Supplementary Information

Coordination-Driven Assembly of Actinide-Organic Polyrotaxanes Involving Crown Ether Macrocycles

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S1. Synthesis and analysis

Synthesis of $UO_2(OTf)_2$[1]: To get uranium trioxide, the solid sample of uranyl nitrate were heated in air at 300 ^{O}C for 8 hours in the muffle oven, in which the temperature went high with a speed of 1 ^{o}C per minute and cooled down at natural rate. The red solid sample of uranium trioxide was added into a 50mL flask, then 2.5 equivalents of triflic acid were added into the flask. The red solid turned yellow at 110 ^{o}C, and 2 hours later the hydrated uranyl triflate $[UO_2(OTf)_2(H_2O)_n]$ was synthesized. Then the hydrated uranyl triflate was put into 80 ^{o}C dry vacuum oven for 48 hours to get $UO_2(OTf)_2$. To avoid water absorption, the $UO_2(OTf)_2$ was dissolved in acetonitrile formulating a 0.1M solution.

Synthesis of 4, 4'-bipyridine-*N*-monoxide[2, 3]: The 4, 4'-bipyridine (10 g, 64.1 mmol), hydrogen peroxide (30%; 6.65 g, 195 mmol) and 40 mL glacial acetic acid were added into a round flask and heated for 18 hours at 76 ^{o}C. After cooling the reaction mixture, the solvent was removed by a rotary evaporator with the assistance of dichloromethane. The product was further purified by column chromatography with an ethyl acetate/methanol mixture (3:1) to give the product 4, 4'-bipyridine-*N*-monoxide. Yield: 5.66 g, 51.3%. ^{1}H NMR (500 MHz, DMSO-d^{6}, δ ppm): 8.67 (d, 2H, J = 6.0 Hz); 8.34 (d, 2H, J = 7.2 Hz), 7.93 (d, 2H, J = 7.1 Hz), 7.81 (d, 2H, J = 6.0 Hz). ESI-MS (m/z): 173.06 ($[M+H]^+$), 345.17 ($[2M+H]^+$). IR (KBr): υ= 1593, 1564, 1540, 1480, 1410, 1339, 1324, 1259, 1288, 1234, 1189, 1100, 1073, 1027, 992, 869, 851, 815, 734, 710, 654, 576, 490, 420, cm^{-1}.

Synthesis of bis(4,4′-bipyridinium *N*-monoxide)ethane bromide ($[EBBPYO]Br_2$) and bis(4,4′-bipyridinium *N*-monoxide)ethane trifluoromethanesulfonate ($[EBBPYO](OTf)_2$)[4]: the mixture of 4, 4'-bipyridine-*N*-monoxide (2.00 g, 11.6 mmol) and 1, 2-dibromoethane (400 μL, 4.62 mmol) was dissolved in 10 mL *N*, *N*-Dimethylformamide (DMF), and heated at 80 ^{o}C for 48 hours. After immediate filtration, $[EBBPYO]Br_2$ was gained as light brown precipitation. Yield: 0.64g, 38.3%. ^{1}H NMR (500 MHz, DMSO-d^{6}, δ ppm): 9.16 (d, 4H, J = 6.2 Hz); 8.69 (d, 4H, J = 6.1 Hz), 8.51 (d, 4H, J = 6.4 Hz), 8.23 (d, 4H, J = 6.5 Hz), 5.29 (s, 4H). ESI-MS (m/z): 186.07 ($[M\text{-}2Br]^{2+}$), 451.10 ($[M\text{-}Br]^+$). Anal. calcd for

