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Supporting Information

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Switching the Interior Hydrophobicity of a Self-Assembled Spherical Complex through the Photoisomerization of Confined Azobenzene Chromophores

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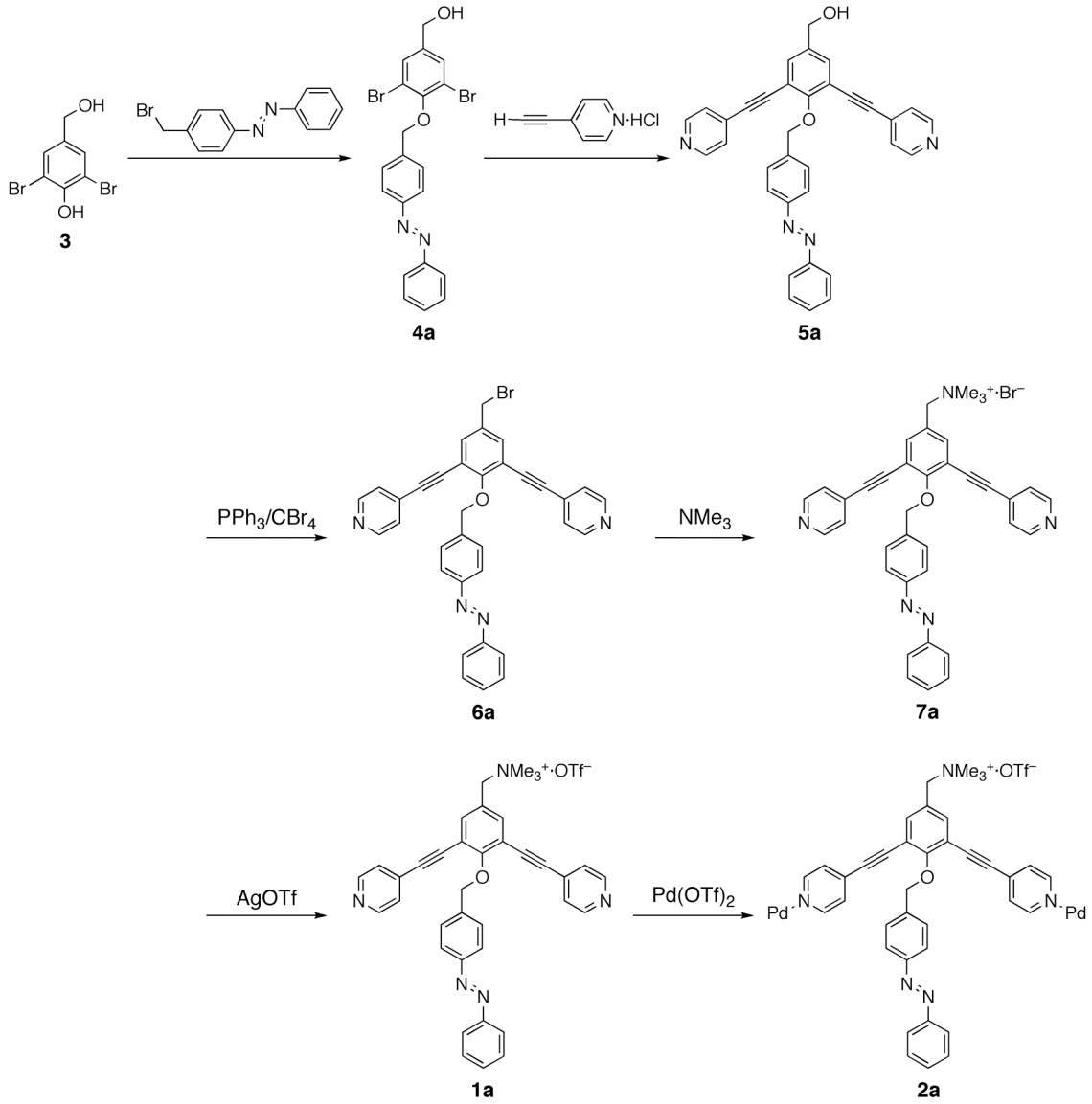
Contents

General

NMR spectra were recorded on Bruker DRX-500 and AV-500 (500 MHz) spectrometer. All NMR spectral data were collected at 300 K and the chemical shift values reported here are with respect to an internal TMS standard for $CDCl_3$ and CD_3CN. MALDI-TOF (LD+, dithranol) mass spectra were recorded on Applied Biosystems Voyager DE-STR. CSI-MS (cold-spray ionization mass spectrometry) spectra were measured on a four-sector (BE/BE) tandem mass spectrometer (JMS-700C, JEOL) equipped with a CSI source. UV-Vis absorption spectra were recorded on a Shimadzu UV-3150 spectrometer. IR measurements were carried out as KBr pellets using a Varian Scimitar FTS-2000 instrument. The synchrotron X-ray diffraction study was carried out at 80.0 K (λ = 0.6890 Å) at PF-AR of the High Energy Accelerator Research Organization (KEK). The diffraction data were collected by Rigaku CrystalClear, and cell refinement and data reduction were performed using the HKL2000 program. Structural solution was performed using the SHELXS-97 (Sheldrick, 1990) program, and structural refinement was performed using the SHELXL-97 (Sheldrick, 1997) program.

Solvents and reagents were purchased form TCI CO., Ltd., WAKO Pure Chemical Industries Ltd., and Sigma-Aldrich Co. All the chemicals were of reagent grade and used without any further purification.

Ligand 1a and complex 2a were synthesized as follows:



3,5-Dibromo-4-hydroxybenzyl alcohol (**3**)[1] and 4-(bromomethyl)azobenzene[2] were prepared as described in the literatures.

[1] A. Sudalai, G. S. K. Rao, *Indian J. Chem., Sect. B* **1989**, *28*, 858–859.

[2] N. Iyi, T. Fujita, C. V. Yalamaggad, F. L. Arbeloa, *Appl. Clay Sci.* **2001**, *19*, 47–58.

1,3-Dibromo-5-hydroxymethyl-2-[[4-(phenylazo)phenyl]methoxy]benzene (4a). 3,5-Dibromo-4-hydroxybenzyl alcohol **3** (3.04 g, 10.8 mmol) and 4-(bromomethyl)azobenzene (2.76 g, 10.0 mmol) were dissolved in DMF (80 mL). Potassium carbonate (3.07 g, 22.2 mmol) was added, and the resulting mixture was stirred at 100 ºC for 12 h. The solvent was evaporated, and the residue was redissolved in $CHCl_3$. The precipitates were filtered off and the filtrate was concentrated *in vacuo*. The crude product was purified by column chromatography on silica gel (ethyl acetate/hexane = 1:3) to give **4a** as an orange powder (2.16 g, 4.53 mmol) in 45% yield: mp 124.2–125.2 ºC. ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.97 (d, *J* =

8.4 Hz, 2H), 7.94 (d, *J* = 7.1 Hz, 2H), 7.75 (d, *J* = 8.4 Hz, 2H), 7.57 (s, 2H), 7.53 (t, *J* = 7.1 Hz, 2H), 7.48 (t, *J* = 7.1 Hz, 1H), 5.11 (s, 2H), 4.67 (d, *J* = 5.9 Hz, 2H), 1.75 (t, *J* = 5.9 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ: 152.7 (C), 152.6 (C), 152.0 (C), 139.8 (C), 139.1 (C), 131.1 (2CH), 129.1 (CH), 129.0 (CH), 123.0 (CH), 122.9 (CH), 118.6 (C), 74.1 (CH_2), 63.5 (CH_2). IR (KBr, cm^{-1}): 3327, 3060, 2883, 1702, 1546, 1468, 1454, 1399, 1377, 1267, 1258, 1155, 1056, 1015, 984, 836, 766, 739, 684, 547. MALDI-TOF MS *m/z* calcd for $[M + H]^+$: 476.96; found 476.79. Anal. Calcd for $C_{20}H_{16}Br_2N_2O_2$: C, 50.45; H, 3.39; N, 5.88. Found: C, 50.18; H, 3.42; N, 5.68.

5-Hydroxymethyl-2-[4-(phenylazo)phenyl]methoxy-1,3-bis(4-pyridylethynyl)benzene (5a). Tri-*t*-butylphosphine (0.90 mL, 0.30 mmol; 10% solution in hexane) and diisopropylamine (4.5 mL, 32 mmol) were added to a mixture of compound **4a** (1.21 g, 2.53 mmol), 4-ethynylpyridine hydrochloride (1.08 g, 7.70 mmol), $Pd(PhCN)_2Cl_2$ (61.6 mg, 0.161 mmol), and copper(I) iodide (21.3 mg, 0.112 mmol) in degassed dioxane (18 mL). This mixture was stirred at 50 ºC for 21 h under argon atmosphere. The reaction mixture was diluted with $CHCl_3$ (20 mL), filtrated, evaporated *in vacuo*, and redissolved in $CHCl_3$. The $CHCl_3$ layer was washed with ethylenediamine-containing water and brine, dried over anhydrous Na_2SO_4, filtrated, and concentrated *in vacuo*. The crude product was purified by column chromatography on silica gel (gradient elution from $CHCl_3$ to $CHCl_3$/MeOH = 30:1) to give **5a** as an orange powder (1.26 g, 2.42 mmol) in 96% yield: mp 172.5–173.5 ºC. ^{1}H NMR (500 MHz, $CDCl_3$) δ: 8.60 (d, *J* = 5.5 Hz, 4H), 7.93 (d, *J* = 7.2 Hz, 2H), 7.91 (d, *J* = 8.3 Hz, 2H), 7.69 (d, *J* = 8.3 Hz, 2H), 7.59 (s, 2H), 7.53 (t, *J* = 7.2 Hz, 2H), 7.49 (t, *J* = 7.2 Hz, 1H), 7.30 (d, *J* = 5.5 Hz, 4H), 5.43 (s, 2H), 4.72 (d, *J* = 5.8 Hz, 2H), 2.01 (br t, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ: 160.3 (C), 152.6 (C), 152.5 (C), 149.9 (CH), 139.7 (C), 137.1 (C), 133.0 (CH), 131.2 (CH), 131.0 (C), 129.2 (CH), 128.7 (CH), 125.4 (CH), 123.0 (CH), 122.9 (CH), 117.1 (C), 91.6 (C), 89.6 (C), 75.7 (CH_2), 63.8 (CH_2). IR (KBr, cm^{-1}): 3253, 3071, 3043, 2887, 2208, 1597, 1539, 1492, 1448, 1415, 1366, 1235, 1153, 1120, 1064, 1003, 968, 871, 819, 767, 685, 548, 498. MALDI-TOF MS *m/z* calcd for $[M + H]^+$: 521.20; found 521.00. Anal. Calcd for $C_{34}H_{24}N_4O_2 \cdot 0.5H_2O$: C, 77.11; H, 4.76; N, 10.58. Found: C, 77.34; H, 4.85; N, 10.43.

