<Supporting Information>

Pseudo-2D Porous Networks via Interpenetration of 1D Zigzag Ladder-type Coordination Polymers: Adsorption and Separation of Xylene Isomers

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■ EXPERIMENTAL SECTION

Materials and Measurements. Silver(I) salts ($AgPF_6$ and $AgClO_4$) and 1, 3, 5-tris(bromomethyl)benzene were purchased from Aldrich, and 4-hydroxybenzaldehyde and isonicotinoyl chloride hydrochloride were purchased from Tokyo Chemical Industry and Alfa, respectively. ^1H and ^{13}C NMR spectra were recorded on a Varian Mercury Plus 300 operating at 300.00 MHz and 75.00 MHz, respectively, and the chemical shifts were relative to the internal Me_4Si. Infrared spectra were obtained on a Nicolet 380 FT-IR spectrophotometer with samples prepared as KBr pellets. Thermal analyses were carried out under a dinitrogen atmosphere at a scan rate of 10 °C/min using a Labsys TGA-DSC 1600.

(((Benzene-1,3,5-triyltris(methylene))tris(oxy))tris(benzene-4,1-diyl))tris(methylene)triisonicotinate (L). Potassium carbonate anhydrous (35 mmol, 4.83 g) was added to a stirred mixture of 1, 3, 5-tris(bromomethyl)benzene (5 mmol, 1.78 g) and 4-hydroxybenzaldehyde (25 mmol, 3.05 g) in tetrahydrofuran (100 mL) at 70 °C. The reaction mixture was refluxed for 24 h. The solution was evaporated on rota vapor and workup with saturated $NaHCO_3$ aqueous solution and chloroform several times. The chloroform layer was dried using magnesium sulfate and filtered. Evaporation of the chloroform gave a white solid product 4,4',4''-((benzene-1,3,5-triyltris(methylene))tris(oxy))tribenzaldehyde in a 95% yield. A mixture of sodium borohydride (2mmol, 0.076 g) and the product (5 mmol, 0.48 g) in 1:4 ratio of ethanol and chloroform solution was stirred for 12 hours at room temperature. The reaction mixture was evaporated on rota vapor and workup with chloroform and water. The chloroform layer was dried using magnesium sulfate and filtered. Evaporation of the chloroform layer was gave a white solid product (((benzene-1,3,5-triyltris(methylene))tris(oxy))tris(benzene-4,1-diyl))trimethanol in a 90% yield. Isonicotinoyl chloride hydrochloride (25mmol, 4.45 g) was slowly added to a stirred mixture of N,N-diisopropylethylamine (10mmol, 8.71 mL) and the product (5mmol, 2.43 g) in chloroform

(100 mL) at 60 °C. The reaction mixture was refluxed for 24hours. The solution was washed with saturated $NaHCO_3$ aqueous solution several times. The chloroform layer was dried using magnesium sulfate and filtered. Evaporation of the chloroform gave a yellow solid product in a 86% yield. Anal. calcd for $C_{48}H_{39}N_3O_9$: C, 71.90; H, 4.90; N, 5.24%. Found: C, 70.80; H, 4.88; N, 5.17%. IR (KBr, cm^{-1}): 1726 (s), 1610 (s), 1587 (w), 1562 (w), 1514 (s), 1460 (m), 1406 (m), 1378 (m), 1325 (m), 1277 (s), 1240 (s), 1178 (m), 1120 (s), 1058 (w), 1041 (w), 1014 (m), 993 (w), 949 (w), 924 (w), 891 (m), 851 (w), 825 (s), 783 (w), 758 (s), 708 (s), 675 (m), 644 (w), 633 (w), 615 (w), 563 (m), 505 (m). ^1H NMR ($Me_2SO - d_6$, δ): 8.78 (d, J = 5.87 Hz, 6H), 7.82 (d, J = 5.87 Hz, 6H), 7.50 (s, 3H), 7.42 (d, J = 8.8 Hz, 6H), 7.04 (d, J = 8.8 Hz, 6H), 5.31 (s, 6H), 5.15 (s, 6H).

