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Supporting Information

Efficient Fixation of Atmospheric CO_2 as Carbonate in a Capsule of a Neutral Receptor and its Release under Mild Condition.

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Materials and Methods:

Tris-(2-aminoethyl)amine, pentafluorophenyl isocyanate, *n*-tetrabutylammonium hydroxide and *n*-tetraethylammonium bicarbonate were purchased from Sigma-Aldrich, USA and were used as purchased without further purification. Dichloromethane (DCM) and dimethylsulfoxide (DMSO) were purchased from Spectrochem Ltd., India. Elemental analyses were performed on a Perkin Elmer CHN 2400 Ser II Elemental Analyzer. ^{1}H-NMR (300 MHz) and ^{13}C NMR (75 MHz) spectra were recorded on a Bruker DPX 300 FT-NMR spectrometer. Chemical shifts for ^{1}H- and ^{13}C-NMR were reported in parts per million (ppm), calibrated to the residual solvent peak set, with coupling constants reported in Hertz (Hz). Infrared (IR) spectra were recorded on a Perkin Elmer FTIR spectrometer. The spectra were obtained in KBr pressed disks in solid state. X-ray powder patterns were collected on a Bruker D8 SWAX X-ray diffractometer (CuKα = 1.5418 Å) with a scan rate of 0.3 min/deg in the 5º < 2θ < 55º range with a step size of 0.05º.

Synthesis of Tripodal Receptor L

L was synthesized following our recent report.[1] 2.6 mL (20 mmol) of pentafluorophenyl isocyanate was dissolved in 25 mL of dry DCM at room temperature in a 100 mL 2-neck round bottom flask equipped with a dropping funnel. Then tren (1.0 mL, 6.5 mmol) was dissolved in 25 mL of dry DCM and was added drop-wise using a dropping funnel with constant stirring. The resulting solution was stirred for another 1 h at room temperature in N_2 atmosphere. The colorless precipitate formed was filtered off and washed with DCM twice. The precipitate collected was dried in air. Yield of **L** is 98%.Melting point: 216°C. ^{1}H-NMR (300 MHz, DMSO-d_6): δ 2.55 (m, 6H, NCH_2), 3.15 (m, 6H, NCH_2CH_2), 6.55 (br, 3H, NH_a), 8.352 (br, 3H, NH_b). ^{13}C NMR (75.47 MHz, DMSO-d_6): δ 38.9 (NCH_2), 54.5 (NCH_2CH_2), 115.7 (m of s, Ar, *C*C-F, J_{CCF} = 15Hz), 137.9 (m of d, Ar, *C*-F, J_{CF} = 247 Hz), 138.8 (m of d, Ar, *C*-F J_{CF} = 247 Hz), 143.6 (m of d, Ar, *C*-F, J_{CF} = 246 Hz), 155.4 (s, *C*=O). HRMS (+ESI) calcd for $[C_{27}H_{19}F_{15}N_7O_3]^+$, $\mathbf{L}^+$ 774.1309, found 774.2267.

Synthesis of Complex 1.

Complex **1** was synthesized by reacting **L** and *n*-$Bu_4N^+OH^-$ in an open vessel. In the present case, 77 mg (0.1 mmol) of **L** was dissolved in 10 mL of DMSO in a 25 mL beaker and 25 mg of *n*-$Bu_4N^+OH^-$ (52 mg, 0.2 mmol) was added in one shot to DMSO solution of **L**. The colorless clear solution was allowed to crystallize at laboratory conditions in an open vessel. Colorless single crystals of the carbonate complex of **L**, [2**L** (CO_3^{2-})]·2(n-$Bu)_4N^+$ (**1**), suitable for X-ray diffraction was obtained within a day. Isolated Yield of **1** is 98%. Melting point: 157°C. ^{1}H-NMR (300 MHz, CD_3CN): δ 0.920 (t, 24H, $NCH_2CH_2CH_2CH_3$, J = 7.5 Hz), 1.30 (m, 16H, $NCH_2CH_2CH_2CH_3$), 1.55 (m, 16H, $NCH_2CH_2CH_2CH_3$), 2.38 (m, 12H, NCH_2), 3.03 (m, 28H, NCH_2CH_2, $NCH_2CH_2CH_2CH_3$), 8.09 (br, 6H, NH_a), 9.69 (br, 6H, NH_b). ^{13}C NMR (75.47 MHz, CD_3CN): δ 12.85 ($NCH_2CH_2CH_2CH_3$), 19.42 ($NCH_2CH_2CH_2CH_3$), 23.40 ($NCH_2CH_2CH_2CH_3$) 38.25 (NCH_2), 54.33 (NCH_2CH_2), 58.41 ($NCH_2CH_2CH_2CH_3$), 116.09 (m of s, Ar, *C*C-F, J_{CCF} = 15 Hz), 137.43 (m of d, Ar, *C*-F, J_{CF} = 247 Hz), 138.00

(m of d, Ar, *C*-F J_{CF} = 247 Hz), 143.29 (m of d, Ar, *C*-F, J_{CF} = 247 Hz), 155.72 (s, *C*=O), 169.60 (s, CO_3^{2-}). Anal. Calcd for $C_{87}H_{108}F_{30}N_{16}O_9$: C, 49.95; H, 5.20; N, 10.71%. Found: C, 50.10; H, 5.12; N, 10.55%.