Trimethyl[[[4-[4-(phenylazo)phenyl]methoxy-3,5-bis(4-pyridylethynyl)]phenyl]methyl]ammonium bromide (7a). Triphenylphosphine (561 mg, 2.14 mmol) and carbon tetrabromide (931 mg, 2.81 mmol) were added sequentially to a solution of compound **5** (500 mg, 0.960 mmol) in dry THF (45 ml) at room temperature under argon atmosphere. After stirring the mixture for 3 h, the quantitative formation of compound **6a** (not isolated) in the solution was confirmed by MALDI-TOF MS (*m/z* calcd for $[M + H]^+$: 585.11; found 584.85). The above solution was treated with trimethylamine (22 ml, 94.6 mmol; 4.3 M solution in water) and stirred at room temperature for 21 h. The solvent was evaporated, and the residue was dissolved in $CHCl_3$. The $CHCl_3$ layer was washed with NaBr-containing water, dried over

anhydrous Na_2SO_4, filtrated, and concentrated *in vavuo*. The crude product was purified by column chromatography on silica gel (gradient elution from CH_3CN_3/H_2O (10 wt% NaBr) = 50:1 to CH_3CN_3/H_2O (10 wt% NaBr) = 10:1). The product was redissolved in $CHCl_3$, washed with water, dried over anhydrous Na_2SO_4, filtrated, and concentrated *in vavuo* to give **7a** as an orange powder (580 mg, 0.902 mmol) in 94% yield: mp 182.5–183.5 ºC. ^{1}H NMR (500 MHz, CD_3CN) δ: 8.60 (d, *J* = 6.0 Hz, 4H), 7.90 (d, *J* = 7.8 Hz, 2H), 7.85 (d, *J* = 8.2 Hz, 2H), 7.79 (s, 2H), 7.75 (d, *J* = 8.2 Hz, 2H), 7.62–7.55 (m, 3H), 7.41 (d, *J* = 6.0 Hz, 4H), 5.57 (s, 2H), 4.45 (s, 2H), 3.08 (s, 9H). ^{13}C NMR (125 MHz, CD_3CN) δ: 163.6 (C), 153.6 (C), 153.5 (C), 151.0 (CH), 141.1 (C), 140.0 (CH), 132.6 (CH), 131.3 (C), 130.5 (CH), 130.4 (CH), 126.4 (CH), 125.2 (C), 123.8 (CH), 123.7 (CH), 118.8 (C), 93.3 (C), 89.3 (C), 76.9 (CH_2), 68.6 (CH_2), 53.6 (CH_3). IR (KBr, cm^{-1}): 3023, 2884, 2216, 1594, 1538, 1487, 1447, 1411, 1375, 1240, 1220, 1142, 1068, 990, 926, 880, 820, 768, 687, 546, 508. MALDI-TOF MS *m/z* calcd for $[M - Br^-]^+$: 562.26; found 562.04. Anal. Calcd for $C_{37}H_{32}BrN_5O{\cdot}2.5H_2O$: C, 64.63; H, 5.42; N, 10.18. Found: C, 64.37; H, 5.54; N, 9.95.

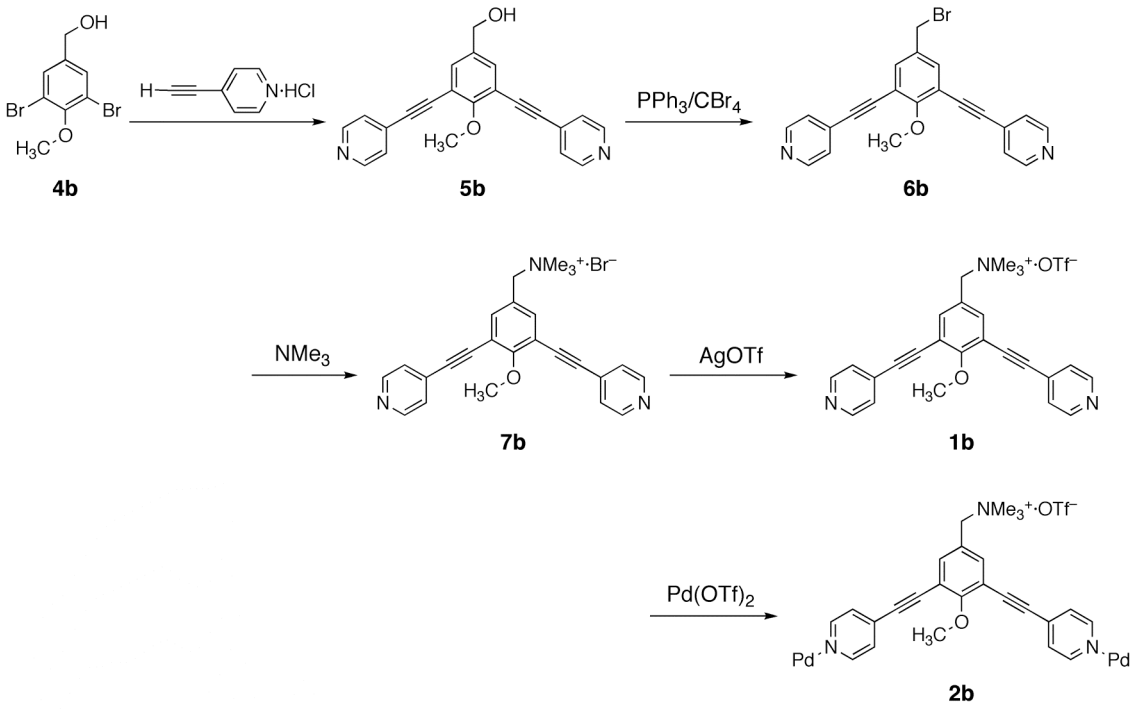
Trimethyl[[[4-[4-(phenylazo)phenyl]methoxy-3,5-bis(4-pyridylethynyl)]phenyl]methyl]ammonium trifluoromethanesulfonate (1a). Compound **7a** (94.6 mg, 0.147 mmol) and silver trifluoromethanesulfonate (37.9 mg, 0.147 mmol) were dissolved in a CH_3CN (8 mL). The resulting mixture was stirred at room temperature for 12 h under argon atmosphere. The reaction mixture was filtrated and concentrated *in vacuo* to give **1a** as an orange powder (96.9 mg, 0.136 mmol) in 93% yield: mp 176.8–177.8 ºC. ^{1}H NMR (500 MHz, CD_3CN) δ: 8.61 (d, *J* = 6.0 Hz, 4H), 7.90 (d, *J* = 6.7 Hz, 2H), 7.89 (d, *J* = 8.4 Hz, 2H), 7.75 (s, 2H), 7.75 (d, *J* = 8.4 Hz, 2H), 7.61–7.56 (m, 3H), 7.40 (d, *J* = 6.0 Hz, 4H), 5.58 (s, 2H), 4.38 (s, 2H), 3.05 (s, 9H). ^{13}C NMR (125 MHz, CD_3CN) δ: 163.6 (C), 153.6 (C), 153.5 (C), 151.1 (CH), 141.1 (C), 139.9 (CH), 132.5 (CH), 131.2 (C), 130.5 (CH), 130.4 (CH), 126.3 (CH), 125.0 (C), 123.8 (CH), 123.7 (CH), 118.8 (C), 93.3 (C), 89.2 (C), 76.9 (CH_2), 68.8 (CH_2), 53.6 (CH_3). (The peak of $CF_3SO_3^-$ is probably overlapped with that of solvent CD_3CN (δ: 118.4).) IR (KBr, cm^{-1}): 3040, 2883, 2217, 1595, 1539, 1489, 1440, 1412, 1370, 1259, 1225, 1160, 1031, 880, 821, 769, 689, 639, 547, 518. MALDI-TOF MS *m/z* calcd for $[M - CF_3SO_3^-]^+$: 562.26; found 561.83. Anal. Calcd for $C_{38}H_{32}F_3N_5O_4S{\cdot}H_2O$: C, 62.54; H, 4.70; N, 9.60. Found: C, 62.80; H, 4.94; N, 9.44.

Complex 2a. Compound **1a** (12.6 mg, 17.7 μmol) was treated with $Pd(CF_3SO_3)_2$ solution (1.8 mL, 8.9 μmol; 4.9 mM solution in CD_3CN) at 50 ºC for 4 h. The quantitative formation of complex **2a** was confirmed by ^{1}H NMR. The title compound was precipitated as an orange solid by adding diethyl ether to the solution. Isolated yield was 14.4 mg (0.658 μmol, 89%): mp > 160 ºC (decomposed). ^{1}H NMR (500 MHz, CD_3CN) δ: 8.97 (d, *J* = 6.4 Hz, 96H), 7.80 (s, 48H), 7.77 (d, *J* = 7.3 Hz, 48H), 7.71 (d, *J* = 8.4 Hz, 48H), 7.54 (d, *J* = 8.4 Hz, 48H), 7.52 (d, *J* = 6.4 Hz, 96H), 7.51 (d, *J* = 7.3 Hz, 48H), 7.44 (t, *J* = 7.3 Hz, 24H), 5.39 (s, 48H), 4.39 (s, 48H), 3.02

(s, 216H). ^{13}C NMR (125 MHz, CD_3CN) δ: 164.0 (C), 153.4 (C), 153.3 (C), 152.2 (CH), 141.2 (CH), 140.3 (C), 135.9 (C), 132.4 (CH), 130.3 (C), 130.1 (CH), 129.6 (CH), 125.3 (C), 123.7 (CH), 123.6 (CH), 123.3 (C), 120.8 (C), 94.2 (C), 91.4 (C), 76.9 (CH_2), 68.2 (CH_2), 53.4 (CH_3). IR (KBr, cm^{-1}): 3055, 2883, 2216, 1765, 1613, 1496, 1444, 1371, 1256, 1161, 1065, 1030, 925, 879, 836, 769, 690, 639, 561, 517. CSI-MS ($CF_3SO_3^-$ salt, CH_3CN): *m/z* 2294.1 $[M–6(CF_3SO_3^-)]^{6+}$, 1945.4 $[M–7(CF_3SO_3^-)]^{7+}$, 1683.1 $[M–8(CF_3SO_3^-)]^{8+}$, 1479.3 $[M–9(CF_3SO_3^-)]^{9+}$, 1316.6 $[M–10(CF_3SO_3^-)]^{10+}$, 1183.3 $[M–11(CF_3SO_3^-)]^{11+}$, 1072.0 $[M–12(CF_3SO_3^-)]^{12+}$, 978.1 $[M–13(CF_3SO_3^-)]^{13+}$, 897.5 $[M–14(CF_3SO_3^-)]^{14+}$. Anal. Calcd for $C_{936}H_{768}F_{144}N_{120}O_{168}S_{48}Pd_{12}\cdot 90H_2O$: C, 47.72; H, 4.06; N, 7.13. Found: C, 47.50; H, 3.79; N, 6.85.