$2C_4H_8O_2$@[Ag(PF_6)L]. A methanol solution (5 mL) of $AgPF_6$ (mg, 0.0125 mmol) was slowly diffused into a 1,4-dioxane solution (5mL) of L (mg, 0.0125 mmol). Colorless crystal of formed at the interface. Anal. Calcd for $C_{56}H_{55}AgF_6N_3O_{13}P$: C, 54.64; H, 4.50; N, 3.41%. Found: C, 54.30; H, 4.65; N, 3.61%. IR (KBr, cm^{-1}): 1726 (s), 1610 (s), 1587 (w), 1562 (w), 1514 (s), 1454 (m), 1419 (m), 1378 (m), 1330 (m), 1282 (s), 1240 (s), 1219 (s), 1178 (m), 1120 (s), 1081 (w), 1058 (m), 1014 (w), 1001 (w), 922 (w), 838 (s), 764 (m), 704 (m), 685 (w), 613 (w), 582 (w), 557 (s), 507 (w), 461 (w), 405 (w). ^1H NMR ($Me_2SO - d_6$, δ): 8.79 (d, J = 5.87 Hz, 6H), 7.83 (d, J = 5.87 Hz, 6H), 7.50 (s, 3H), 7.42(d, J = 8.61 Hz, 6H), 7.04 (d, J = 8.61 Hz, 6H), 5.31 (s, 6H), 5.15 (s, 6H), 3.57(s, 16H).

Adsorption of Xylenes.

***p*-X@[Ag(PF_6)L].** Single crystals of $2C_4H_8O_2$@[Ag(PF_6)L] were left in *p*-xylene media at 40 °C for 3 days, resulting in the transformation of single crystals of *p*-X@[Ag(PF_6)L] suitable for single-crystal X-ray diffraction. Anal. Calcd. $C_{48}H_{39}N_3O_9$ $C_{56}H_{49}AgF_6N_3O_9P$: C, 57.94; H, 4.25; N, 3.62%. Found: C, 55.80; H, 4.35; N, 3.69%. ^1H NMR (Me_2SO-d_6, δ): 8.79 (d, J = 5.28 Hz, 6H), 7.83 (d, J = 5.87Hz, 6H), 7.50 (s, 3H), 7.43 (d, J = 8.8Hz, 6H), 7.04 (d,

J = 8.61Hz, 10H), 5.31 (s, 6H), 5.16 (s, 6H), 2.24 (s, 6H).

***m*-X@[Ag(PF$_6$)L].** Single crystals of $2C_4H_8O_2$@[Ag(PF$_6$)L] were left in *m*-xylene media at 40 °C for 5 days, resulting in the transformation of single crystals of *m*-X@[Ag(PF6)L] suitable for single-crystal X-ray diffraction. Anal. Calcd. $C_{56}H_{49}AgF_6N_3O_9P$: C, 57.94; H, 4.25; N, 3.62%. Found: C, 56.30; H, 4.35; N, 3.69%. ^1H NMR (Me$_2$SO-d_6, δ): 8.79 (d, J = 5.28 Hz, 6H), 7.83 (d, J = 5.28 Hz, 6H), 7.50 (s, 3H), 7.43 (d, J = 8.22 Hz, 6H), 7.13 (m, J = 15.26 Hz, 2H), 7.04 (d, J = 8.22 Hz, 6H), 6.96 (d, J = 12.91 Hz, 2H), 5.31 (s, 6H), 5.16(s, 6H), 2.25(s, 6H).