^{1}H-NMR Titration Studies:

Binding constant was obtained by ^{1}H-NMR (300 MHz Bruker) titrations of **L** with $[n\text{-Et}]_4N^+HCO_3^-$ in DMSO-d_6 at 25ºC. The initial concentration of **L** was 20 mM. Aliquots of anions were added from a stock solutions of 50 mM. Tetramethylsilane (TMS) in DMSO-d_6 was used as an internal reference, and titration was performed by 25 measurements at room temperature. All proton signals were referred to TMS. The overall association constant,[2] β value was calculated by WINEQNMR 2 fitting the change in the N-H chemical shift with a 1:2 association model with non-linear least square analysis.

The stepwise binding constants[3] were defined as

$$\mathbf{L} + HCO_3^- \underset{}{\overset{K_{11}}{\rightleftharpoons}} \mathbf{L}\cdot HCO_3^- \quad K_{11} = \frac{[\mathbf{L}\cdot HCO_3^-]}{[\mathbf{L}][HCO_3^-]}\ M^{-1}$$

$$\mathbf{L} + \mathbf{L}\cdot HCO_3^- \underset{}{\overset{K_{12}}{\rightleftharpoons}} 2L\cdot HCO_3^- \quad K_{12} = \frac{[2\mathbf{L}\cdot HCO_3^-]}{[\mathbf{L}][\mathbf{L}\cdot HCO_3^-]}\ M^{-1}$$

The overall binding constant is defined as

$$2\cdot\mathbf{L} + HCO_3^- \underset{}{\overset{\beta_{12}}{\rightleftharpoons}} 2\mathbf{L}\cdot HCO_3^- \quad \beta_{12} = \frac{[2\mathbf{L}\cdot HCO_3^-]}{[\mathbf{L}]^2[HCO_3^-]}\ M^{-2}$$

$$\beta_{12} = K_{11}K_{12}$$

Single-crystal X-ray studies:

The crystallographic data and details of data collection and refinement for complex **1** were listed below. In the present case, a single crystal of suitable size was selected from the mother liquor and immersed in paratone oil and then mounted on the tip of a glass fibre and cemented using epoxy resin. Intensity data for this crystal was collected using MoKα (λ = 0.7107 Å) radiation on a Bruker SMART APEX II diffractometer equipped with CCD area detector at 100 K. Reflections were measured from a hemisphere of data collected with each frame covering 0.5º in ω. The data integration, reduction and structure solutions/refinements were carried out using the software package of Bruker SMART APEX. Graphics were generated using PLATON 97[4] and MERCURY 2.2.[5] In complex **1**, the non-hydrogen atoms were refined anisotropically until convergence. All the hydrogen atoms in this complex were geometrically fixed at idealized positions and refined isotropically.

Figure 1S: ^{1}H-NMR Spectrum of Complex **1** in CD_3CN at 298 K.