$C_{22}H_{20}Br_2N_4O_2$ (%): C, 49.65; H, 3.79; N, 10.53; Found (%): C, 49.12; H, 4.82; N, 10.31. IR (KBr): υ= 1567, 1544, 1484; 1438, 1408, 1359, 1330, 1273, 1241, 1210, 1185, 1122, 1024, 970, 942, 882, 854, 840, 825, 787, 741, 694, 672, 654, 577, 563, 541, 517, 490, 447, cm^{-1}. The light brown precipitate (1.20g, 2.26mmol) was dissolved in a minimum amount of H_2O. Five equivalents of [Na][OTf] (1.93g, 11.22mmol) were added and the mixture was heated until the solution was homogeneous. The solution was then cooled and bis(4,4′-bipyridinium N-monoxide)ethane $[OTf]_2$ isolated as a light tan powder.[5] Yield: 0.42 g, 27.9%. ^1H NMR (500 MHz, CD_3OD, δ ppm): 9.05 (d, 4H, *J* = 6.8 Hz); 8.58 (d, 4H, *J* = 6.8 Hz), 8.50 (d, 4H, *J* = 7.2 Hz), 8.17 (d, 4H, *J* = 7.2 Hz), 5.34 (s, 4H). ESI-MS (m/z): 185.92 ($[M\text{-}2OTf]^{2+}$), 521.02 ($[M\text{-}OTf]^{+}$). IR (KBr): υ= 1575, 1555, 1490, 1442, 1357, 1266,1192, 1172, 1035, 844, 786, 759, 711, 696, 672, 638, 578, 547, 518, 494, 419, cm^{-1}. It should be mentioned that the ion exchange is not complete as expected. The residual Br^- measured by ion chromatography is 0.1 g per gram of as-synthesized bis(4,4′-bipyridinium N-monoxide)ethane $[OTf]_2$, which is corresponding to 38.6% of residual Br^- for each OTf^- ion.

S2. Supplementary figures

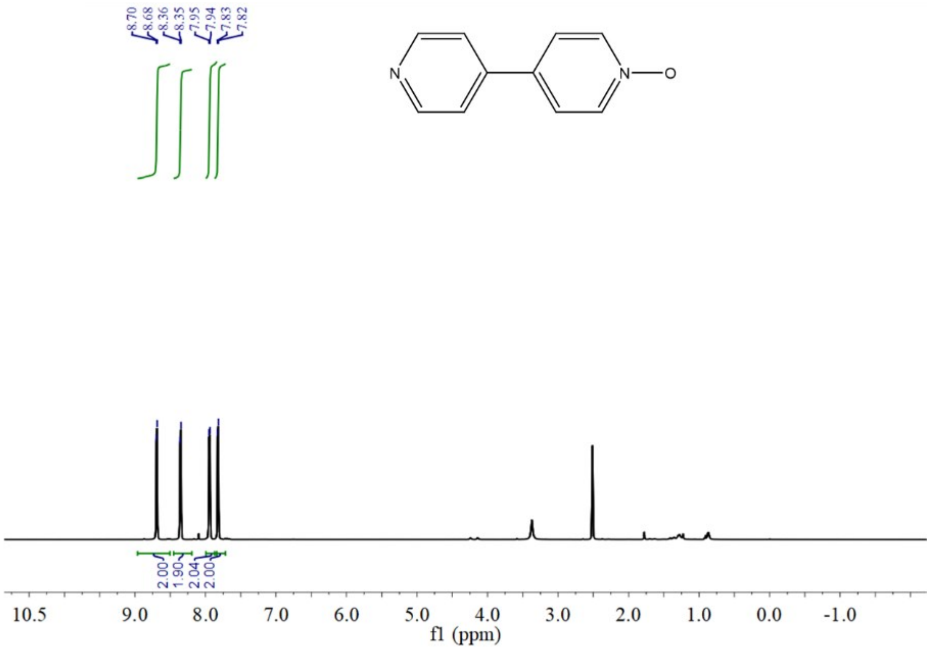

Figure S1. ^{1}H NMR spectra of 4, 4'-bipyridine-*N*-monoxide recorded in DMSO-d^6 (500 MHz).