Crystal structure determination. X-ray data of $2C_4H_8O_2$@[Ag(PF$_6$)L] were collected on a Bruker SMART automatic diffractometer with graphite-monochromated Mo Kα radiation (λ = 0.71073 Å). Thirty-six (36) frames of 2D diffraction images were collected and processed to obtain the cell parameters and orientation matrix. The data were corrected for Lorentz and polarization effects. The absorption effects were corrected using the multi-scan method (SADABS).[S1] The diffraction data of the *p*-X@[Ag(PF$_6$)L] and *m*-X@[Ag(PF$_6$)L] single crystals were measured at 120 K, respectively, with synchrotron radiation (λ = 0.7000 Å, respectively) on a Rayonix MX225HS detector at 2D SMC with a silicon (111) double crystal monochromator (DCM) at the Pohang Accelerator Laboratory, Korea. The PAL BL2D-SMDC program[S2] was used for data collection (detector distance was 66 mm, omega scan; $\Delta\omega$ = 1°, exposure time was 1 s per frame) and HKL3000sm (ver. 703r)[S3] was used for cell refinement, reduction, and absorption correction. The structures were solved using the direct method (SHELXS) and refined by full-matrix least squares techniques (SHELXL 2018/3).[S4] The non-hydrogen atoms were refined anisotropically, and the hydrogen atoms were placed in calculated positions and refined only for the isotropic thermal factors. The crystal parameters and procedural information corresponding to the data collection and structure refinement are listed in Table S1.

(S1) Sheldrick, G. M. *SADABS, A program for Empirical Absorption Correction of Area Detector Data*; University of Göttingen: Germany, **1996**.

(S2) Shin, J. W.; Eom, K.; Moon, D. *J. Synchrotron Radiat*. **2016**, 23, 369–373.

(S3) Otwinowski, Z.; Minor, W. *Methods in Enzymology*, ed. Carter Jr., C. W.; Sweet, R. M. Academic Press, New York, **1997**, 276, 307.

(S4) Sheldrick, G. M. *Acta Crystallogr. Sect. C-Struct. Chem*. **2015**, 71, 3-8.

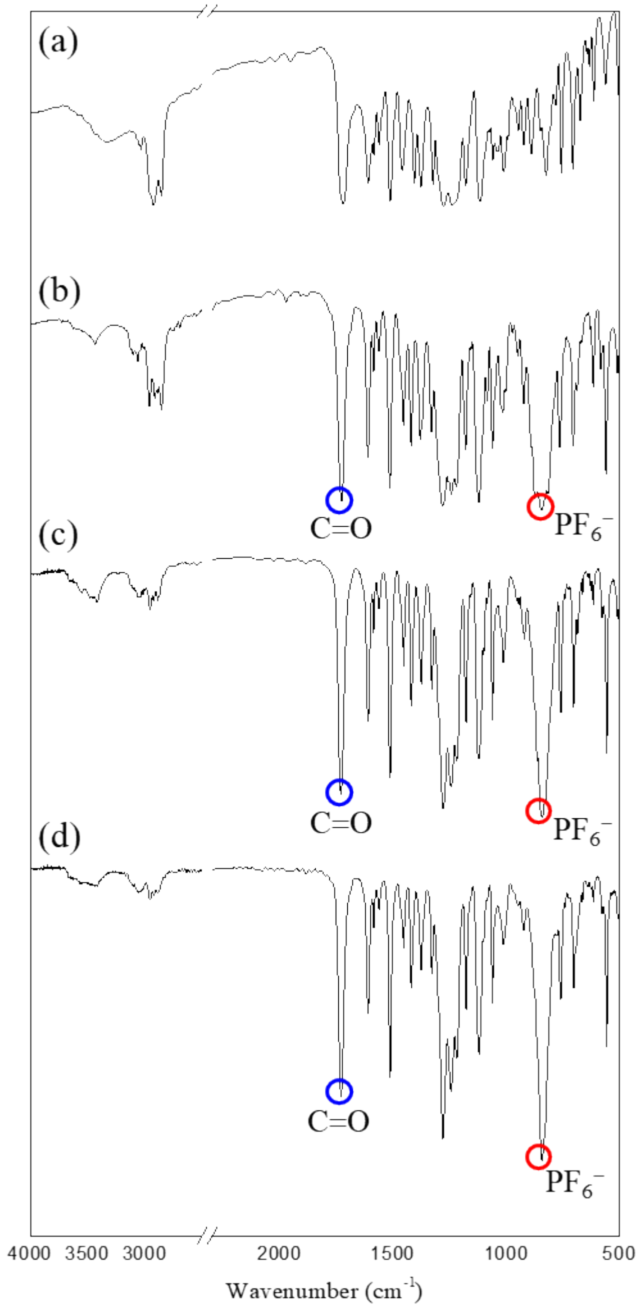

Figure S1. IR spectra of L (a), $2C_4H_8O_2$@[Ag(PF_6)L] (b), *p*-X@[Ag(PF_6)L] (c), and *m*-X[Ag(PF_6)L] (d).