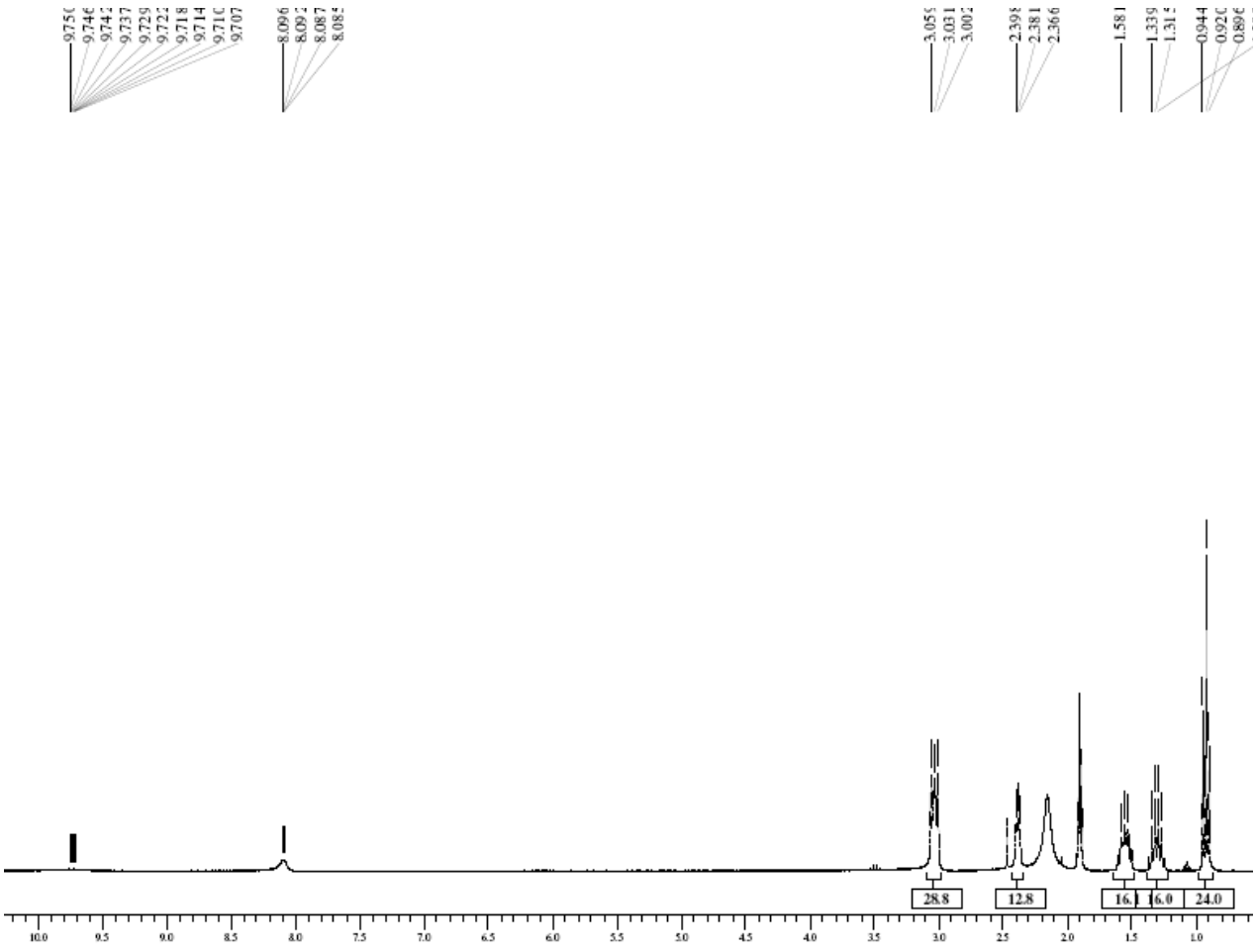
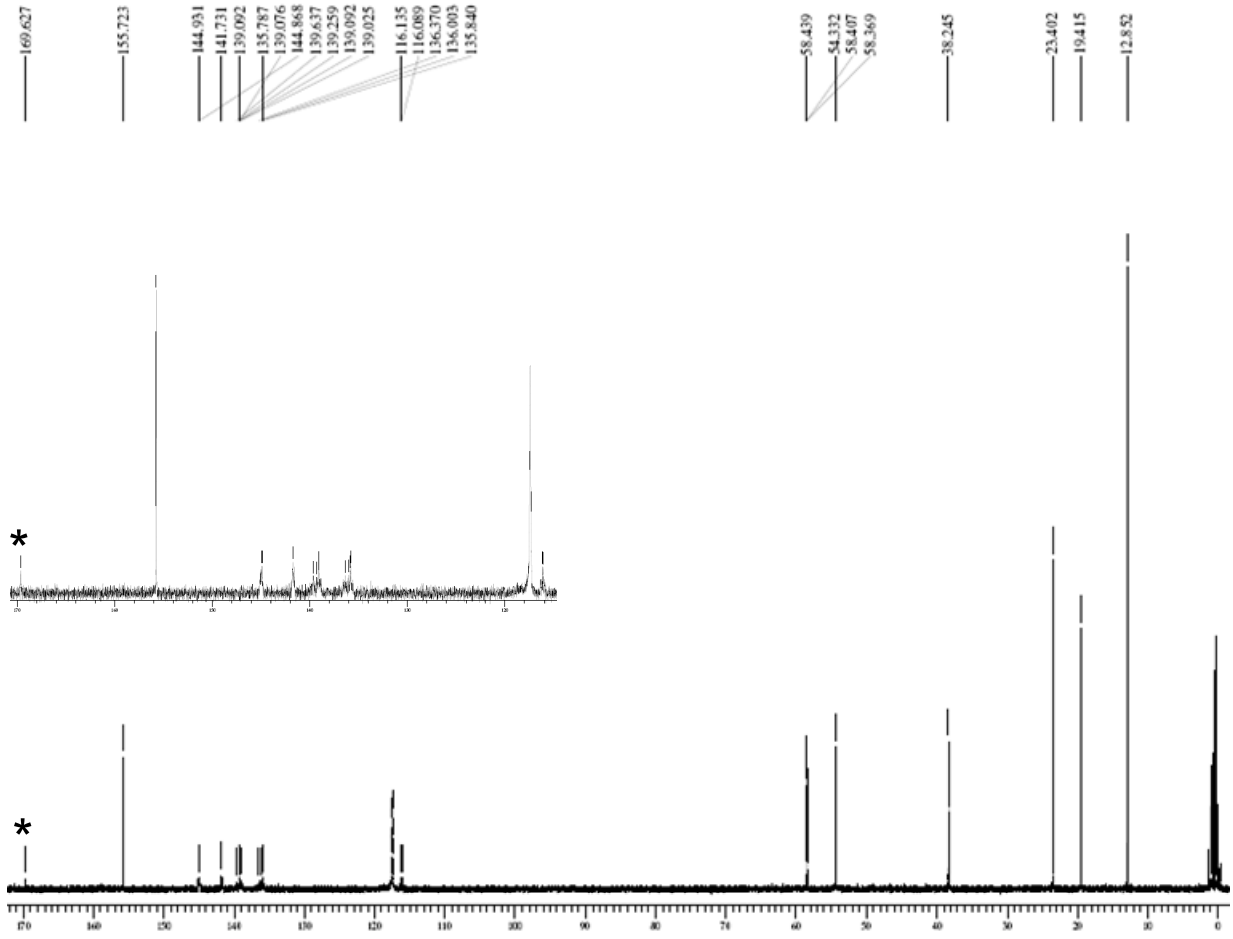


Figure 2S: ^{13}C-NMR Spectrum of Complex **1** in CD_3CN at 298 K.