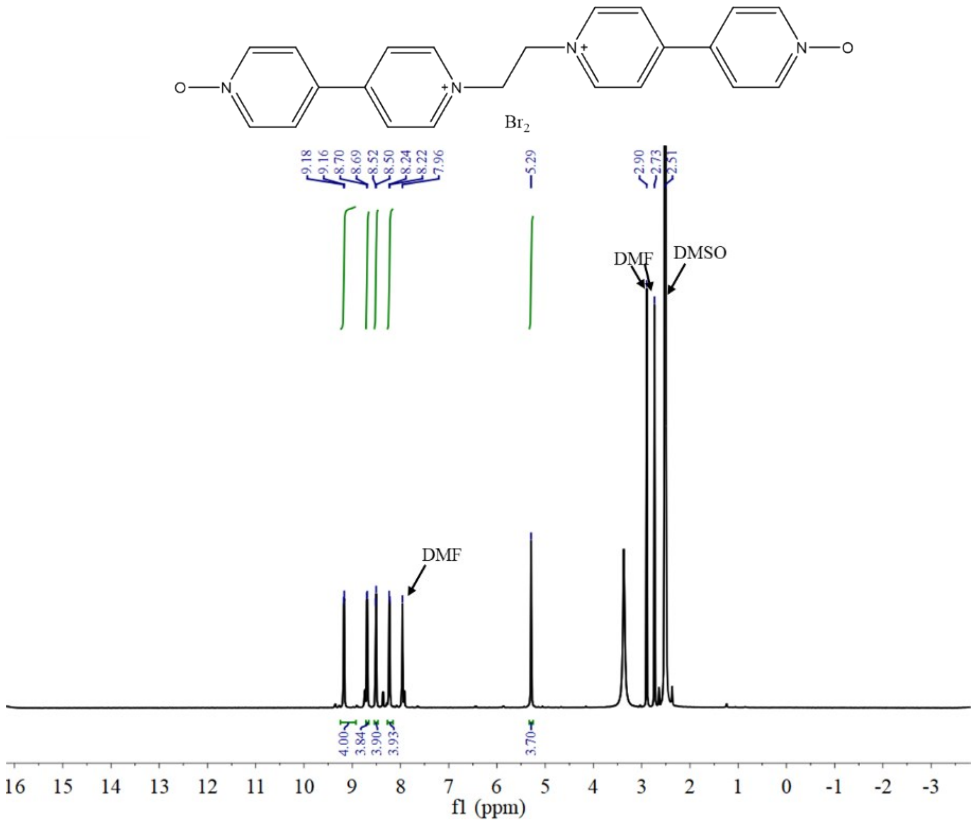

Figure S2. ^{1}H NMR of [EBBPYO]Br$_2$ recorded in in DMSO-d^6 (500 MHz).

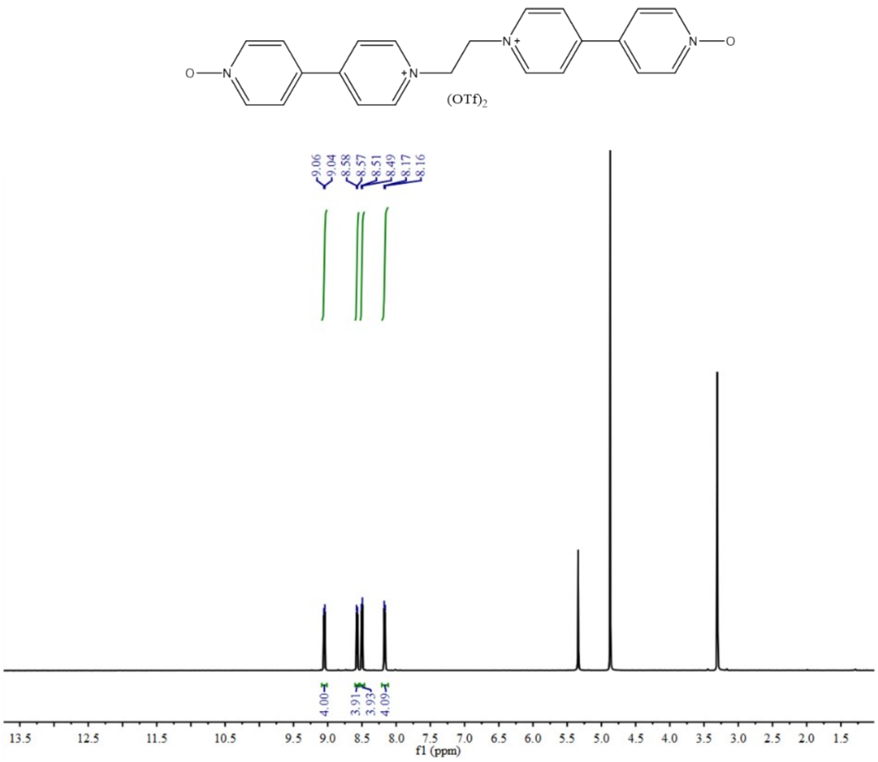

Figure S3. ^{1}H NMR of [EBBPYO][OTf]$_2$ recorded in CD_3OD (500 MHz).