X-ray crystallographic analysis of 2a. Single crystals of complex **2a** were obtained by slow vapor diffusion of 1,4-dioxane into a CH_3CN solution of **2a** at 17 ºC. The diffraction data were measured at 80.0 K [wavelength (λ) = 0.6890 Å] at Photon Factory–Advanced Ring for Pulse X-rays (PF-AR) of the High Energy Accelerator Research Organization (KEK). Space group $Fm\bar{3}m$, temperature (*T*) = 80.0 ± 0.1 K, *a* = 61.794 ± 0.007 Å, volume (*V*) = 235,959 ± 47 Å^3, atomic number (*Z*) = 4. Anisotropic least-squares refinement for the palladium atoms and isotropic refinement for the other atoms on 3231 independent merged reflections (R_{int} = 0.5704) converged at residual $wR_2(F^2)$ = 0.3816 for all data; residual $R_1(F)$ equals 0.2943 for 1149 observed data [$I > 2\sigma(I)$], and goodness of fit (GOF) equals 1.726. CCDC-637523 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Ligand 1b and complex 2b were synthesized as follows:



3,5-Dibromo-4-methoxybenzyl alcohol (**4b**) was prepared as described in the literatures.[3]

[3] a) J. Boukouvalas, N. Lachance, M. Ouellet, M. Trudeau, *Tetrahedron Lett*. **1998**, *39*, 7665–7668; b) D. Zuev, J. A. Michne, H. Huang, B. R. Beno, D. Wu, Q. Gao, J. R. Torrente, C. Xu, C. M. Conway, J. E. Macor, G. M. Dubowchik, *Org*. *Lett*. **2005**, *7*, 2465–2468.

5-Hydroxymethyl-2-methoxy-1,3-bis(4-pyridylethynyl)benzene (5b). Tri-*t*-butylphosphine (1.5 mL, 0.50 mmol; 10% solution in hexane) and diisopropylamine (5.0 mL, 36 mmol) were added to a mixture of 3,5-dibromo-4-methoxybenzyl alcohol **4b** (1.22 g, 4.11 mmol), 4-ethynylpyridine hydrochloride (1.48 g, 10.6 mmol), $Pd(PhCN)_2Cl_2$ (94.7 mg, 0.247 mmol), and copper(I) iodide (31.8 mg, 0.167 mmol) in degassed dioxane (20 mL). This mixture was stirred at 50 ºC for 27 h under argon atmosphere. The reaction mixture was diluted with ethyl acetate (20 mL), filtrated, evaporated *in vacuo*, and redissolved in ethyl acetate. The ethyl acetate layer was washed with ethylenediamine-containing water and brine, dried over anhydrous Na_2SO_4, filtrated, and concentrated *in vacuo*. The crude product was purified by column chromatography on silica gel (gradient elution from $CHCl_3$ to $CHCl_3$/MeOH = 30:1) to give **5b** as a grayish white powder (0.942 g, 2.77 mmol) in 67% yield: mp 150.0–151.0 ºC. ^{1}H NMR (500 MHz, $CDCl_3$) δ: 8.62 (d, *J* = 5.0 Hz, 4H), 7.55 (s, 2H), 7.40 (d, *J* = 5.0 Hz, 4H), 4.69 (s, 2H), 4.15 (s, 3H), 2.54 (br s, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ: 161.6 (C), 149.8 (CH), 136.8 (C), 133.1 (CH), 131.2 (C), 125.5 (CH), 116.5 (C), 91.2 (C), 89.5 (C), 63.8 (CH_2), 61.7 (CH_3). IR (KBr, cm^{-1}): 3152, 2943, 2853, 2215, 1602, 1539, 1492, 1466, 1418, 1361,

1296, 1242, 1129, 1048, 1000, 963, 889, 819, 743, 661, 623, 547, 496. MALDI-TOF MS *m/z* calcd for $[M + H]^+$: 341.13; found 341.03. Anal. Calcd for $C_{22}H_{16}N_2O_2 \cdot 0.2H_2O$: C, 76.82; H, 4.81; N, 8.14. Found: C, 77.20; H, 5.14; N, 7.79.

Trimethyl[[[4-methoxy-3,5-bis(4-pyridylethynyl)]phenyl]methyl]ammonium bromide (7b). Triphenylphosphine (561 mg, 2.66 mmol) and carbon tetrabromide (1.19 g, 3.60 mmol) were added sequentially to a solution of compound **5b** (403 mg, 1.18 mmol) in dry THF (60 ml) at room temperature under argon atmosphere. After stirring the mixture for 3 h, trimethylamine (32 ml, 138 mmol; 4.3 M solution in water) was added and the resulting solution was stirred at room temperature for 20 h. The solvent was evaporated, and the residue was dissolved in $CHCl_3$. The product was precipitated from the $CHCl_3$ layer by vigorously shaking with water, filtrated, and dried *in vavuo* to give **7b** as a bright yellow powder (413 mg, 0.893 mmol) in 76% yield: mp > 230 ºC (decomposed). ^{1}H NMR (500 MHz, $CDCl_3$) δ: 8.62 (d, *J* = 6.1 Hz, 4H), 7.85 (s, 2H), 7.39 (d, *J* = 6.1 Hz, 4H), 5.30 (s, 2H), 4.22 (s, 3H), 3.47 (s, 9H). ^{13}C NMR (125 MHz, $CDCl_3$) δ: 163.8 (C), 149.9 (CH), 138.7 (CH), 130.5 (C), 125.4 (CH), 123.0 (C), 117.3 (C), 92.9 (C), 88.0 (C), 67.0 (CH_2), 61.7 (CH_3), 52.9 (CH_3). IR (KBr, cm^{-1}): 3035, 3019, 2984, 2219, 1594, 1534, 1491, 1473, 1417, 1250, 1213, 1141, 993, 883, 822, 551, 510. MALDI-TOF MS *m/z* calcd for $[M - Br^-]^+$: 382.19; found 382.06. Anal. Calcd for $C_{25}H_{24}BrN_3O \cdot H_2O$: C, 62.50; H, 5.46; N, 8.75. Found: C, 62.18; H, 5.47; N, 8.59.

Trimethyl[[[4-methoxy-3,5-bis(4-pyridylethynyl)]phenyl]methyl]ammonium trifluoromethanesulfonate (1b). Compound **7b** (200 mg, 0.433 mmol) and silver trifluoromethanesulfonate (111 mg, 0.434 mmol) were dissolved in a CH_3CN (20 mL). The resulting mixture was stirred at room temperature for 10 h under argon atmosphere. The reaction mixture was filtrated and concentrated *in vacuo* to give **1b** as a light brown powder (207 mg, 0.389 mmol) in 90% yield: mp > 195 ºC (decomposed). ^{1}H NMR (500 MHz, CD_3CN) δ: 8.64 (d, *J* = 5.9 Hz, 4H), 7.74 (s, 2H), 7.49 (d, *J* = 5.9 Hz, 4H), 4.39 (s, 2H), 4.24 (s, 3H), 3.06 (s, 9H). ^{13}C NMR (125 MHz, CD_3CN) δ: 164.8 (C), 151.1 (CH), 140.0 (CH), 131.3 (C), 126.3 (CH), 124.5 (C), 118.0 (C), 93.1 (C), 89.0 (C), 68.8 (CH_2), 62.7 (CH_3), 53.5 (CH_3). (The peak of $CF_3SO_3^-$ is probably overlapped with that of solvent CD_3CN (δ: 118.4).) IR (KBr, cm^{-1}): 3037, 2983, 2218, 1596, 1538, 1491, 1474, 1421, 1277, 1260, 1226, 1159, 1031, 989, 881, 826, 757, 640, 574, 548, 518. MALDI-TOF MS *m/z* calcd for $[M - CF_3SO_3^-]^+$: 382.19; found 381.99. Anal. Calcd for $C_{26}H_{24}F_3N_3O_4S$: C, 58.75; H, 4.55; N, 7.91. Found: C, 58.58; H, 4.81; N, 7.77.

Complex 2b. Compound **1b** (9.49 mg, 17.9 μmol) was treated with $Pd(CF_3SO_3)_2$ solution (1.8 mL, 9.0 μmol; 5.0 mM solution in CD_3CN) at 50 ºC for 4 h. The quantitative formation of complex **2b** was confirmed by ^{1}H NMR. The title compound was precipitated as a pale yellow solid by adding diethyl ether to the

solution. Isolated yield was 9.46 mg (0.537 μmol, 72%): mp > 175 ºC (decomposed). ^{1}H NMR (500 MHz, CD_3CN) δ: 9.07 (d, *J* = 6.5 Hz, 96H), 7.78 (s, 48H), 7.67 (d, *J* = 6.5 Hz, 96H), 4.36 (s, 48H), 4.20 (s, 72H), 3.00 (s, 216H). ^{13}C NMR (125 MHz, CD_3CN) δ: 165.9 (C), 152.3 (CH), 141.3 (CH), 136.1 (C), 129.8 (CH), 124.7 (C), 116.9 (C), 94.3 (C), 91.3 (C), 68.4 (CH_2), 63.2 (CH_3), 53.4 (CH_3). IR (KBr, cm^{-1}): 3049, 2882, 2825, 2215, 1613, 1498, 1476, 1421, 1256, 1160, 1065, 1029, 988, 880, 837, 757, 638, 561, 517. CSI-MS ($CF_3SO_3^-$ salt, CH_3CN): *m/z* 2052.1 $[M–8(CF_3SO_3^-)]^{8+}$, 1807.7 $[M–9(CF_3SO_3^-)]^{9+}$, 1611.9 $[M–10(CF_3SO_3^-)]^{10+}$, 1452.2 $[M–11(CF_3SO_3^-)]^{11+}$, 1318.5 $[M–12(CF_3SO_3^-)]^{12+}$, 1205.8 $[M–13(CF_3SO_3^-)]^{13+}$, 1108.8 $[M–14(CF_3SO_3^-)]^{14+}$, 1024.8 $[M–15(CF_3SO_3^-)]^{15+}$, 951.8 $[M–16(CF_3SO_3^-)]^{16+}$, 887.1 $[M–17(CF_3SO_3^-)]^{17+}$. Anal. Calcd for $C_{648}H_{576}F_{144}N_{72}O_{168}S_{48}Pd_{12}·48H_2O$: C, 42.12; H, 3.67; N, 5.46. Found: C, 41.93; H, 3.94; N, 5.23.

