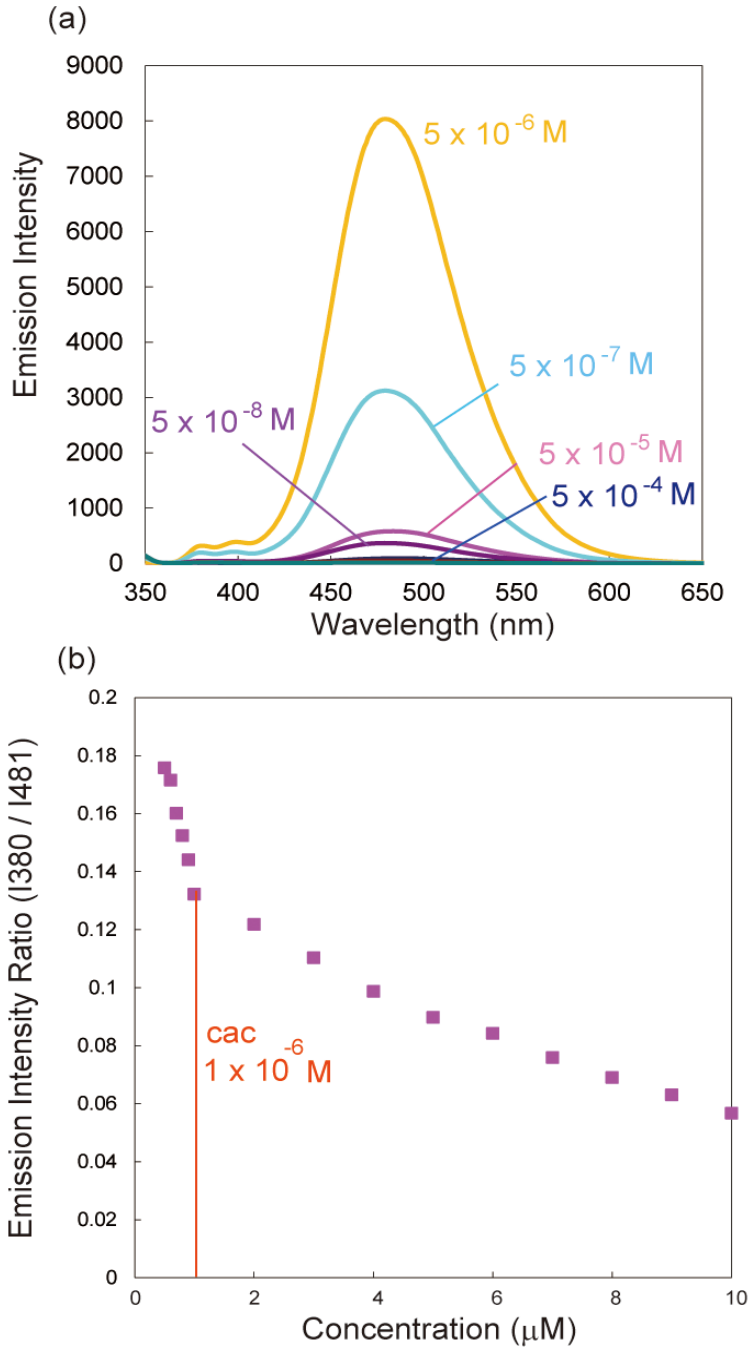

Figure 9S. (a) Concentration dependence of the emission spectra of **3c** (1.0×10^{-6} M) in DMSO (excited at 345 nm). (b) Emission intensity ratio [I380 (from monomer emission) / I481 (from excimer emission)] vs. concentration of **3c**. Critical association concentration (cac) value was determined from the flexion point of the emission intensity ratio.

Variable-Temperature UV-Vis Spectra of 3c and 4

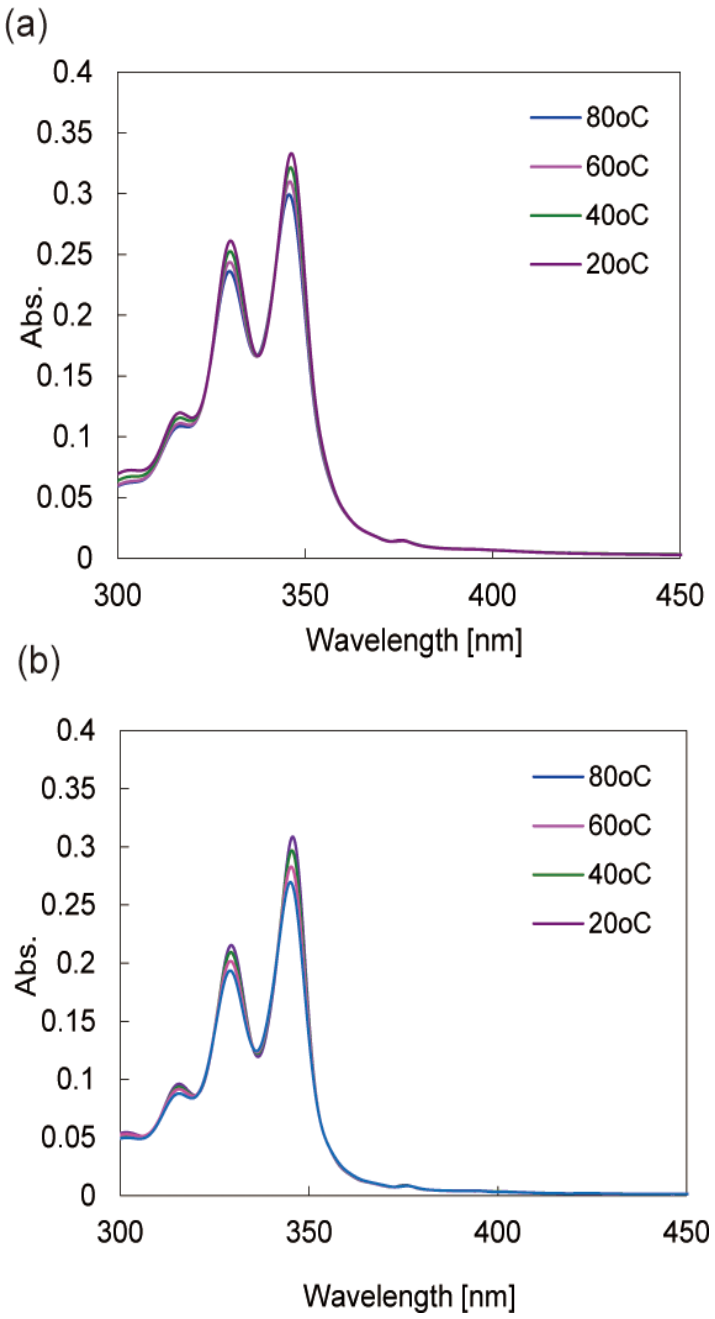

Figure 10S. Variable temperature UV-Vis absorption spectra of (a) **3c** (1.0×10^{-6} M) and (b) **4 (**5.0×10^{-6} M) in DMSO.

References

1) T. Ogoshi, T. Aoki, K. Kitajima, S. Fujinami, T. Yamagishi and Y. Nakamoto, *J. Org. Chem.*, 2011, **76**, 328.
2) Z. Xu, N. J. Singh, J. Lim, J. Pan, H. N. Kim, S. Park, K. S. Kim and J. Yoon, *J. Am. Chem. Soc.*, 2009, **131**, 15528.