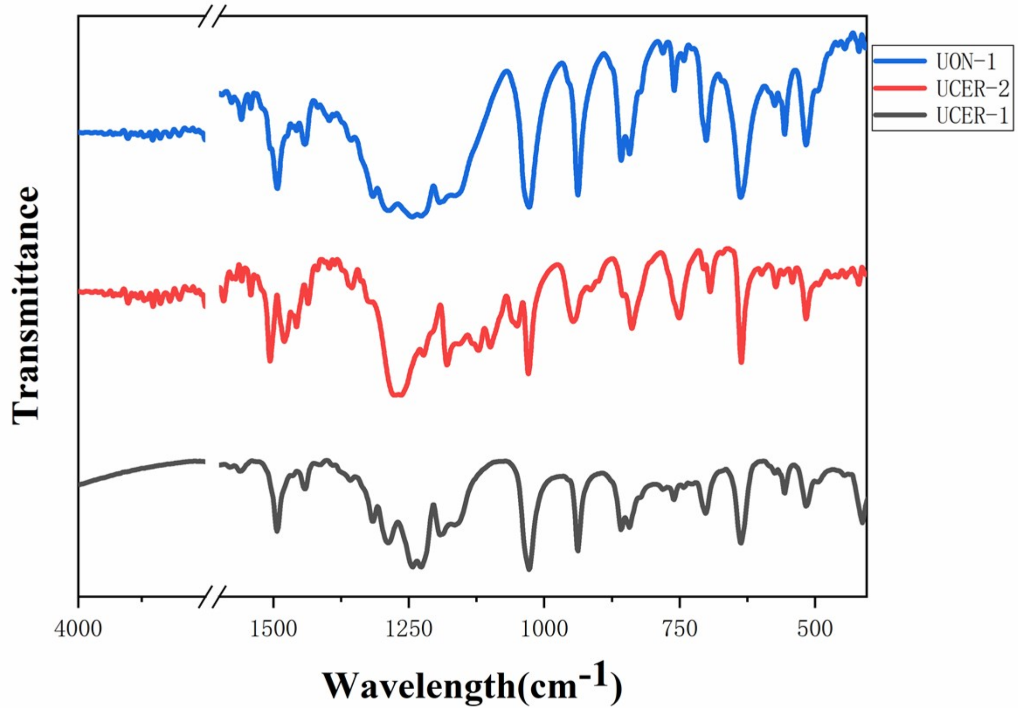

Figure S4. Infrared (IR) spectra for UCER-1,UCER-2,UON-1.