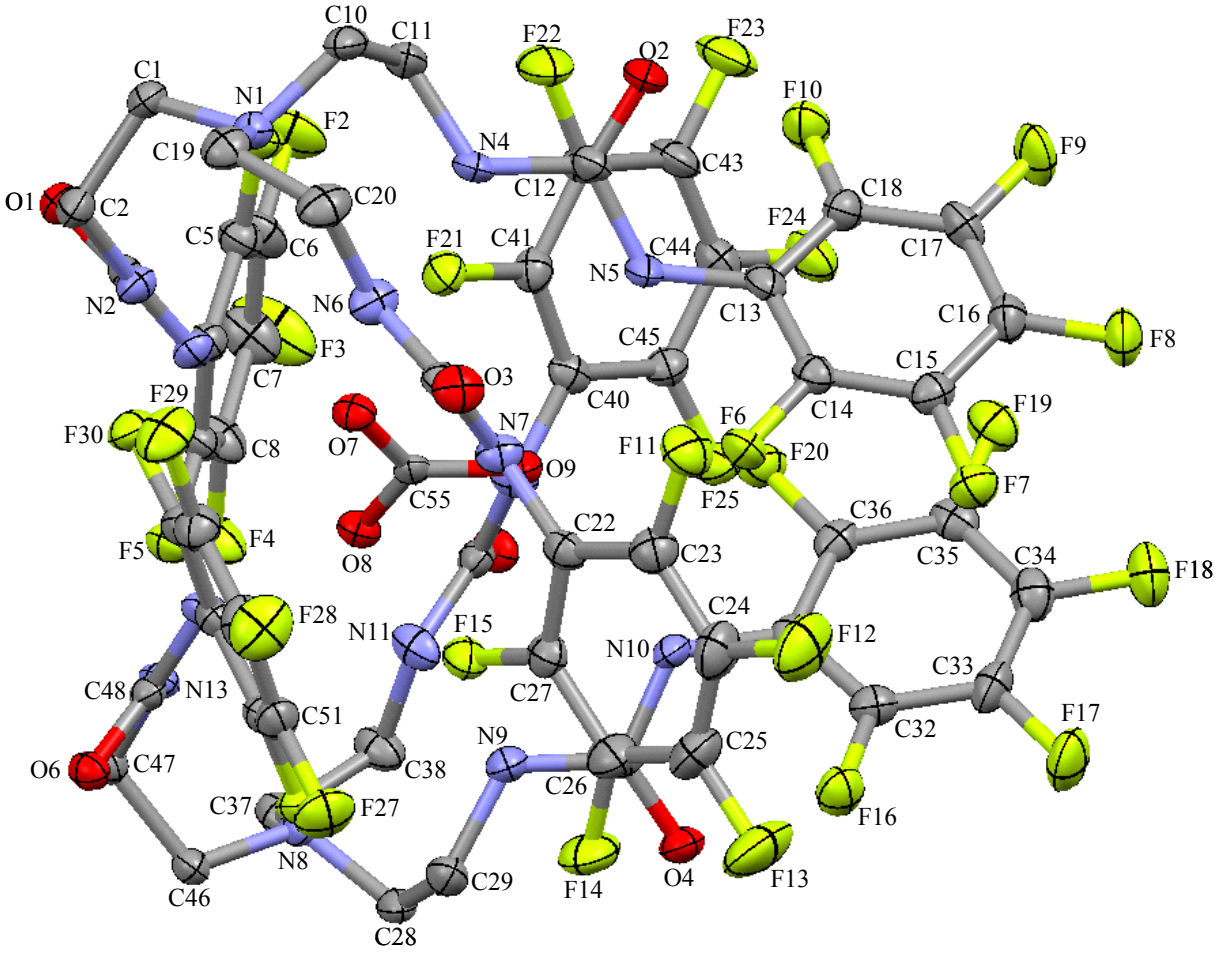
Note: The peak marked as * assigned as the carbon atom in the encapsulated CO_3^{2-}.

Table 1S: Crystallographic table for the complex 1.

	1
Chemical formula	$C_{87}H_{108}F_{30}N_{16}O_9$
Formula weight	2091.89
Temperature (K)	100
Radiation type	MoKα
Radiation wavelength	0.71073
Crystal system	Monoclinic
Space group	Cc
a (Å)	21.923(3)
b (Å)	19.069(3)
c (Å)	23.089(3)
α (deg)	90.00
β (deg)	95.027(2)
γ (deg)	90.00
Cell volume ($Å^3$)	9615(2)
Z	4
Calcd density (g/cm^3)	1.445
Absorption coefficient, μ (mm^{-1})	0.134
F(000)	4336
Crystal color	colorless
Crystal size (mm^3)	0.43 x 0.18 x 0.11
Data collection method	Bruker Apex II CCD diffractometer ω rotation with narrow frames
θ range for data collection	1.42º to 27.50º
Index ranges	h -28 to 28; k -24 to 24; l -29 to 29
Completeness to θ = 25.00º	96.2%
Relfns collected	39541
Independent Reflns	10625 (R_{int} = 0.0373)
Reflections with $F^2>2\sigma$	8930
Absorption correction	semiempirical from equivalents
Min. and max. transmission	0.9447 and 0.9854
Structure solution	direct methods
Refinement method	full-matrix least-