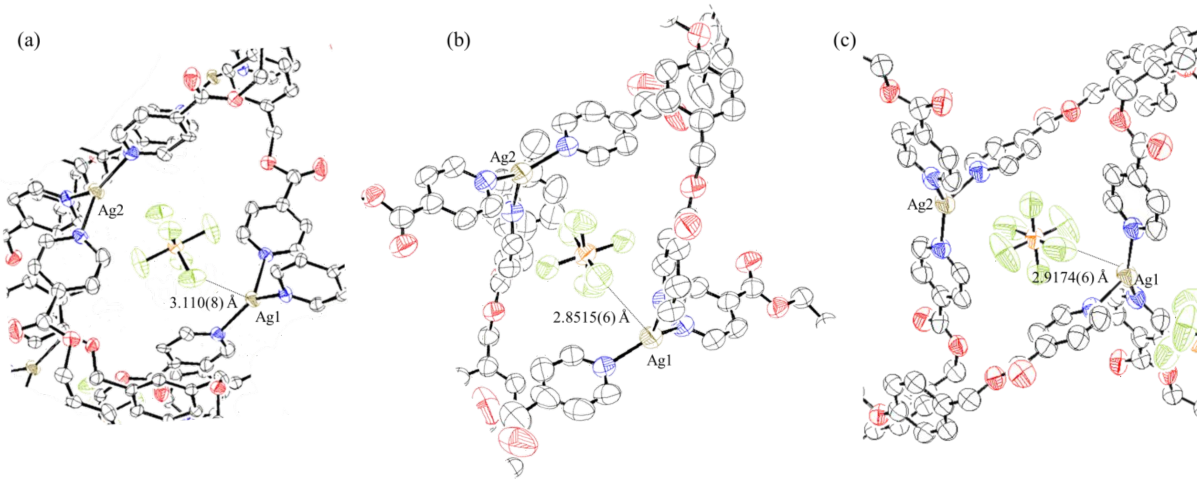

Figure S2. ORTEP drawings (50% ellipsoid probability) including each local geometry around Ag(I) ion. The shortest distance of Ag···FPF_5 is 3.110(8) Å (a, $2C_4H_8O_2$@[Ag(PF_6)L]), 2.8515 Å (b, *p*-X@[Ag(PF_6)L]), and 2.9174(6) Å (c, *m*-X@[Ag(PF_6)L]).

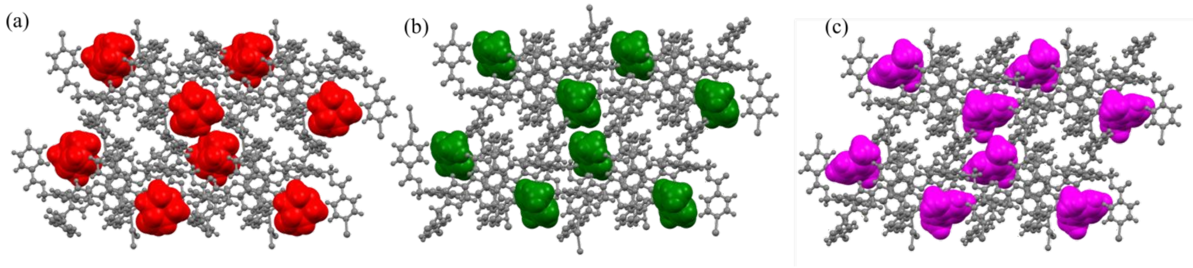

Figure S3. Crystal structures of $2C_4H_8O_2$@[Ag(PF_6)L] (a), *p*-X@[Ag(PF_6)L] (b), and *m*-X@[Ag(PF_6)L] (c). Space-filling indicates the guest molecules. Red: 1,4-dioxane; green: *p*-X; pink: *m*-X.