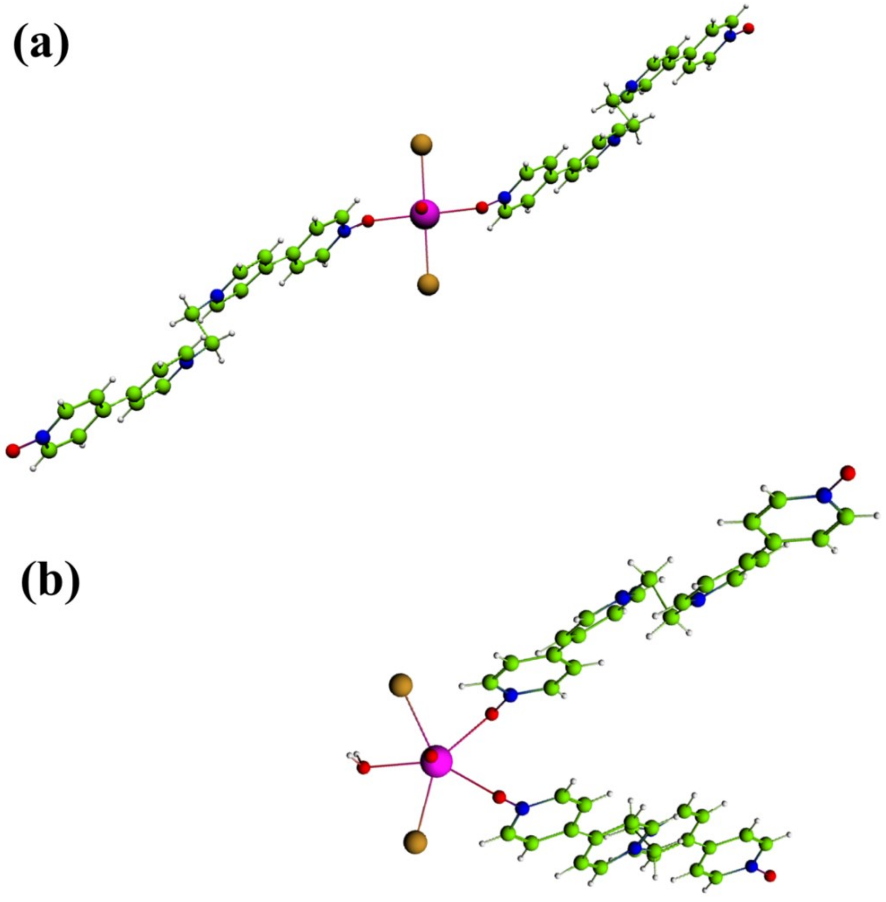

Figure S5. The models of molecular structures of UCER-1 and UCER-2 for theoretical calculation.