3.8.3 Selected NMR and MS Spectra

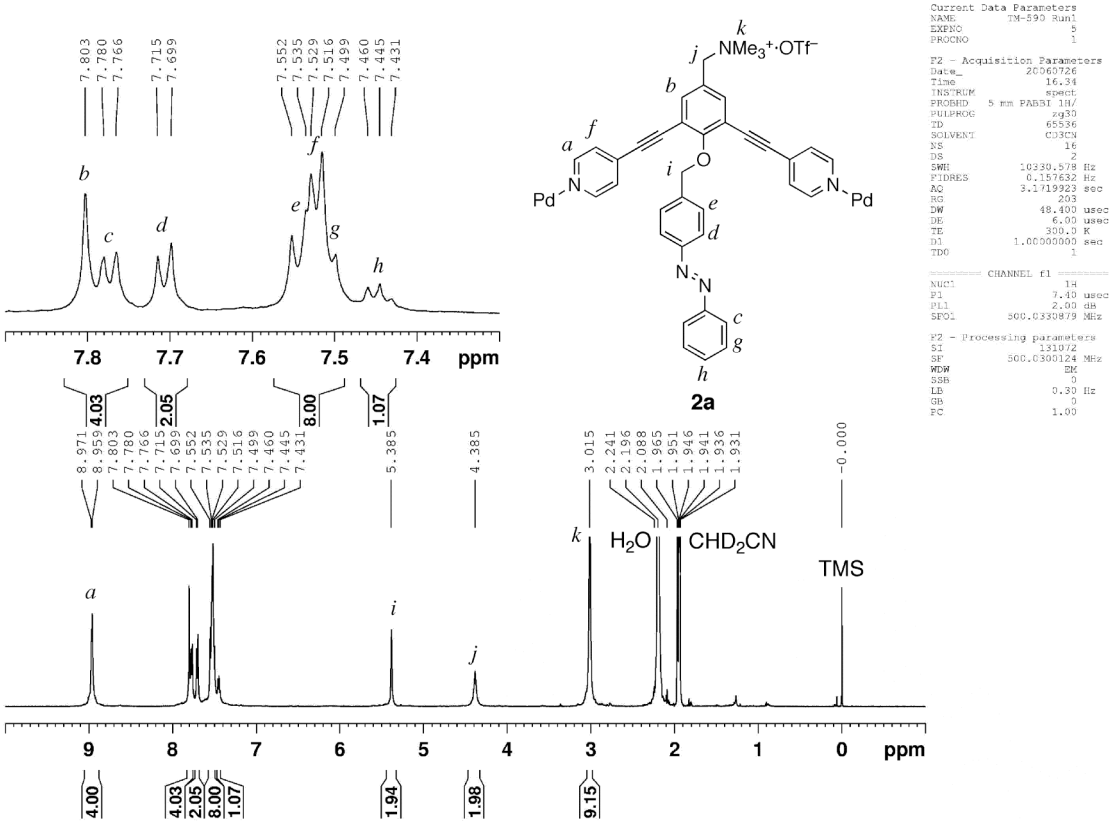


Figure S1. ^{1}H NMR spectrum of **2a**.

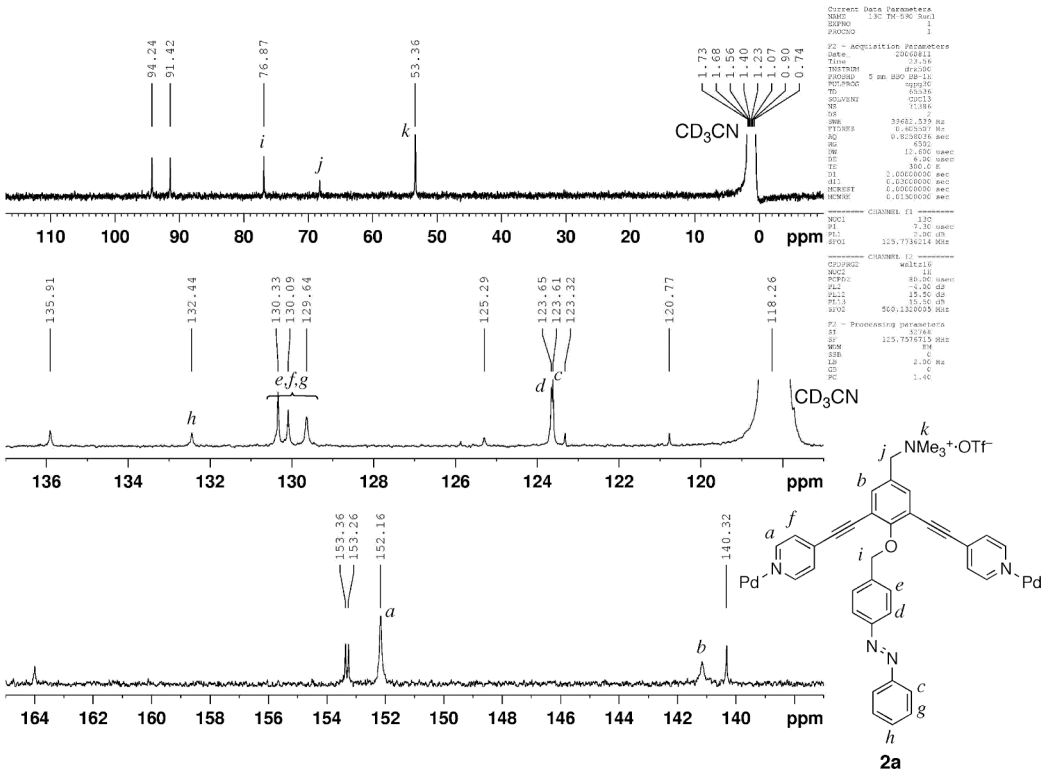


Figure S2. ^{13}C NMR spectrum of **2a**.

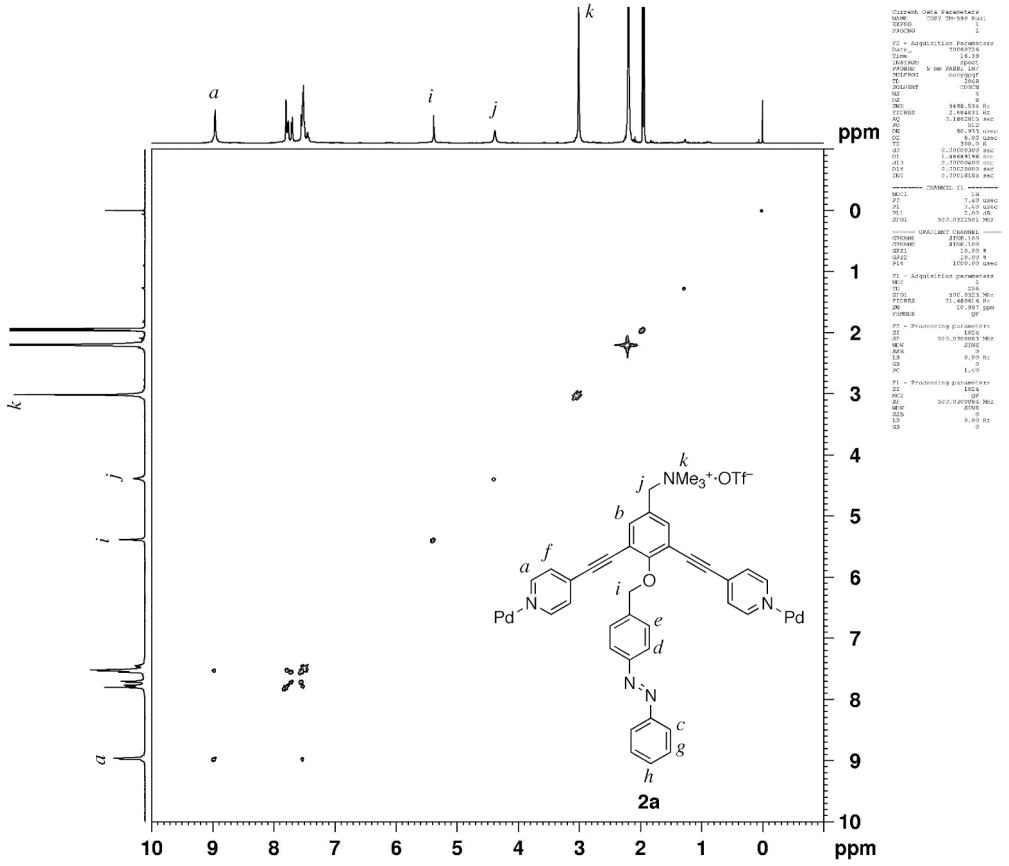


Figure S3. H–H COSY spectrum of **2a**.

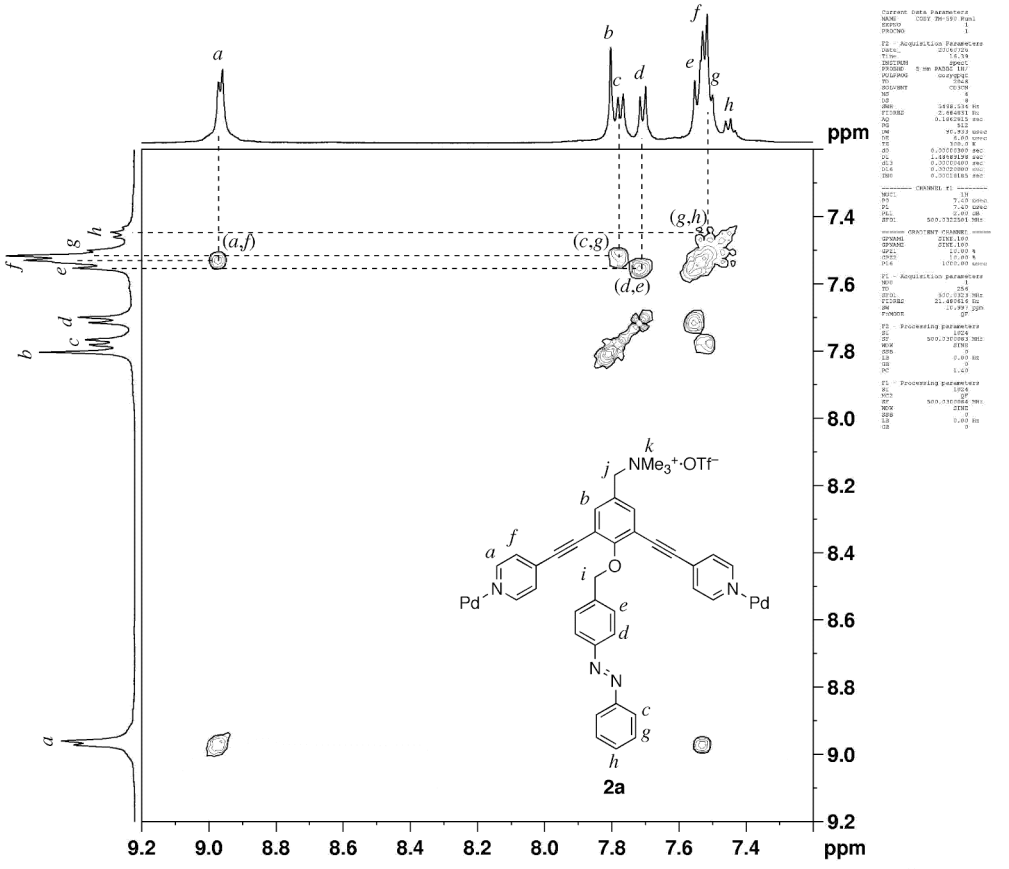


Figure S4. Enlarged H–H COSY spectrum of **2a**.