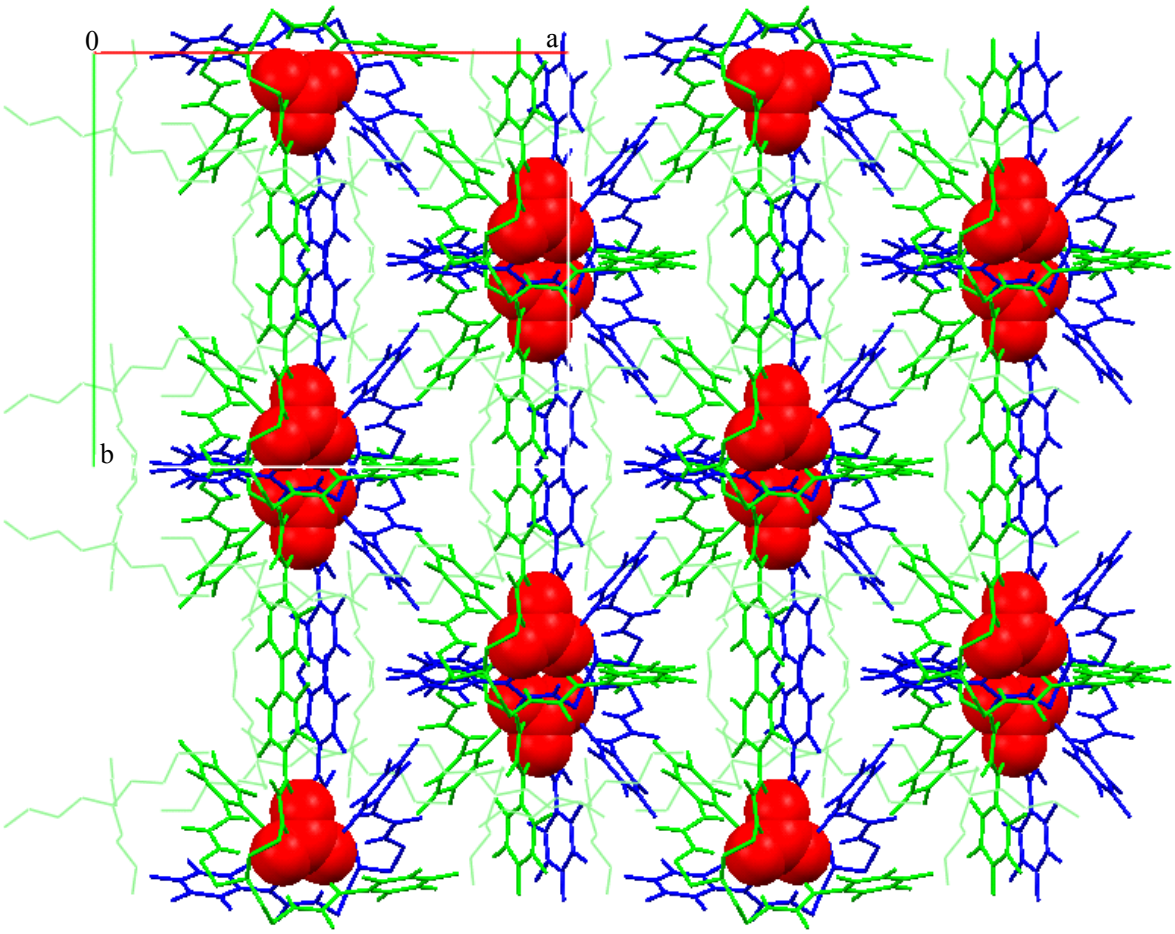
	squares on F^2
Weighting parameters a, b	0.1000, 0.0000
Data/restraints/params	10625/2/1287
Final *R* indices [$F^2>2\sigma$]	R1 = 0.0386, WR2 = 0.1062
R indices (all data)	R1 = 0.0501, WR2 = 0.1168
Goodness-of-fit of F^2	0.850
Largest and mean shift (su)	0.005 and 0.000
Largest diff. peak and hole (e $Å^{-3}$)	0.461 and -0.292

Figure 3S: ORTEP Diagram of Complex **1** with 50% Thermal Ellipsoids.



Note: Hydrogen atoms and *n*-tetrabutylammonium cations are omitted for clarity.

Figure 4S: Packing Diagram of Complex **1** along *c*-axis.



Note: Non-acidic hydrogen atoms are omitted for clarity.

Figure 5S: Partial ^{1}H-NMR Spectra of **L** with aliquots of *n*-$Et_4N^+HCO_3^-$ in DMSO-d_6 at 25ºC.

