

Electronic Supplementary Information (ESI)

**Metallomacrocyclic or helix: Supramolecular isomerism in
bis(pyridylurea) metal complexes**

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S1. Experimental

S1.1 General

¹H NMR spectra were recorded on a Mercury plus-400 spectrometer with calibration against the solvent signal (DMSO-*d*₆ 2.50 ppm for ¹H). IR spectra were obtained using a Nicolet AVATAR 360 FT-IR spectrometer as KBr pellets. Elemental analyses were done on a VarioEL instrument from Elementaranalysensysteme GmbH. ESI-MS measurements were carried out using a Waters ZQ4000 spectrometer in methanol. Melting points were detected on an X-4 Digital Vision MP Instrument. Powder X-Ray diffraction data were obtained with an X'Pert Pro instrument. TGA was carried out under N₂ flow (60 mL min⁻¹) with an STA 449C DSC/DTA-TG instrument.

S1.2 Synthesis of L

To a solution of 3-isocyanatopyridine (0.24 g, 2.0 mmol) in toluene (5 mL) was added butane-1,4-diamine (0.09 g, 1.0 mmol). A mass of precipitate appeared immediately. The reaction mixture was stirred at 60 °C for 1 h, and cooled to room temperature before filtration. The crude solid was purified by recrystallization from CH₃OH/H₂O (1:2) as colorless crystals. Yield: 0.30 g (91%). M.p.: 208–209 °C. Anal. Found: C 58.42, N 25.83, H 5.89; Calcd for C₁₆H₂₀N₆O₂ (328.27): C 58.52, N 25.59, H 6.14%. ESI-MS: *m/z* 165.0 ([L+2H]²⁺), 329.5 ([L+H]⁺). ¹H NMR (DMSO-*d*₆, ppm): 1.43 (t, *J* = 2.0 Hz, 4H, urea-CH₂-CH₂-), 3.07 (dt, *J* = 5.6, 2.0 Hz, 4H, urea-CH₂-), 6.32 (t, *J* = 5.6 Hz; 2H, CH₂-NH), 7.24 (dd, *J* = 8.4, 4.8 Hz, 2H, Py-H5), 7.87 (m, 2H, Py-H4), 8.08 (t, *J* = 4.8 Hz, 2H, Py-H6), 8.50 (d, *J* = 2.4 Hz, 2H, Py-H2), 8.60 (s, 2H, pyridyl-NH-). ¹³C NMR (DMSO-*d*₆): 27.17 (N-CH₂-CH₂-), 38.86 (urea-CH₂-), 123.37 (Py-C5), 124.33 (Py-C4), 137.17 (Py-C3), 139.48 (Py-C2), 141.96 (Py-C6), 155.08 (C=O). FT-IR (KBr, cm⁻¹): 3325, 3080, 2945, 2871, 1682, 1647, 1557, 1482, 1283, 1229, 1026, 812, 703, 608.

S1.3 Synthesis of [Zn₂L₂Cl₄(toluene)] (1)

A methanolic solution (5 mL) of L (32.8 mg, 0.10 mmol) was layered on a toluene/MeOH solution (5 mL,

1:3 v/v) of ZnCl_2 (13.6 mg, 0.10 mmol). Colorless block crystals were obtained after two weeks. Yield: 36.0 mg (70%). Turns to opaque at 140 °C, M.p.: 209–210 °C. Anal. found: C 45.22, H 4.74, N 16.69; Calcd. for $[\text{Zn}_2\text{L}_2\text{Cl}_4(\text{toluene})_{0.9}]$: C 45.45, H 4.70, N 16.60% (about 10% of the guest was lost during the drying of the sample for the analysis). ^1H NMR ($\text{DMSO-}d_6$): 1.43 (s, 8H, urea- $\text{CH}_2\text{-CH}_2$ -), 3.07 (d, $J = 5.6$ Hz, 8H, urea- CH_2 -), 6.34 (t, $J = 5.6$ Hz, 4H, NH), 7.31 (dd, $J = 8.4, 5.2$ Hz, 4H, Py-H5), 7.92 (m, 4H, Py-H4), 8.10 (t, $J = 4.4$ Hz, 4H, Py-H6), 8.56 (s, 4H, Py-H2), 8.72 (s, 4H, pyridyl-NH-), 2.26 (s, 3H, Ar- CH_3), 7.16 (m, 3H, toluene-H2,4), 7.25 (t, $J = 7.2$ Hz, 1H, toluene-H3). ^{13}C NMR ($\text{DMSO-}d_6$), 27.17 (N- $\text{CH}_2\text{-CH}_2$ -), 39.08 (urea- CH_2 -), 123.79 (Py-C5), 125.03 (Py-C4), 137.14 (Py-C3), 139.52 (Py-C2), 141.69 (Py-C6), 155.04 (C=O), 128.17 (Ar-C3), 126.85 (Ar-C2). FT-IR (KBr, cm^{-1}): 3386, 3305, 3082, 2939, 2856, 1712, 1650, 1553, 1483, 1427, 1270, 1231, 1026, 810, 697, 652.