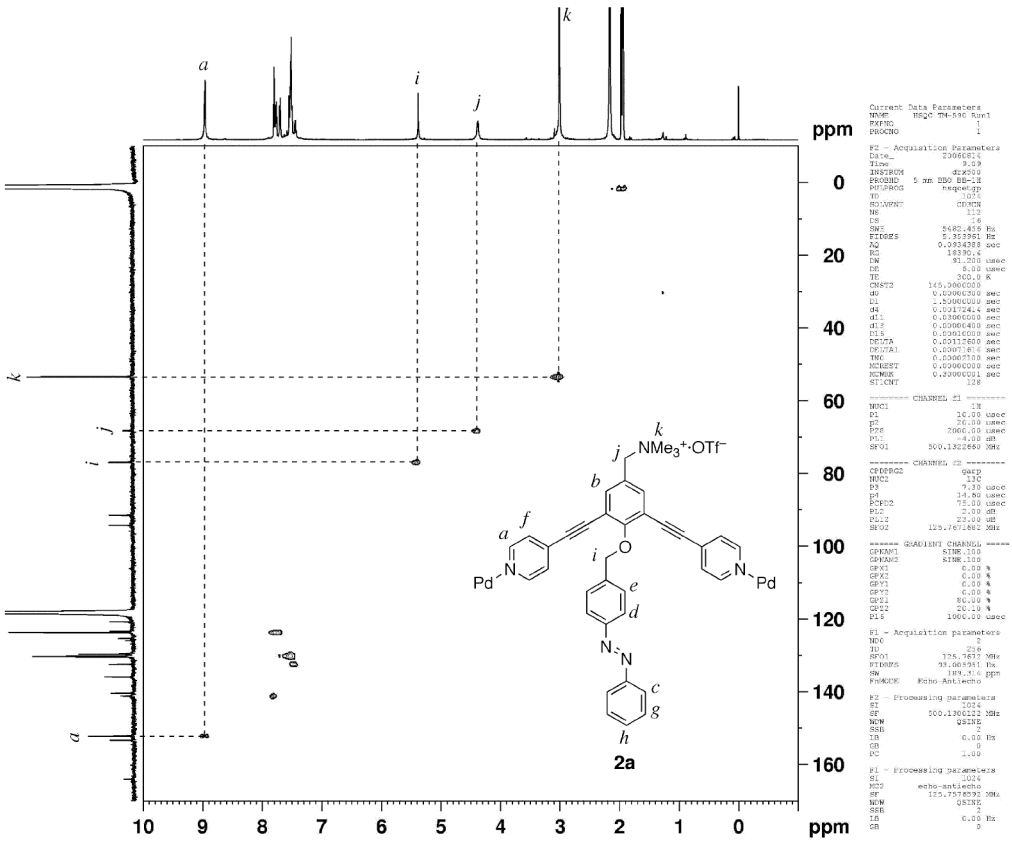


Figure S5. HSQC spectrum of **2a**.

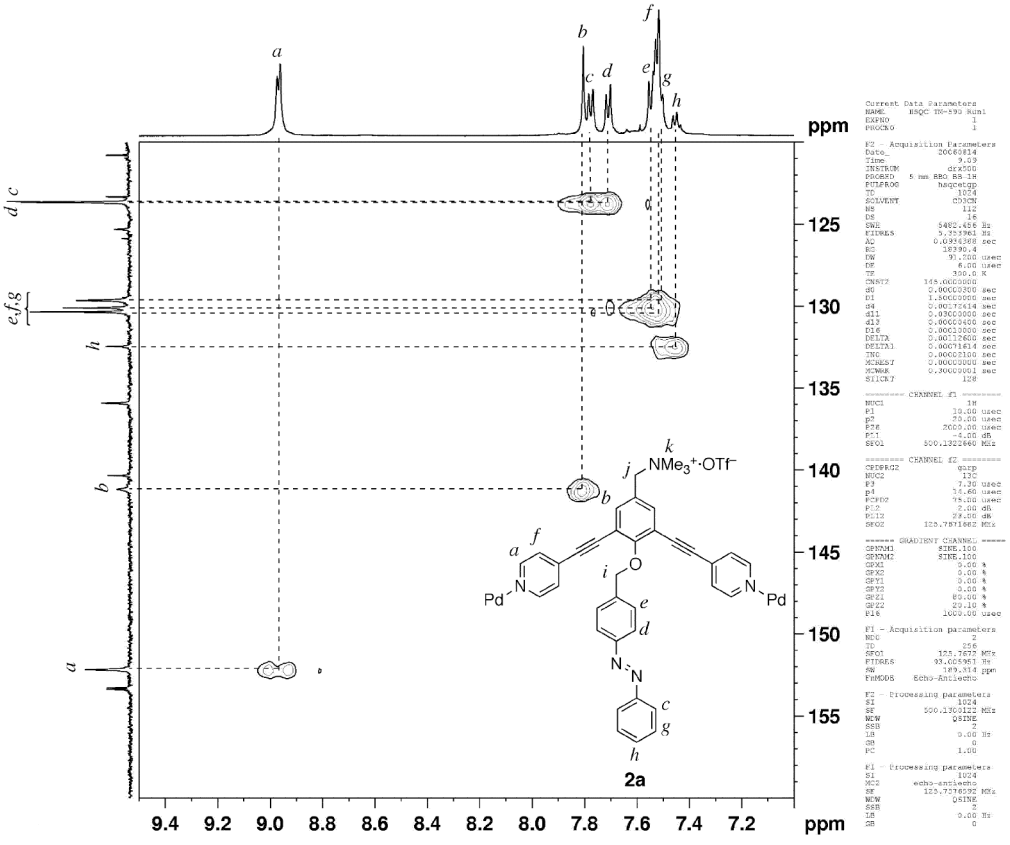


Figure S6. Enlarged HSQC spectrum of **2a**.

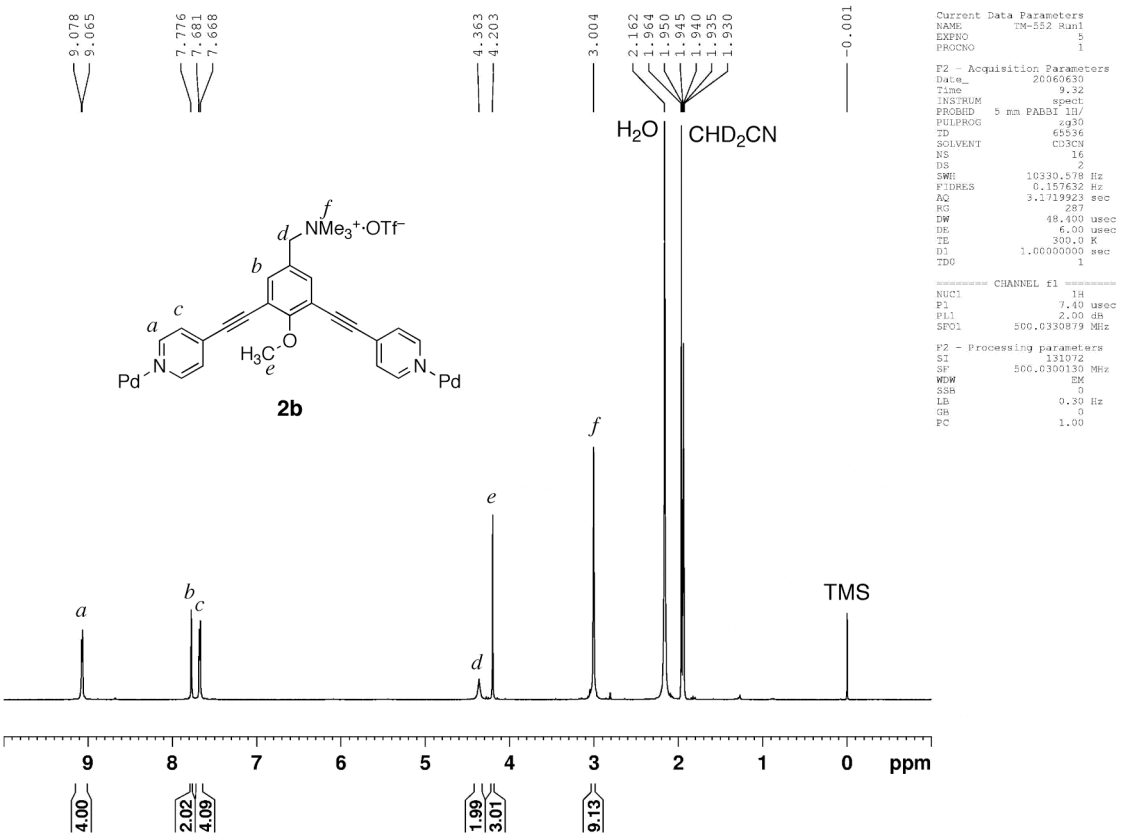


Figure S7. ^{1}H NMR spectrum of **2b**.

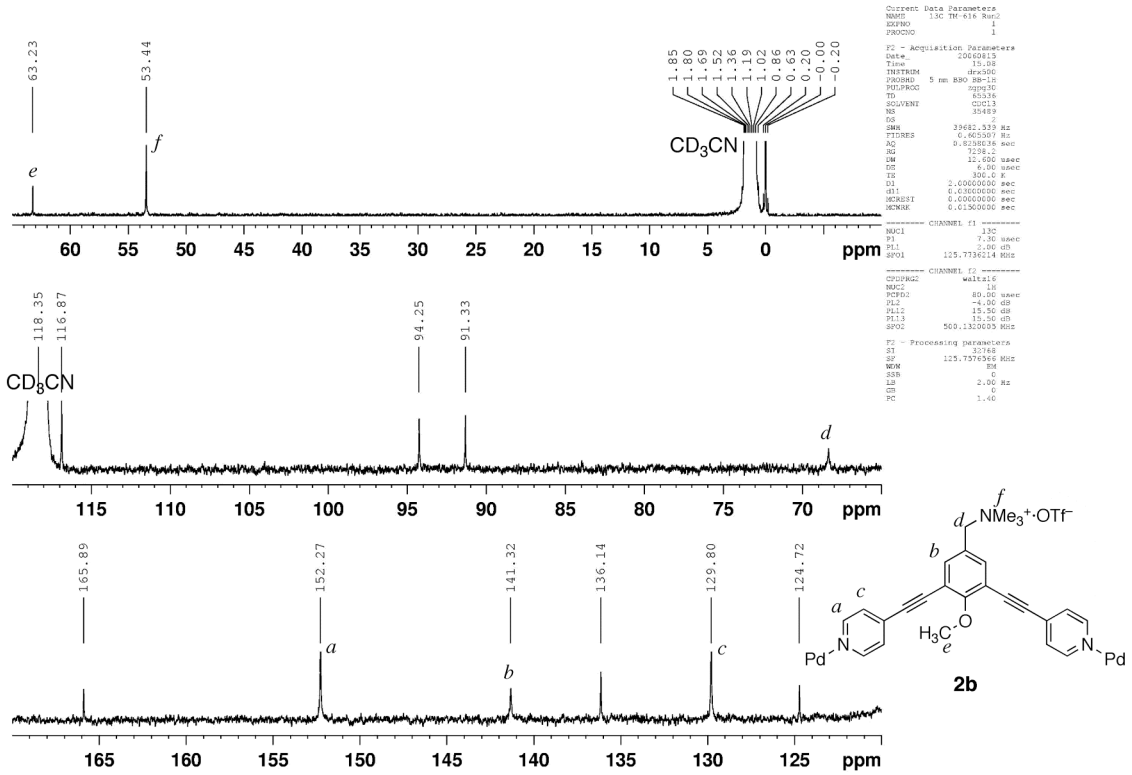


Figure S8. ^{13}C NMR spectrum of **2b**.