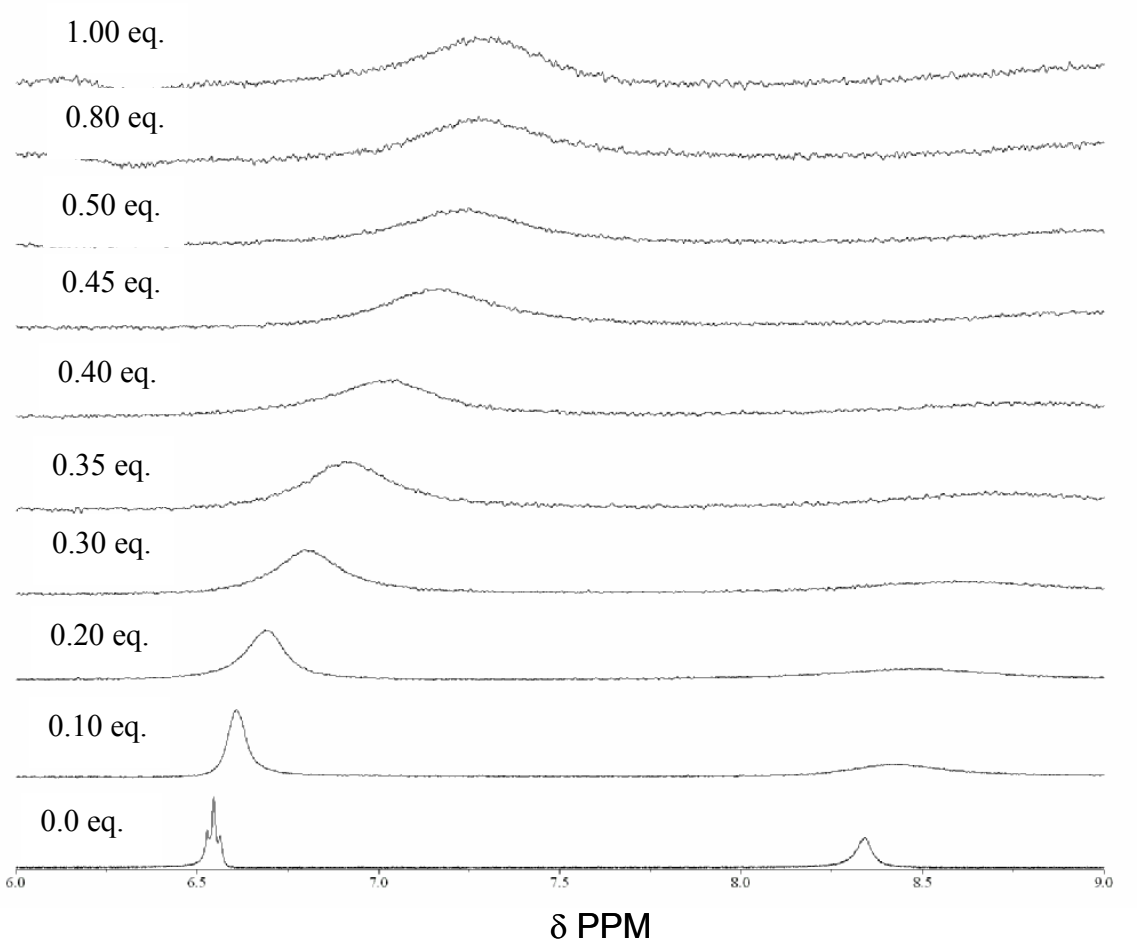


Figure 6S: PXRD pattern of a) simulated **1** and b) complex **1**.

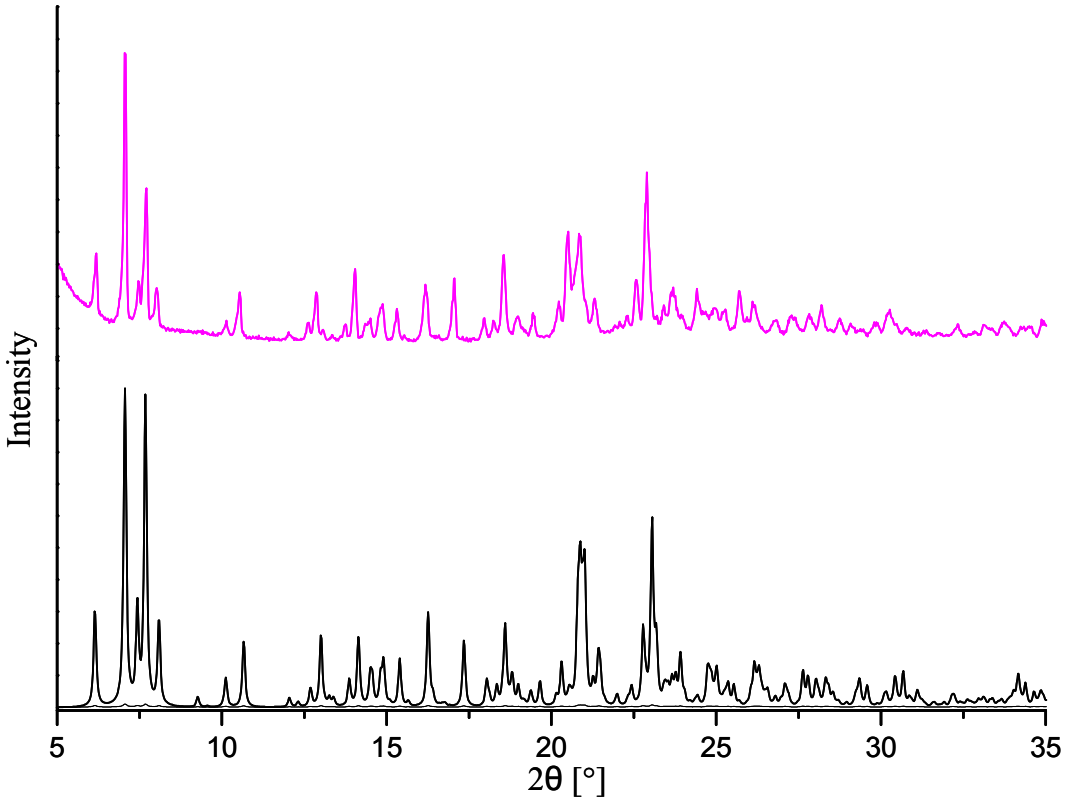
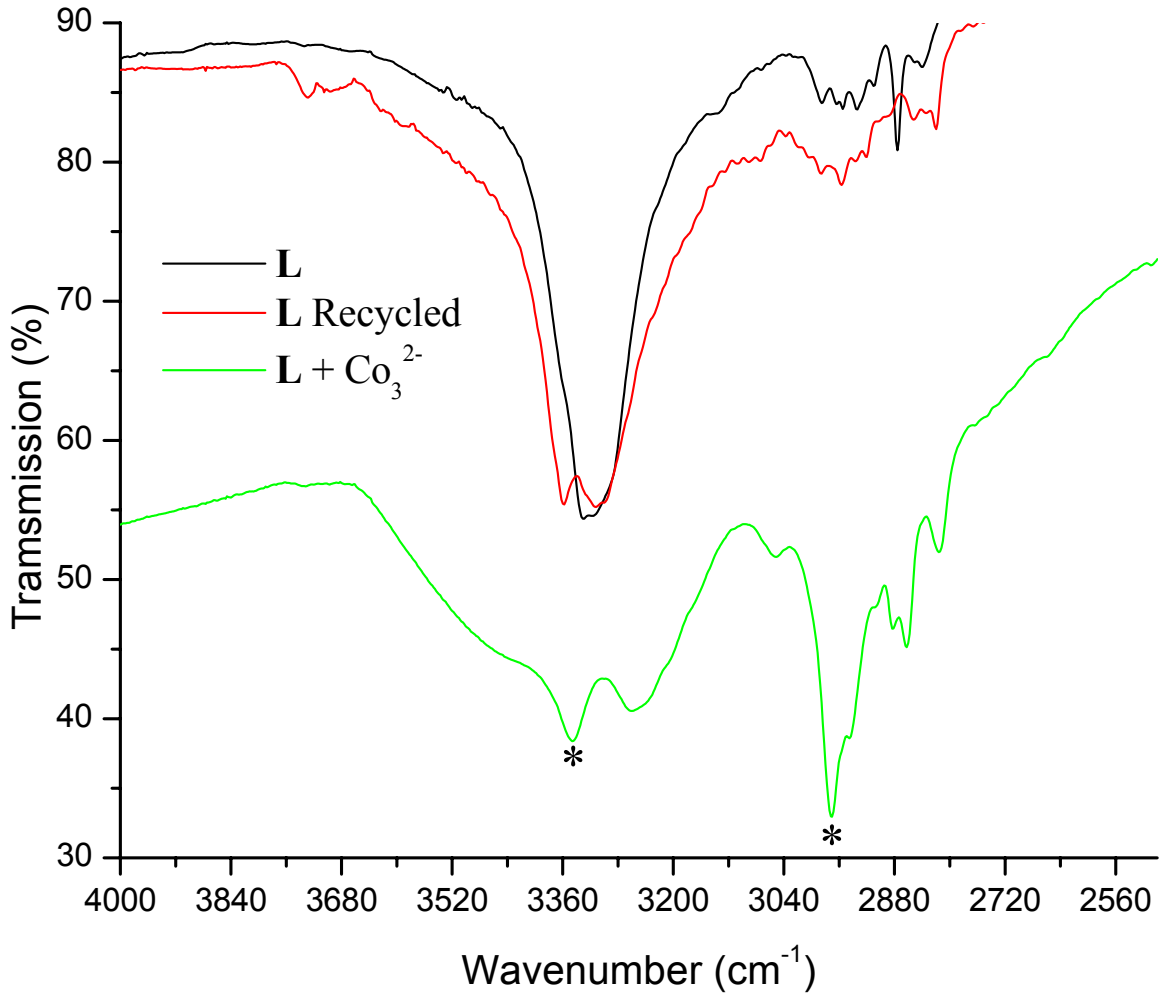