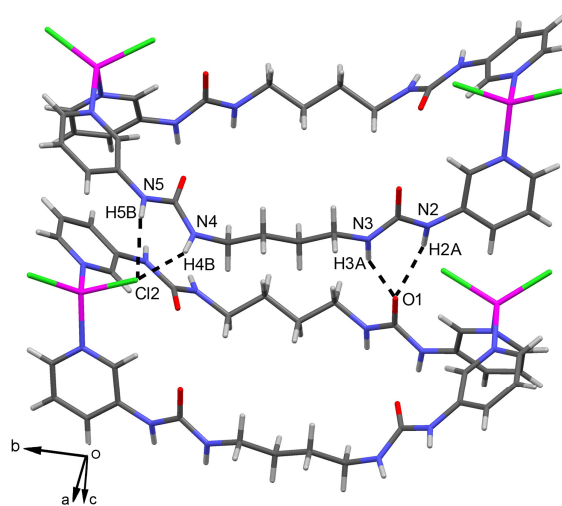


Fig. S1 The intermolecular N–H...O and the N–H...Cl hydrogen bonds in compound 1.

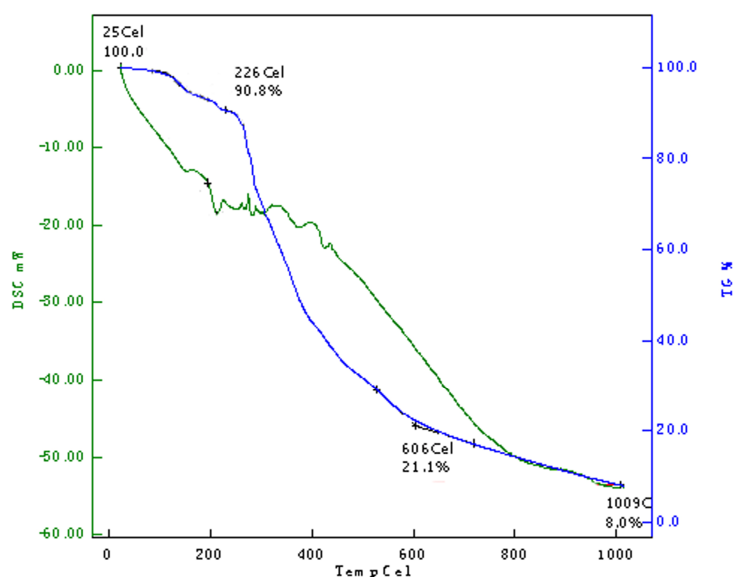


Fig. S2 TGA curve of compound 1.