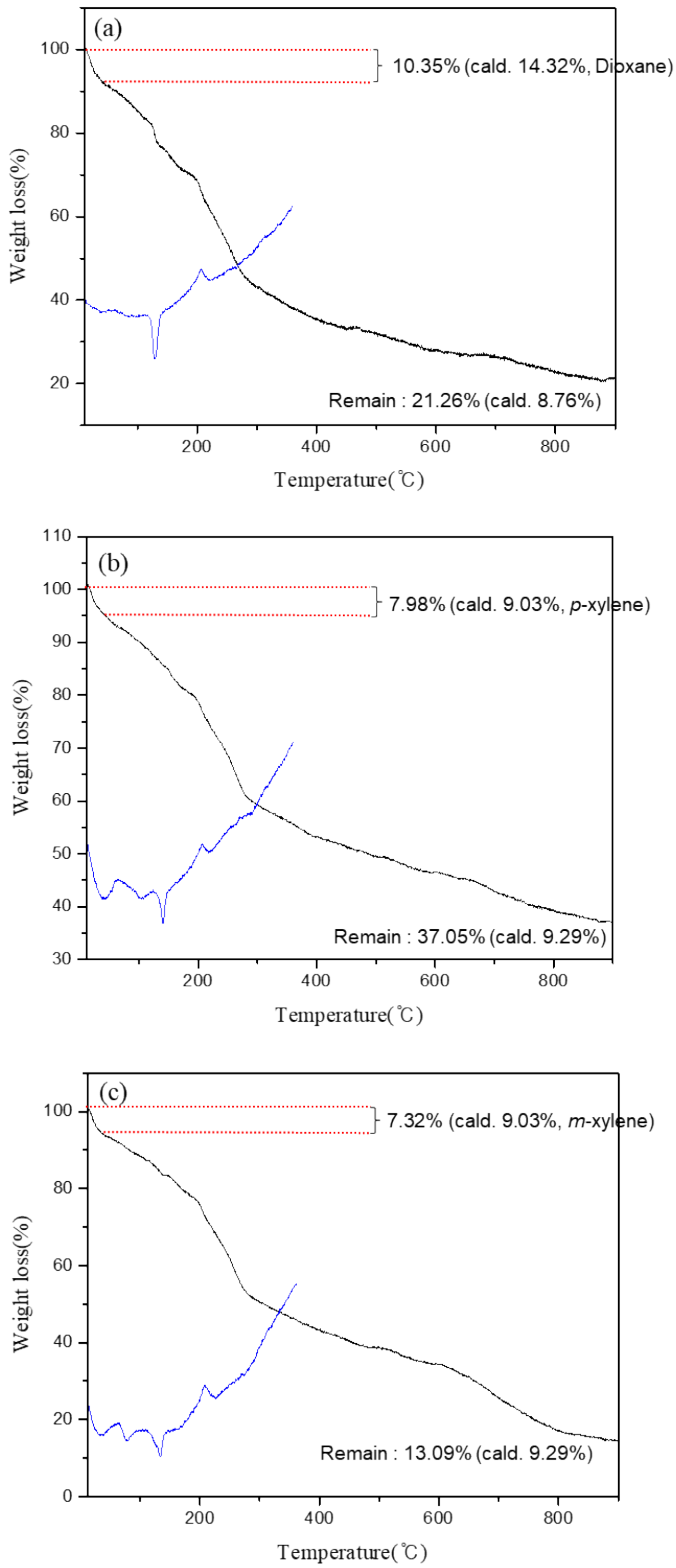

Figure S4. TGA and DSC of $2C_4H_8O_2$@[Ag(PF_6)L] (a), *p*-X@[Ag(PF_6)L] (b), and *m*-X@[Ag(PF_6)L] (c).