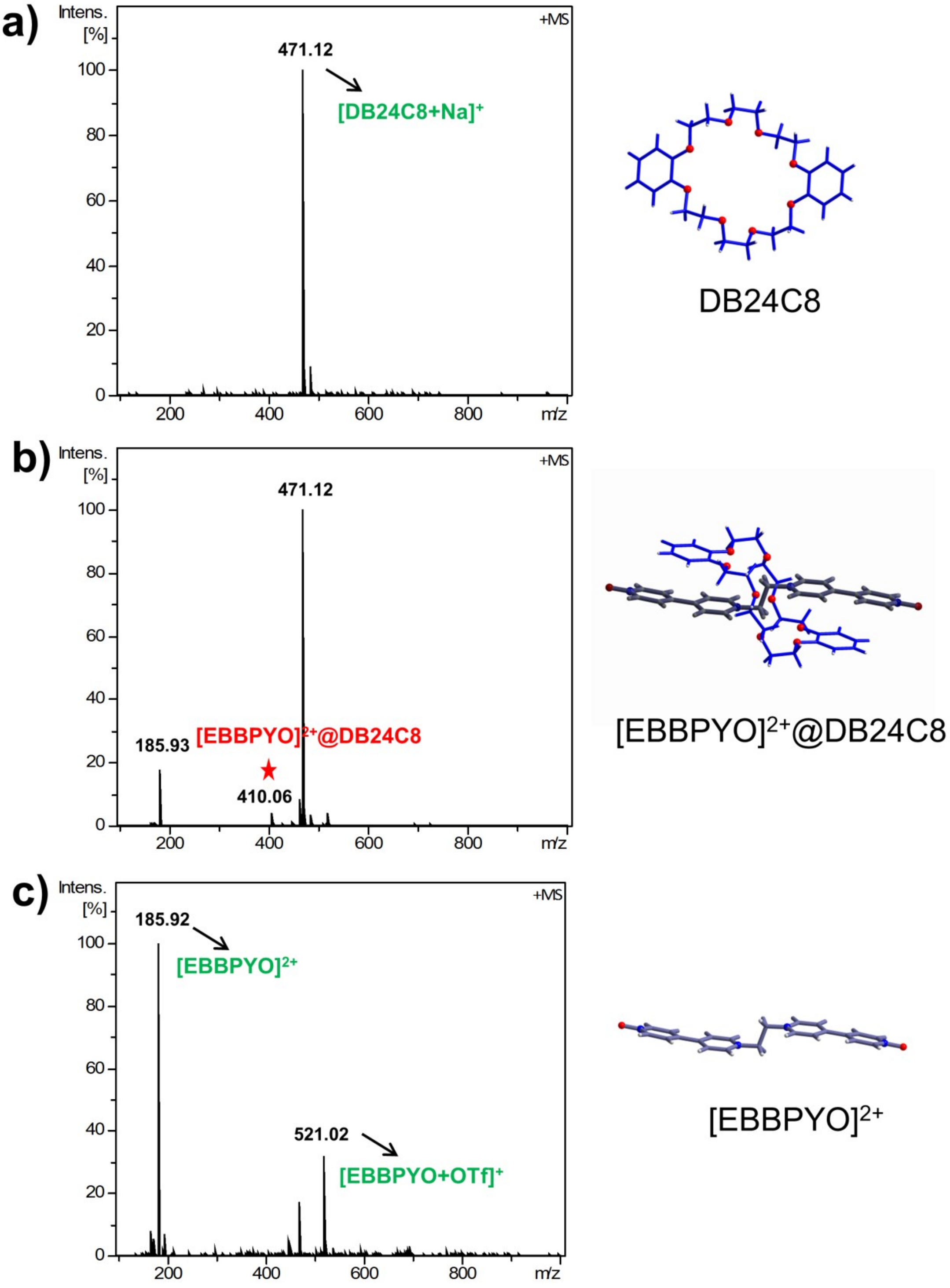

Figure S6. ESI-MS spectrum of a mixture of DB24C8 and [EBBPYO]$^{2+}$ (1:1) with pure DB24C8 and [EBBPYO]$^{2+}$ as the control compounds.