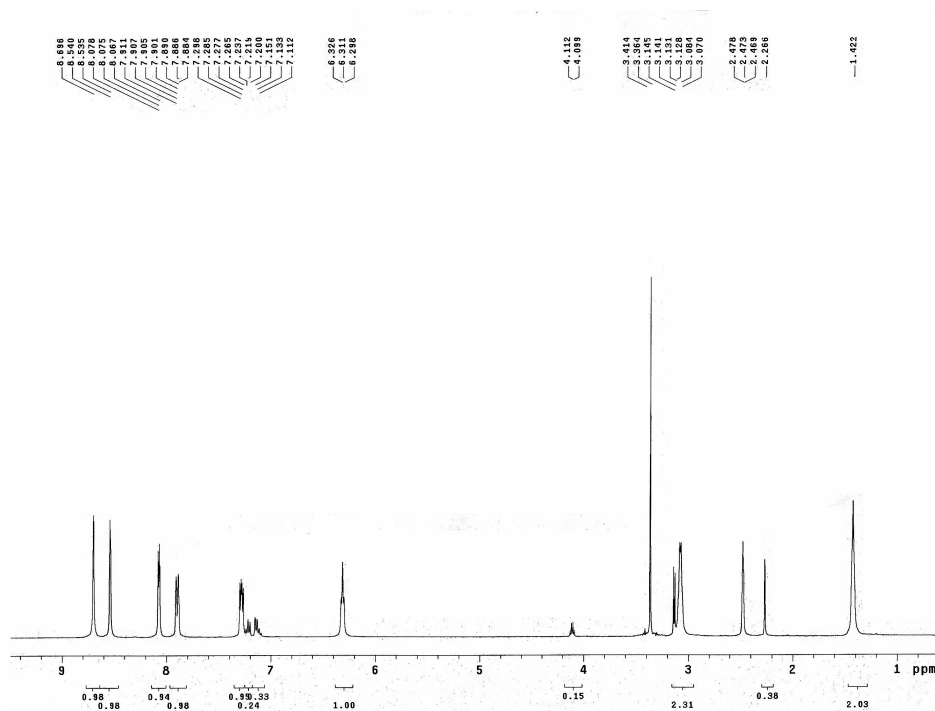


Fig. S3 ^1H NMR Spectrum of compound **1**.

S1.4 Synthesis of $[\text{Zn}_2\text{L}_2\text{Cl}_4(m\text{-xylene})]$ (**2**):

In a similar procedure, $[\text{Zn}_2\text{L}_2\text{Cl}_4(m\text{-xylene})]$ (**2**) was synthesized by layering a methanolic solution (5 mL) of L (32.8 mg, 0.10 mmol) on an *m*-xylene/MeOH solution (5 mL, 1:3 v/v) of ZnCl_2 (13.6 mg, 0.10 mmol) as colorless crystals. Yield: 30.0 mg (53 %). M.p.: 206 °C. Anal found: C 46.16, H 4.55, N 16.05, calc. for $([\text{Zn}_2\text{L}_2\text{Cl}_4(m\text{-xylene})])$ C 46.40, H 4.87, N 16.23%. ^1H NMR (DMSO- d_6), 1.45 (s, 8H, urea- $\text{CH}_2\text{-CH}_2\text{-}$), 3.11 (d, 8H, $J = 4.8$ Hz, urea- $\text{CH}_2\text{-}$), 6.33 (t, 4H, $J = 4.8$ Hz; $\text{CH}_2\text{-NH}$), 7.29 (dd, $J = 8.0$, 4.4 Hz, 4H, Py-H5), 7.91 (m, 4H, Py-H4), 8.10 (d, $J = 4.4$ Hz, 4H, Py-H6), 8.55 (s, 4H, Py-H2), 8.77 (d, 4H, $J = 4.4$ Hz, pyridyl-NH-), 2.25 (s, 6H, xylene- CH_3), 6.96 (t, 1H, $J = 8.0$ Hz, xylene-H2), 7.21 (m, 3H, xylene-H4,5,6). ^{13}C NMR (DMSO- d_6), 27.17 (N- $\text{CH}_2\text{-CH}_2\text{-}$), 39.08 (urea- $\text{CH}_2\text{-}$), 123.65 (Py-C5), 124.77 (Py-C4), 137.38 (Py-C3), 139.30 (Py-C2), 141.80 (Py-C6), 155.05 (C=O), 125.93. FT-IR (KBr, cm^{-1}) 3386, 3303, 3112, 2858, 1712, 1649, 1552, 1482, 1270, 811, 697.

S1.5 Synthesis of $[\text{ZnLCl}_2]_n$ (**3**):

A methanolic solution (5 mL) of **L** (32.8 mg, 0.10 mmol) was layered on a mesitylene/MeOH solution (5 mL, 1:3 v/v) of ZnCl_2 (13.6 mg, 0.10 mmol). After two weeks, colorless crystals were obtained. Yield: 40.8 mg (88 %). M.p.: 235°C–237°C. Anal found: C 41.22, H 4.29, N 17.89; Calcd. for $[\text{ZnLCl}_2]$ (464.69): C 41.36, H 4.34, N 18.09%. ^1H NMR ($\text{DMSO-}d_6$), 1.45 (s, 2H, urea- $\text{CH}_2\text{-CH}_2\text{-}$), 3.11 (d, 2H, $J = 5.6$ Hz, urea- $\text{CH}_2\text{-}$), 6.33 (t, 1H, $J = 5.6$ Hz; NH), 7.31 (dd, 1H, $J = 8.0, 4.4$ Hz, Py-H5), 7.92 (d, 1H, $J = 8.4$ Hz, Py-H4), 8.10 (d, 1H, $J = 4.0$ Hz, Py-H6), 8.57 (s, 1H, Py-H2), 8.72 (s, 1H, pyridyl-NH-). FT-IR (KBr, cm^{-1}): 3358, 3071, 2932, 2853, 1708, 1676, 1546, 1482, 1424, 1302, 1226, 1025, 805, 698, 653.