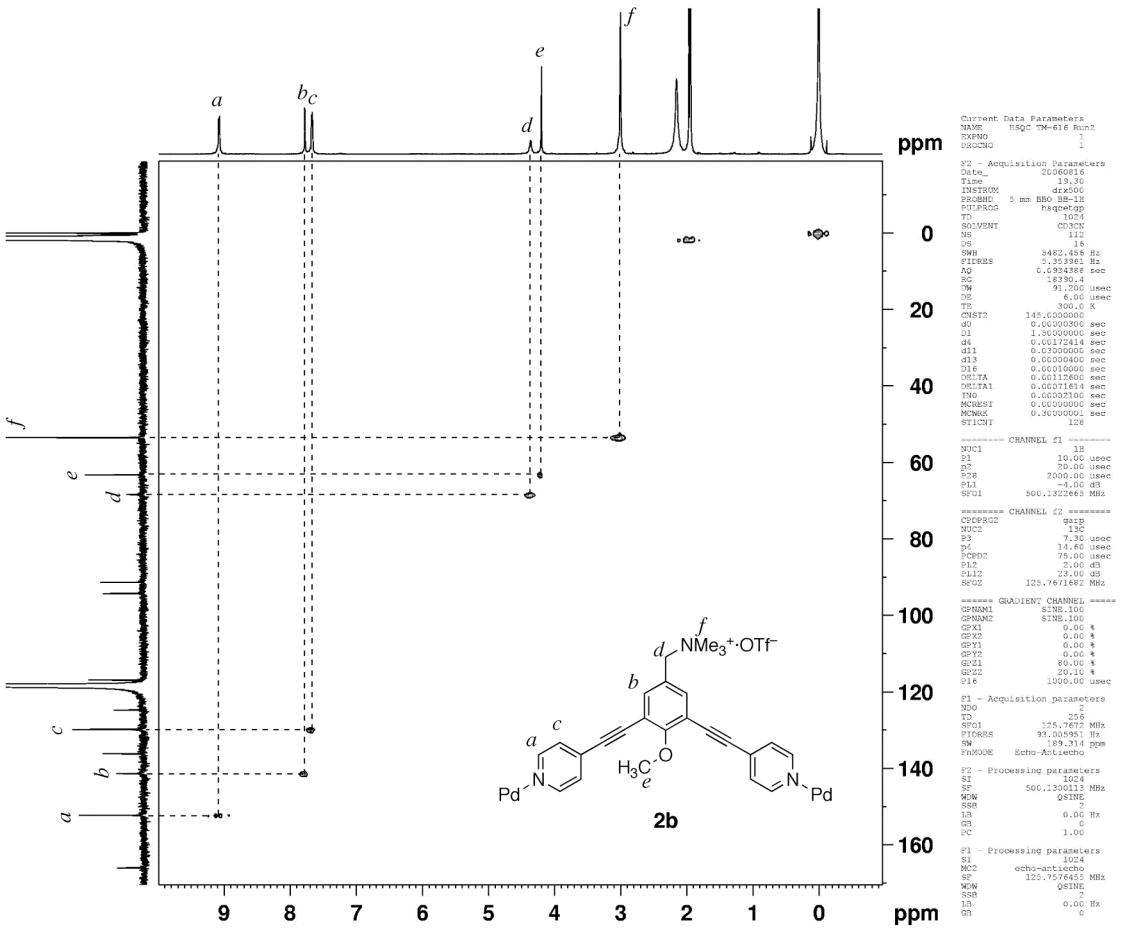


Figure S9. HSQC spectrum of **2b**.

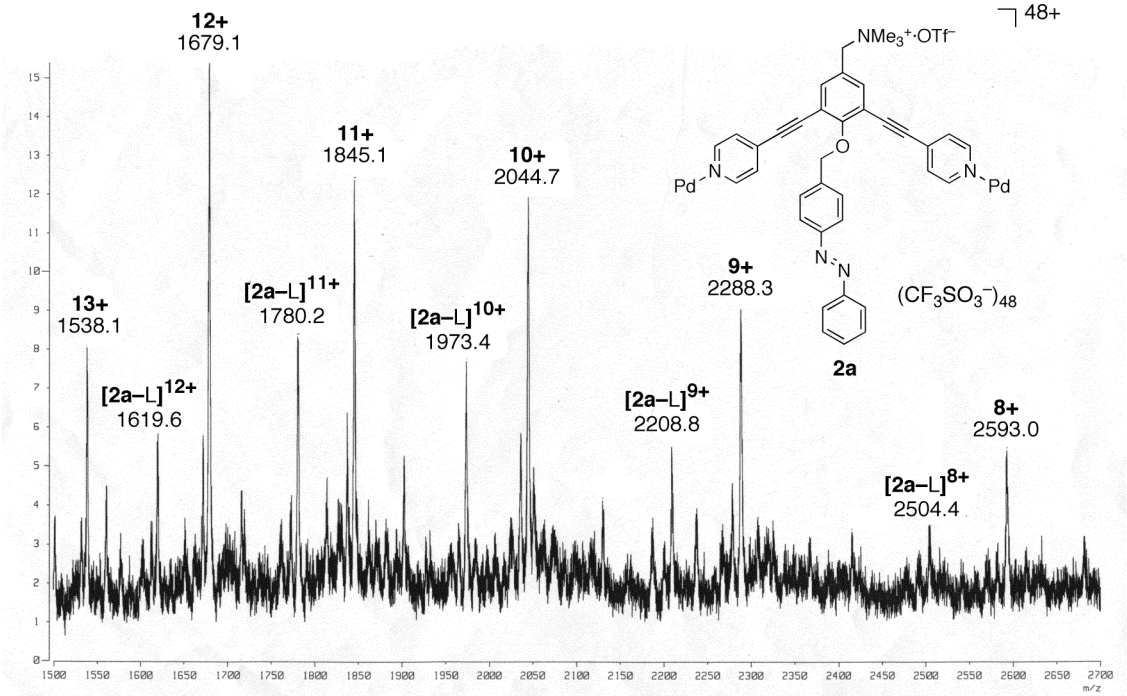


Figure S10. CSI-MS spectrum of **2a**. The decomposition of **2a** was observed, resulting in the appearance of ligand (L)-deficient peaks, [**2a**–L]$^{n+}$.

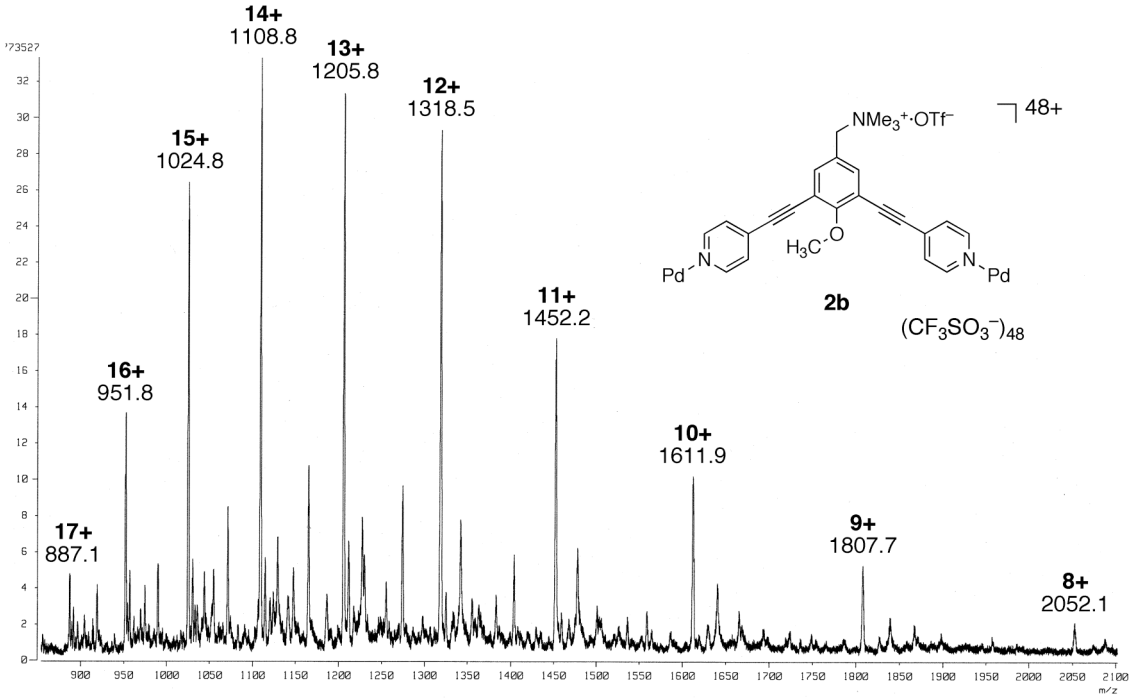


Figure S11. CSI-MS spectrum of **2b**.

Diffusion-ordered NMR spectroscopy (DOSY) tells us diffusion coefficient (*D*) of a molecule at a given temperature in solution and is a powerful method to separate complex mixtures according to *D* values. The DOSY spectra (in CD_3CN, 300 K) of complex **2a** and heterocomplex **2c** showed only one band, respectively, which indicates the quantitative formation of these complexes.