Figure 7S. FTIR analysis of **L** (black)**,** complex **1** (green) and **1** after solvent treatment (red).



Note: The peak marked as * assigned to the –NH stretching and –C-H stretching frequencies of complex 1.

Figure 8S. Photographs of complex 1 in methanol, after treatment with water and after 15 minutes.

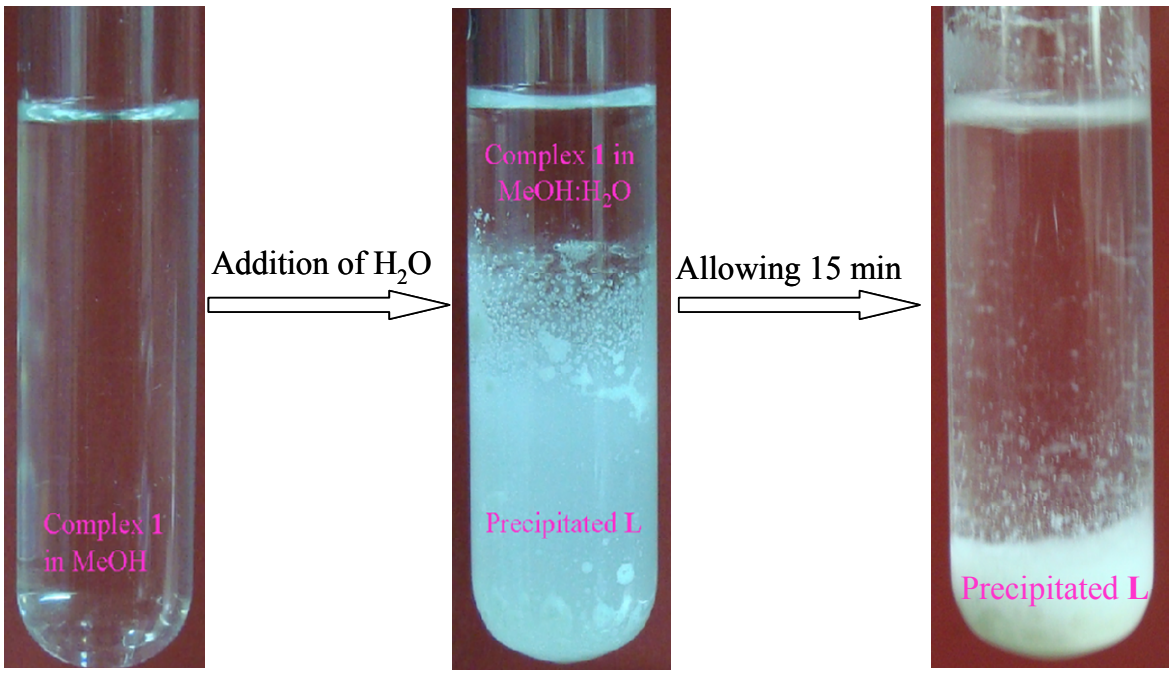


Figure 9S: PXRD pattern of a) freshly prepared **L** and b) **L** recycled from **1**.