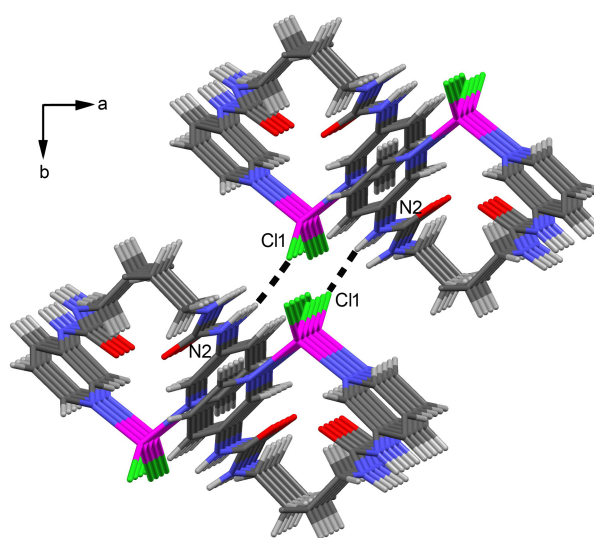


Fig. S7 Racemic helices viewed along the c axis in compound **3**.

S1.6 Experiments on the possible transformation of the macrocyclic and helix isomers:

Powder XRD analyses (Fig. S8) revealed that the metallomacrocyclic $[\text{Zn}_2\text{L}_2\text{Cl}_4(\text{toluene})]$ (**1**) was retained after colorless crystals of **1** were immersed in methanol/mesitylene (10:1, 5:1 and 2:1 v/v, respectively) for two days at different temperature (20 °C and 60 °C). Similar experiments were carried out by placing single crystals of **3** in methanol/toluene, and powder XRD patterns showed no change of the phase (Fig. S9).”

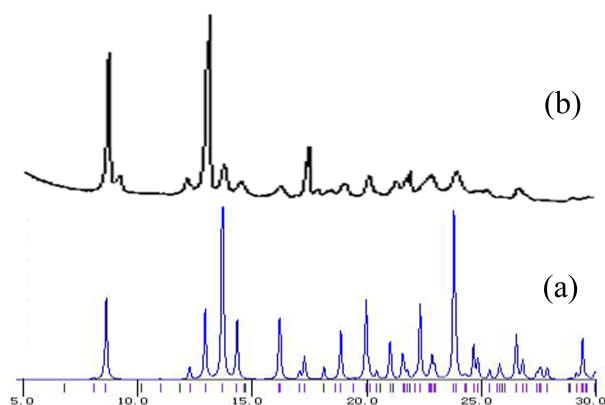


Fig. S8 Power XRD patterns of compound **1**. (a) Simulated pattern; (b) After immersing into methanol/mesitylene (5:1 v/v) at 60 °C.

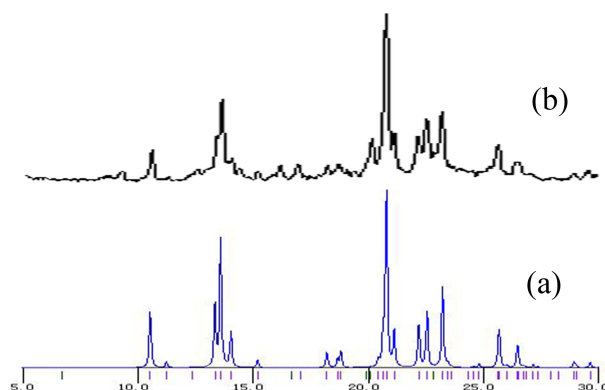


Fig. S9 Power XRD patterns of compound **3**. (a) Simulated pattern; (b) After immersing into methanol/toluene (5:1 v/v) at 60 °C.

S1.7 Experiments on the reversibility of toluene inclusion of compound **1**:

The following experiments were carried out to investigate the reversibility of the toluene inclusion. Colorless crystals of **1** were dried for 24 hours at 160 °C in vacuum and then immersed in toluene for 10 hours at 60 °C. TGA analyses revealed that **1** lost 86.7% of toluene guests upon heating (measured weight loss of the toluene molecule after drying, 1.2%; calculated weight loss for toluene per **1**, 9.0%; Fig. S10). After immersing in toluene, the guest was completely re-introduced (measured weight loss of the toluene molecule, 9.4%; Fig. S12). Powder XRD analyses indicated that the macrocyclic structure was retained during the processes (Fig. S11).