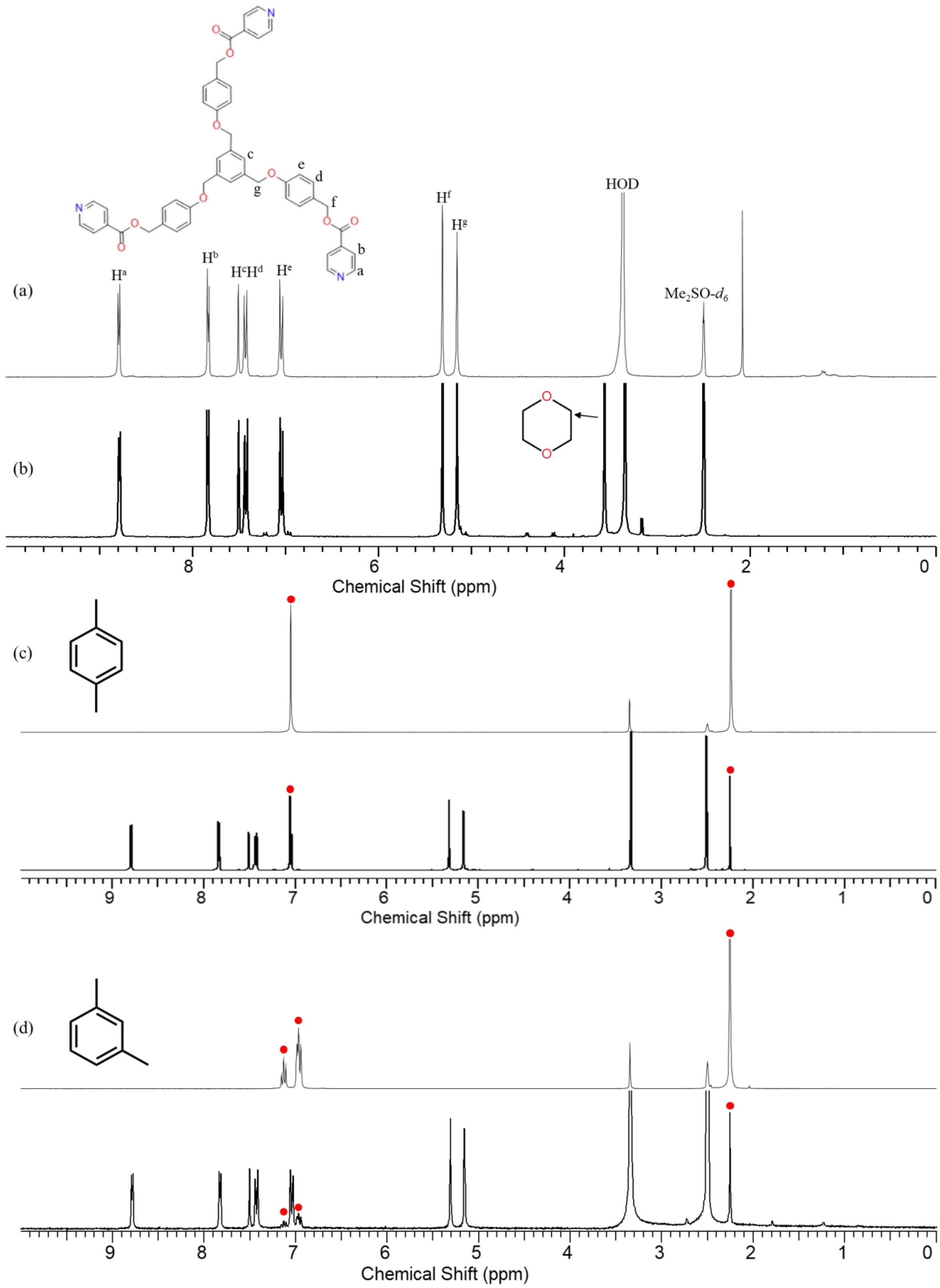

Figure S5. ^{1}H NMR spectra of L (a), $2C_4H_8O_2$@[Ag(PF_6)L] (b), *p*-X@[Ag(PF_6)L] (c), and *m*-X@[Ag(PF_6)L] (d).