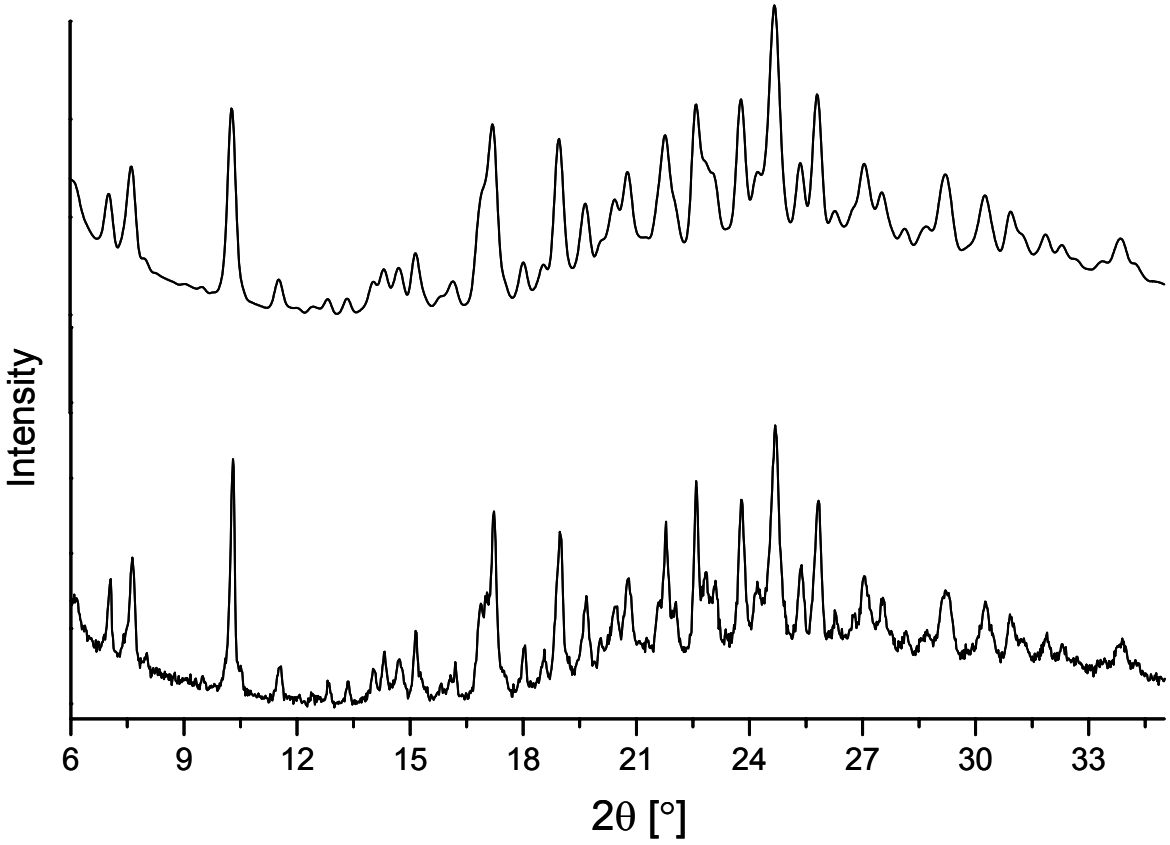
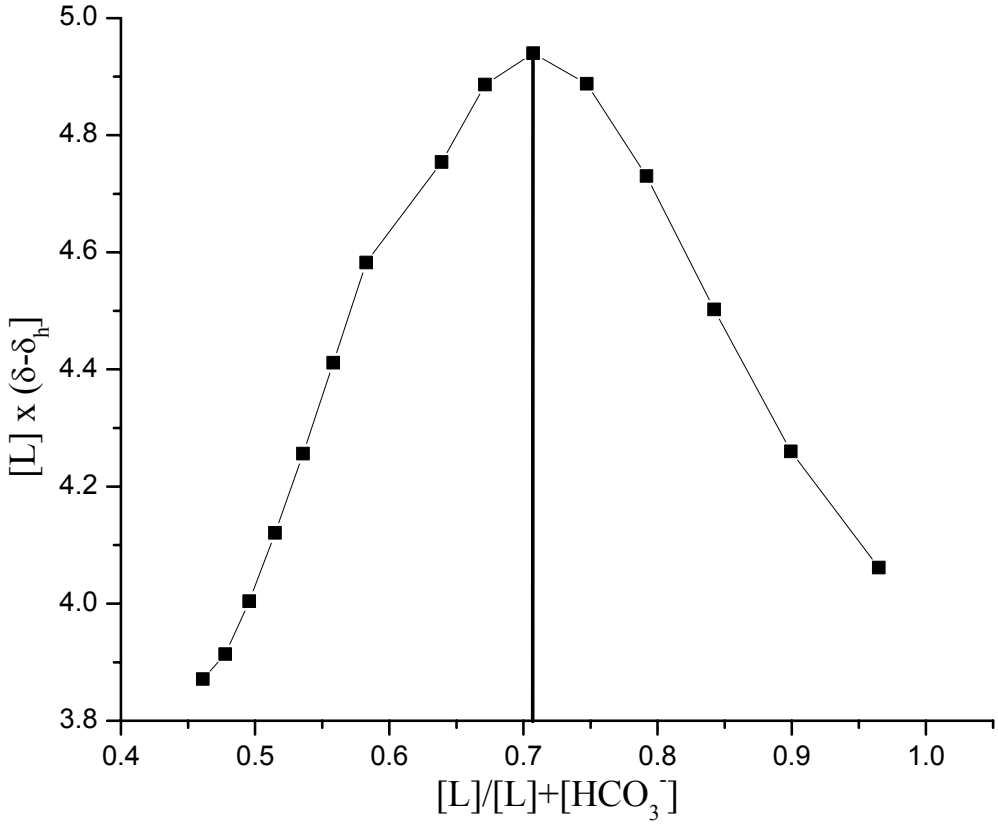


Figure 10S: Job's plot for **L** with *n*-$Et_4N^+HCO_3^-$ in DMSO-d_6 at 25ºC.



References:

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