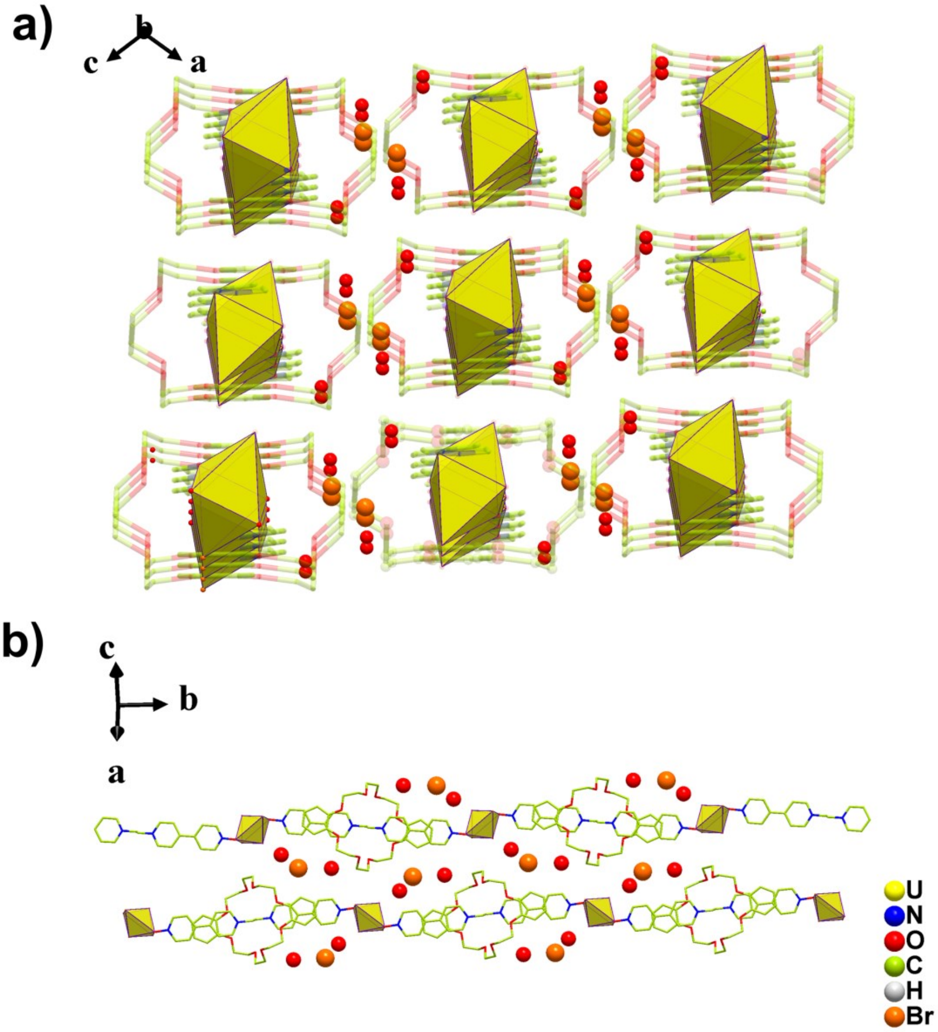

Figure S7. Free bromide counterions dispersed in the gaps of adjacent polyrotaxane chains to balance the net charge in UCER-1: (a) top view of the whole crystal packing; (b) side view of two adjacent chains.

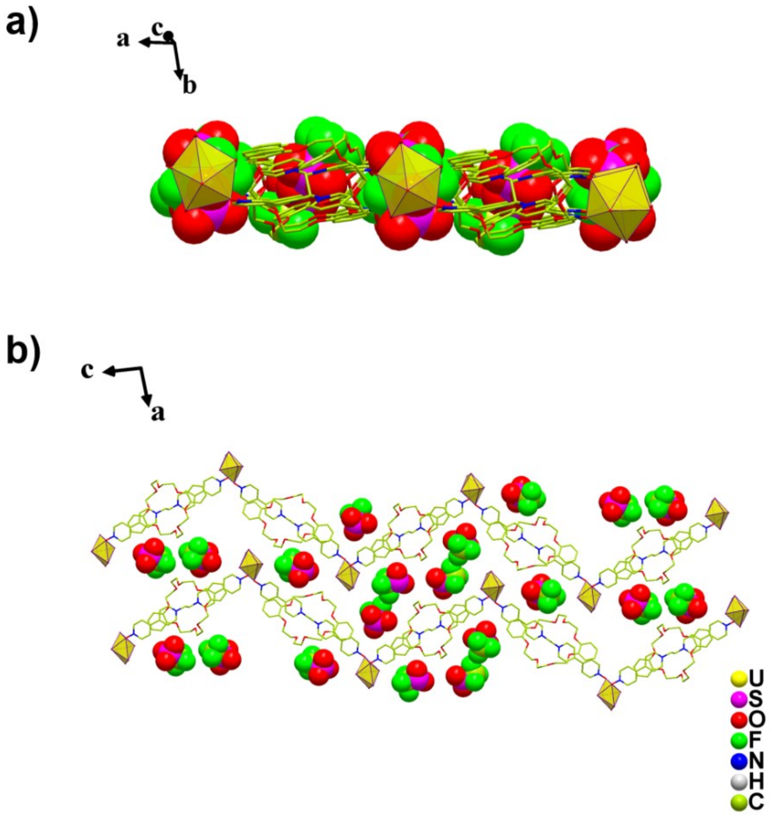

Figure S8. Free OTf⁻ counterions dispersed in the gaps of adjacent polyrotaxane chains to balance the net charge in UCER-2: (a) top view of two adjacent chains; (b) side view of two adjacent chains.

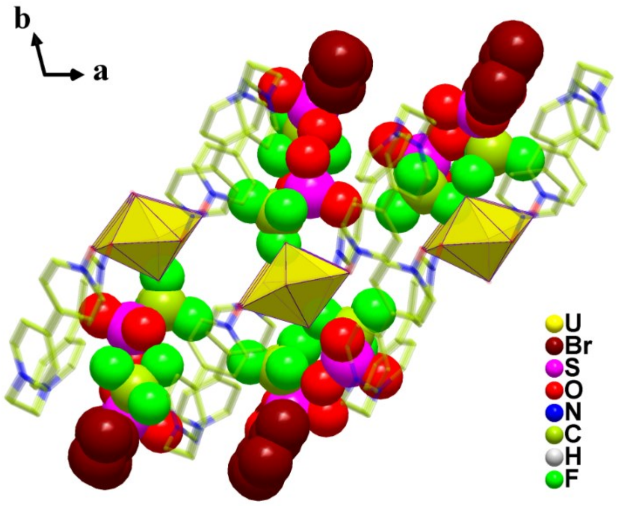

Figure S9. Free bromide and OTf⁻ counterions dispersed in the interlayer space of adjacent polyrotaxane chains to balance the net charge in UON-1.