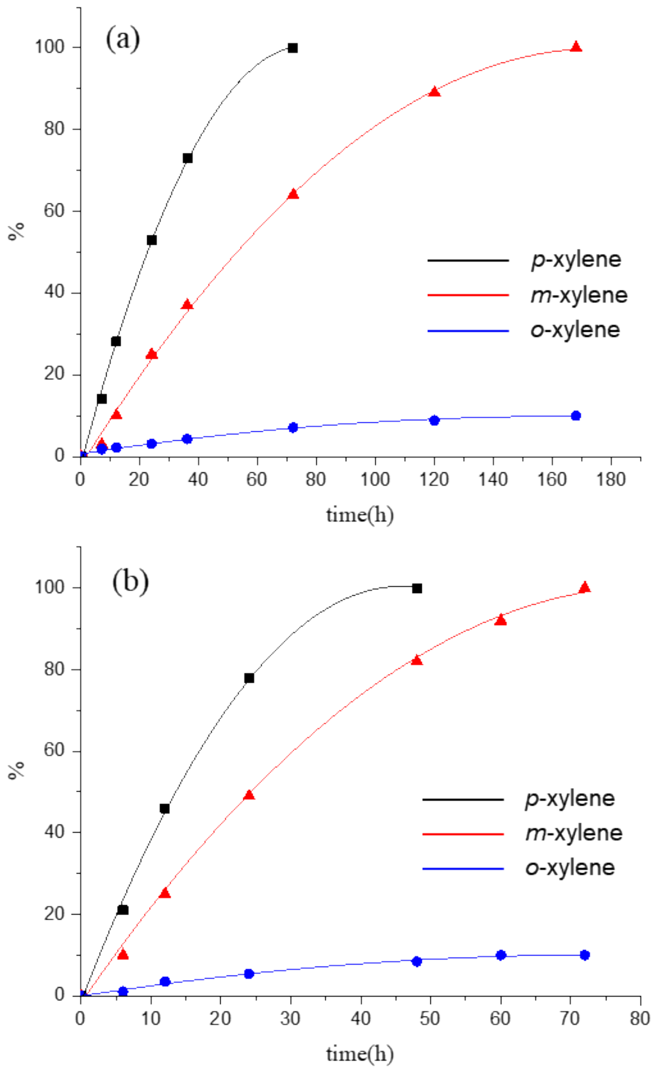

Figure S6. Time-dependent exchange rate at RT (a) and at 60 ^{o}C (b).

Table S1. Crystallographic data

	$2C_4H_8O_2$@[Ag(PF_6)L]	*p*-X@[Ag(PF_6)L]	*m*-X@[Ag(PF_6)L]
Formula	$C_{56}H_{55}AgF_6N_3O_{13}P$	$C_{56}H_{49}AgF_6N_3O_9P$	$C_{56}H_{49}AgF_6N_3O_9P$
M_w	1230.87	1160.82	1160.82
Cryst. sys.	Triclinic	Triclinic	Triclinic
Space group	*P*-1	*P*-1	*P*-1
a (Å)	12.901(4)	12.887(3)	12.844(3)
b (Å)	14.139(5)	13.663(3)	13.802(3)
c (Å)	17.139(6)	16.527(3)	16.745(3)
α (°)	98.120(3)	99.06(3)	99.09(3)
β (°)	107.279(3)	111.22(3)	111.81(3)
γ (°)	99.262(3)	96.68(3)	98.62(3)
V (Å^3)	2886.3(16)	2630.9(11)	2650.0(11)
Z	2	2	2
ρ (g cm^{-3})	1.416	1.465	1.455
μ (mm^{-1})	0.460	0.468	0.465
R_{int}	0.1037	0.0227	0.0450
GoF on F^2	1.267	1.033	1.630
R_1 [I>2σ(I)][a]	0.1408	0.0839	0.1179
wR_2 (all data)[b]	0.3308	0.3228	0.3013

[a]$R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$, [b]$wR_2 = (\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2])^{1/2}$