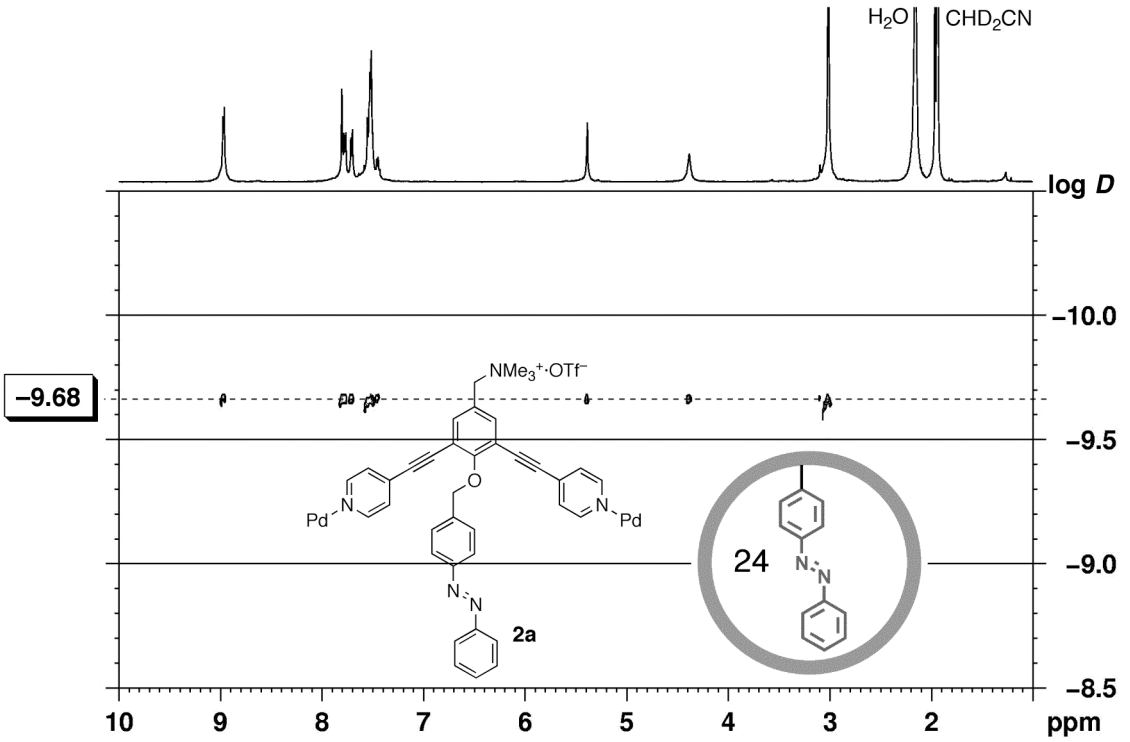


Figure S12. DOSY spectrum of **2a**.

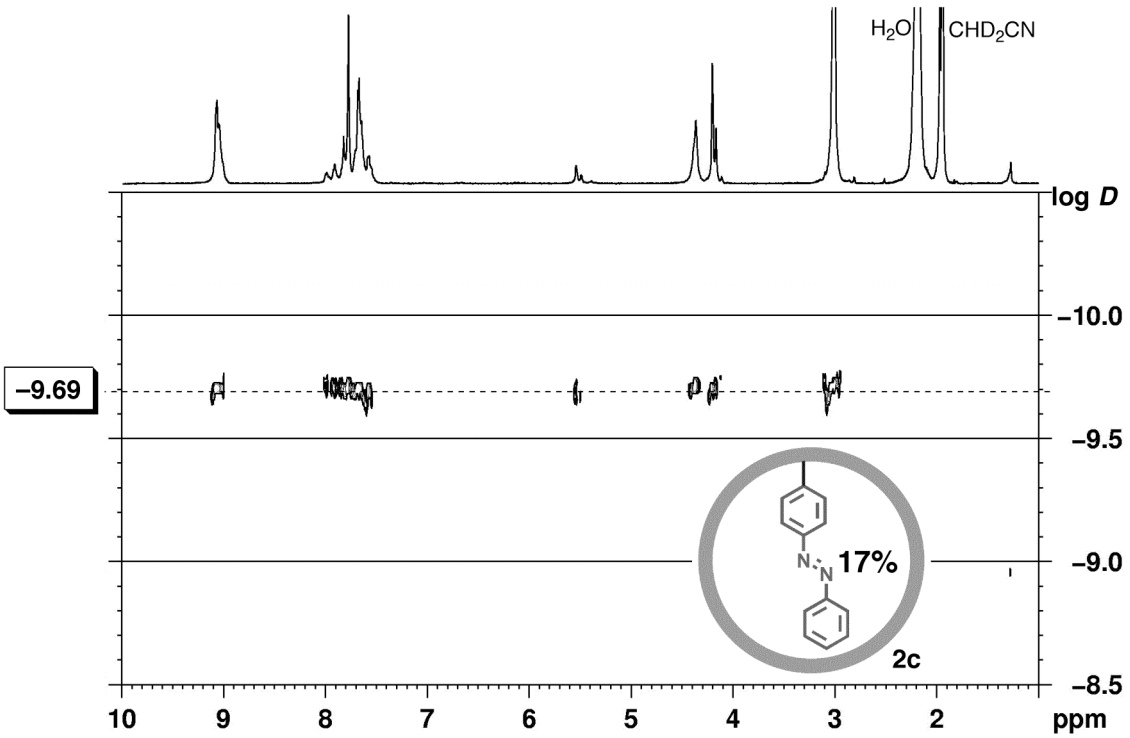


Figure S13. DOSY spectrum of heterocomplex **2c** (17% azobenzene concentration).

Photoisomerization (trans-to-cis)

<UV-Vis spectra>

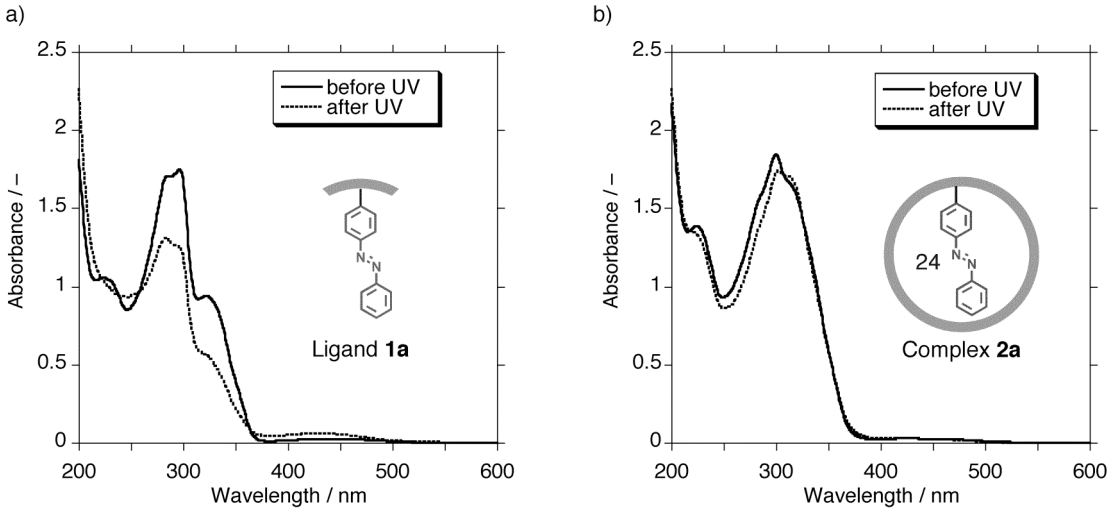


Figure S14. UV-Vis spectra of a) ligand **1a** and b) complex **2a** before and after UV light irradiation. Ligand concentration of complex **2a** is the same as the concentration of ligand **1a**; [**1a**] = 3.0×10^{-5} M in CH_3CN.

<^{1}H NMR spectra>

It is known that aromatic protons in cis-form azobenzene are upfield-shifted, compared to those in trans-form, because the bending structure of cis-form results in receiving a magnetic shielding effect from the counterpart. The shielding effect affects the surroundings of the azobenzene. Actually, upfield shifts of the benzyl protons adjacent to the azobenzene unit in ligand **1a** (5.57 ppm) were observed upon UV light irradiation ($\Delta\delta$ = –0.16 ppm) (Figure S15).

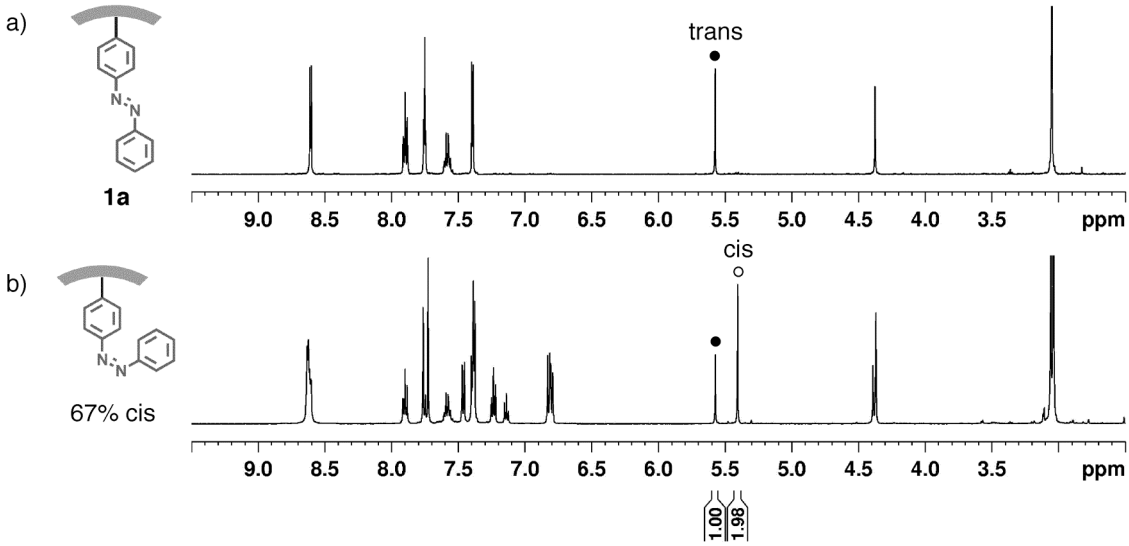


Figure S15. ^{1}H NMR spectra of ligand **1a** a) before and b) after UV light irradiation (500 MHz, CD_3CN, 300 K, TMS).

The ^{1}H NMR spectral changes of complex **2a** were complicated than those of ligand **1a** (Figure S16). After UV irradiation, the peak intensity of the benzyl protons adjacent to the trans-azobenzene units in complex **2a** (5.39 ppm) decreased and three new peaks (5.46, 5.31, and 5.27 ppm) appeared. When one of 24 trans-azobenzene units in complex **2a** is converted to cis-isomer, the spherical symmetry of the complex is disturbed, and thus the magnetic environments around trans-azobenzene units neighboring to and far from the cis-isomer are different. Considered that the benzyl protons adjacent to cis-azobenzene units are upfield-shifted, it can be identified that two peaks in downfield region (5.46 and 5.39 ppm) and the other two peaks in upfield region (5.31 and 5.27 ppm) are assigned to trans- and cis-azobenzene units in complex **2a**, respectively.