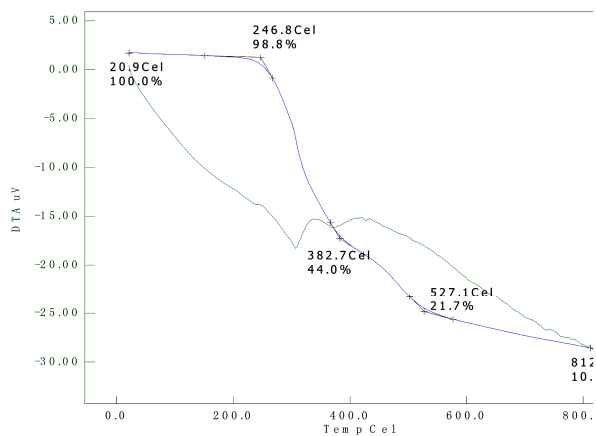


Fig. S10 TGA curve of compound **1** after drying for 24 hours at 160 °C in vacuum.

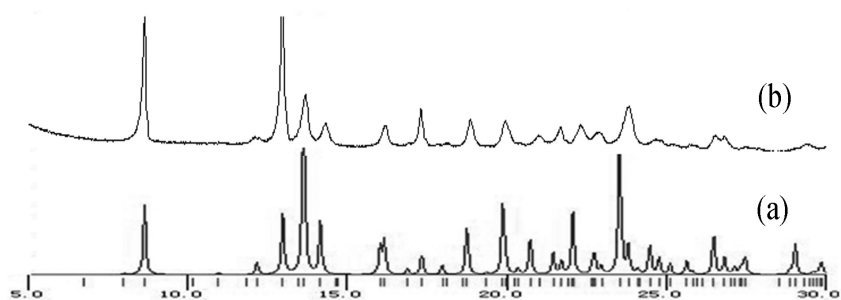


Fig. S11 Powder XRD of **1**. (a) Simulated pattern; (b) After drying for 24 hours at 160 °C in vacuum.

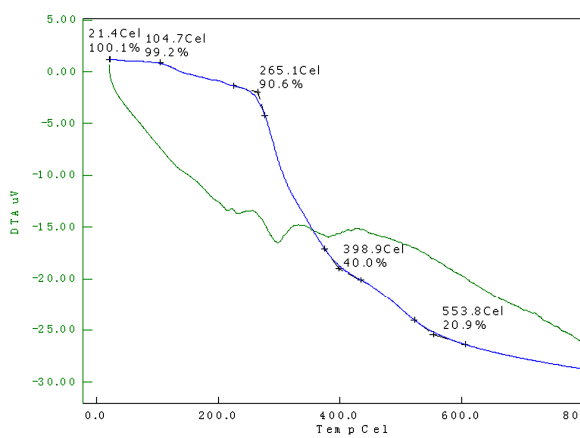


Fig. S12 TGA curve of compound **1** after reversibly reintroducing the toluene guest.

S1.8 X-Ray crystal structure determination:

Diffraction data for the complexes **1–3** were collected on a Bruker SMART APEX II diffractometer at room temperature (293 K) with graphite-monochromated Mo K α radiation ($\lambda = 0.71073 \text{ \AA}$). An empirical absorption correction using SADABS was applied for all data.¹ The structures were solved by direct methods using the SHELXS program.² All non-hydrogen atoms were refined anisotropically by full-matrix least-squares on F^2 by the use of the program SHELXL.² Hydrogen atoms bonded to carbon were included in idealized geometric positions with thermal parameters equivalent to 1.2 times those of the atom to which they were attached. For complex **1**, the methyl group of toluene molecule was refined into two half-occupancy positions, and the hydrogen atom on the carbon attaching disordered methyl group is not included. For complex **3**, the low ratio of observed/unique reflections of 38% is due to the poor quality of the crystal, which led to a large number of weak reflections.

References:

1. Sheldrick, G. M., *SADABS: Area-Detector Absorption Correction*, **1996**, University of Göttingen, Germany.
2. Sheldrick, G. M., *SHELXS-97, SHELXL-97, Programs for Crystal Structure Analysis*, **1997**, University of Göttingen, Germany.