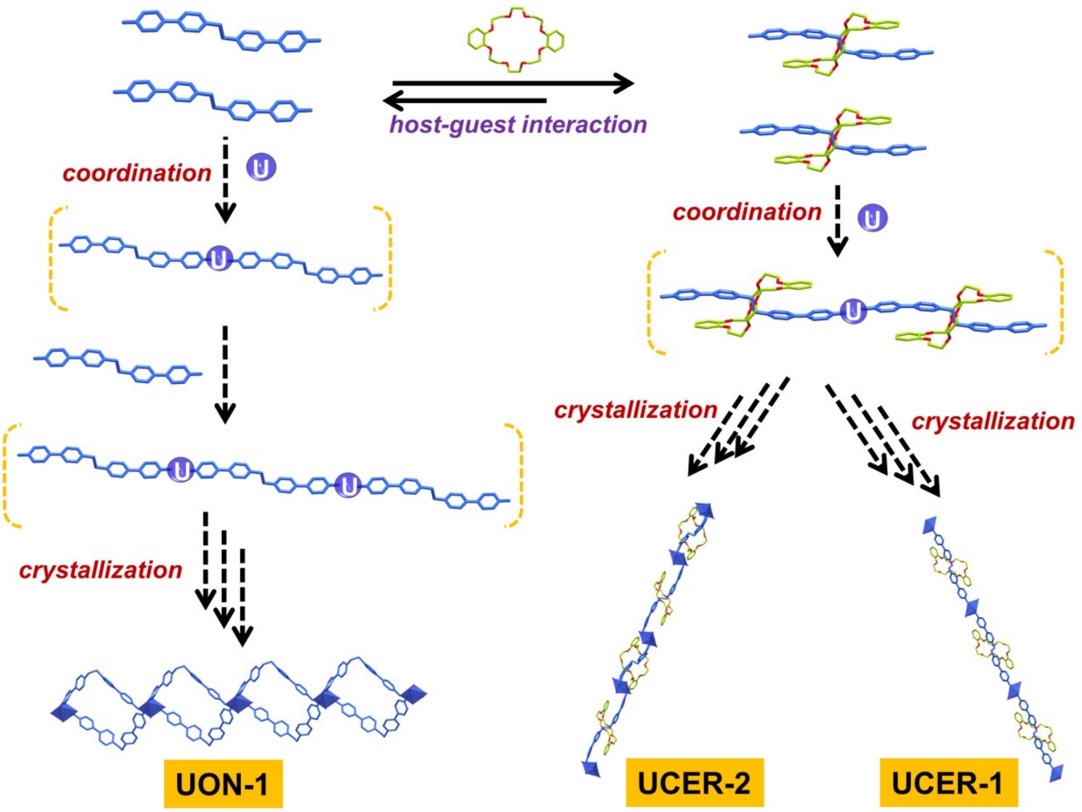

Figure S10. Analysis of the formation mechanisms for UCER-1, UCER-2 and UON-1.

Reference.

[1] K. Lyczko, M. Lyczko, M. Walo and J. Lipkowski, *Inorg. Chem. Commun.*, 2012, **24**, 234-236.

[2] C. B. Aakeroy, K. Epa, S. Forbes, N. Schultheiss and J. Desper, *Chem. Eur. J.*, 2013, **19**, 14998-15003.

[3] D. J. Hoffart, N. C. Habermehl and S. J. Loeb, *Dalton Trans.*, 2007, **27**, 2870-2875.

[4] D. J. Hoffart and S. J. Loeb, *Angew. Chem. Int. Ed.*, 2005, **44**, 901-904.