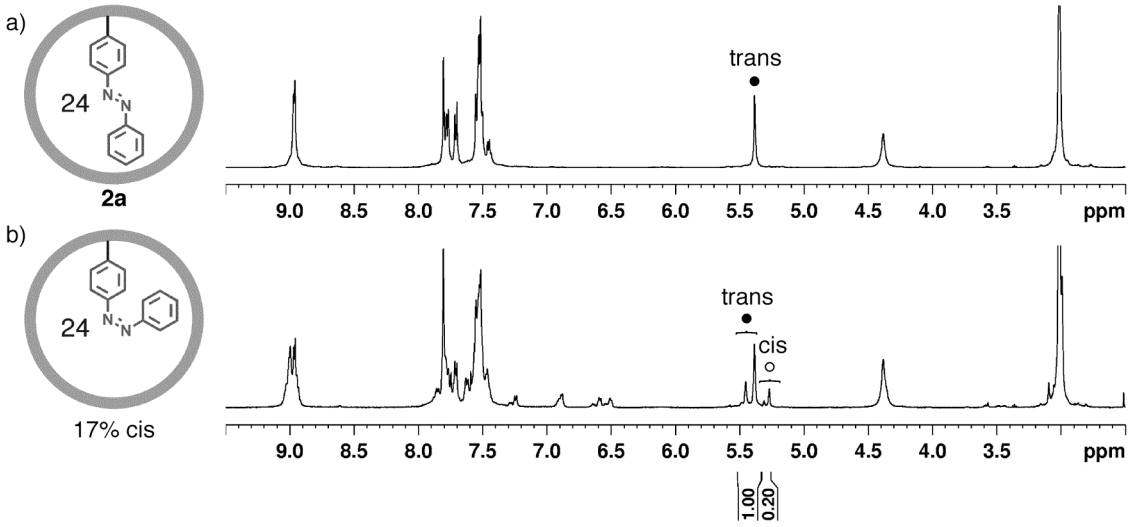


Figure S16. ^{1}H NMR spectra of complex **2a** a) before and b) after UV light irradiation (500 MHz, CD_3CN, 300 K, TMS).

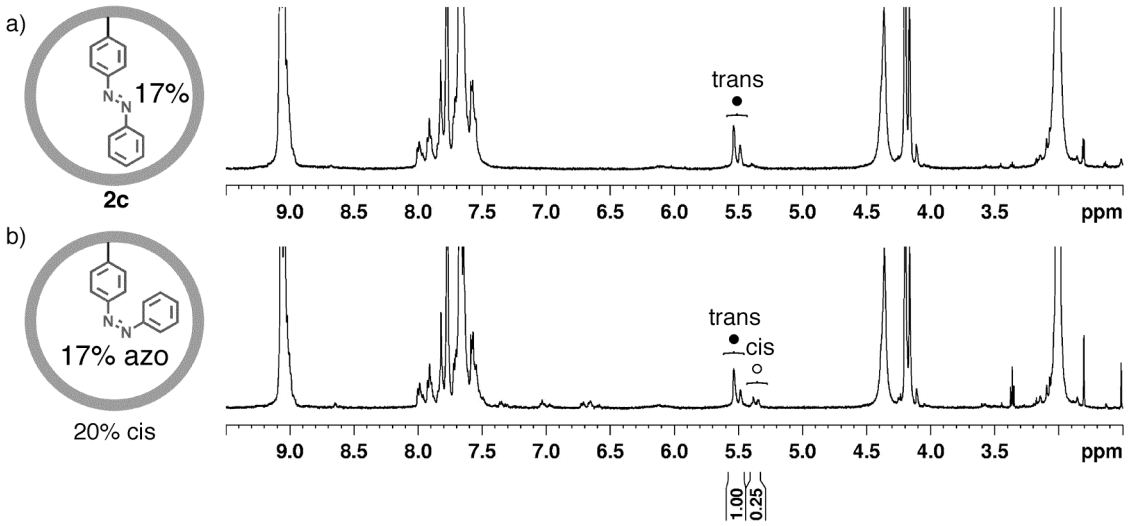


Figure S17. ^{1}H NMR spectra of heterocomplex **2c** a) before and b) after UV light irradiation (500 MHz, CD_3CN, 300 K, TMS).

Pyrene insertion into complex 2a.

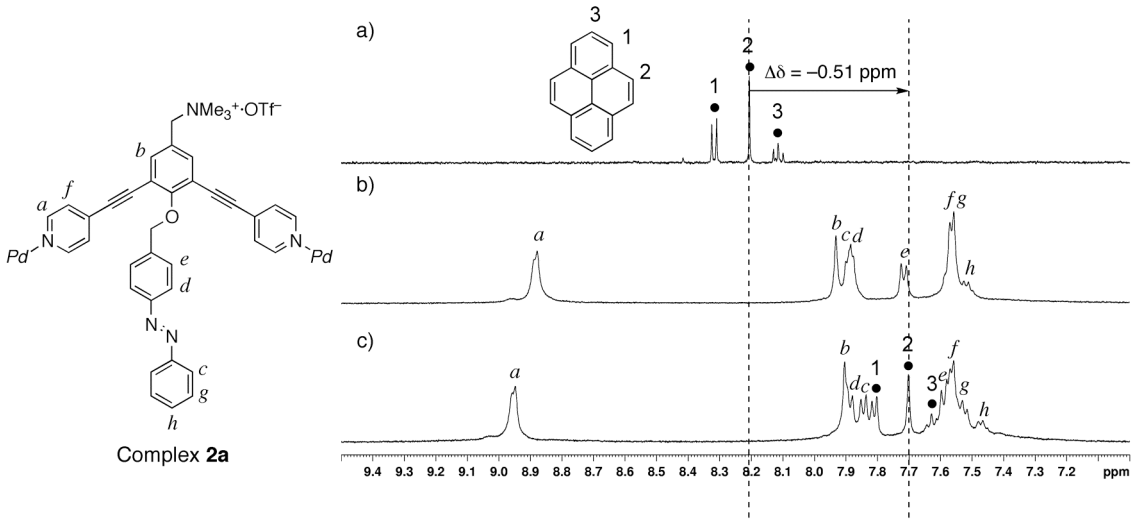


Figure S18. ^{1}H NMR spectra (aromatic region) of a) pyrene, b) complex **2a**, and c) pyrene in the presence of complex **2a** (500 MHz, CD_3CN/D_2O = 1:3, 300 K, TMS).

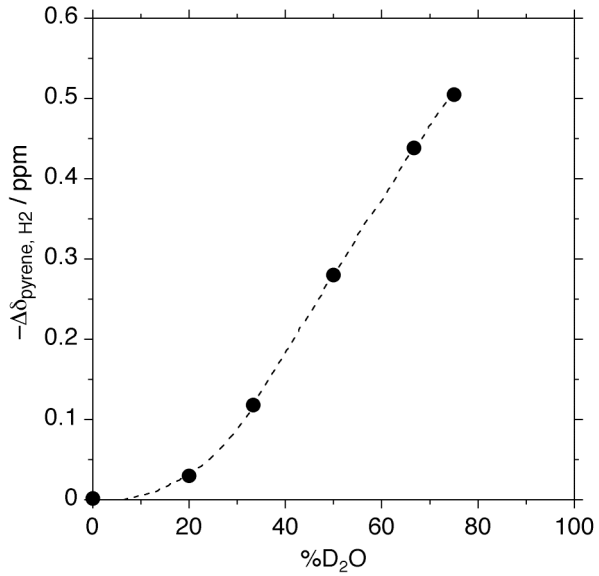


Figure S19. Degree of upfield shift for pyrene ($-\Delta\delta_{pyrene,\ H2}$) in the various volume ratio of $CD_3CN–D_2O$. Complex **2a** was stable up to 75% D_2O solution.

1-Pyrenecarboxaldehyde (3) insertion into complex 2a.

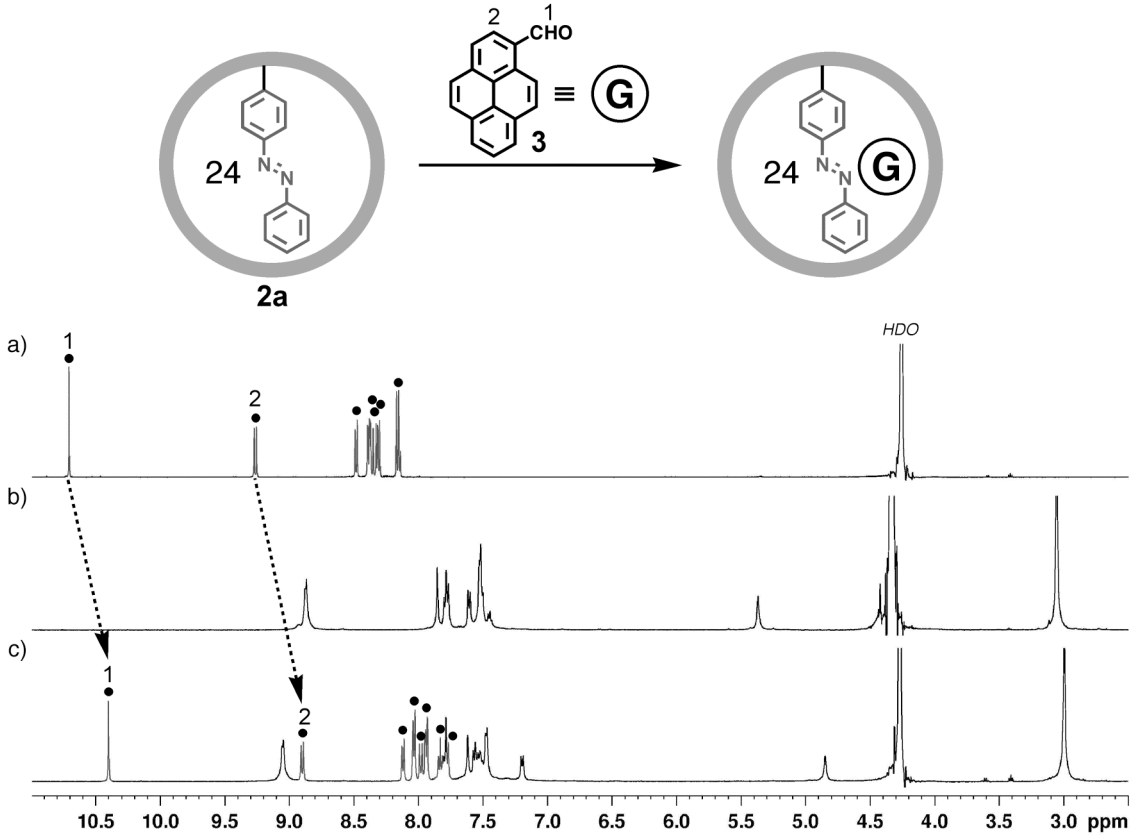


Figure S20. ^{1}H NMR spectra of a) guest **3**, b) complex **2a**, and c) guest **3** + complex **2a** (500 MHz, CD_3CN/D_2O = 1:1, 300 K, TMS).