Supporting Information for "Solid-Liquid Interface Synthesis of Microcrystalline Porous Coordination Networks"

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Introduction

Elemental Analyses

Anal Calcd for $[(ZnCl_2)(C_{18}N_6H_{12})_2]\bullet2(H_2O)$ (**ML₂**): C, 54.25, H; 3.54; N, 21.09. Found: C, 54.20; H, 3.56; N, 21.12.

Anal Calcd for $[(ZnCl_2)(ZnBr_2)_2(C_{18}N_6H_{12})_2]\bullet(CH_3OH)$ (**1**): C, 35.74; H, 2.27; N, 13.52. Found: C, 35.52; H, 2.17; N, 13.60.

Anal Calcd for $[(ZnCl_2)(ZnBr_2)_2(C_{18}N_6H_{12})_2]\bullet2(H_2O)$ (**phase I**): C, 34.66; H, 2.26; N, 13.47. Found: C, 34.66; H, 2.42; N, 13.23.

Anal Calcd for $[(ZnCl_2)(ZnBr_2)_2(C_{18}N_6H_{12})_2]\bullet(C_6H_5NO_2)\ 4(H_2O)$ (**1•G₁**): C, 38.23; H, 3.21; N, 12.33. Found: C, 38.07; H, 2.81; N, 12.29.

Synthesis of ML_2

The complex **ML_2** was synthesized using the solid-liquid interface method by suspension of TPT in a solution of LiCl/methanol (excess) (0.18 mmol, 56.16 mg), and $ZnCl_2$ (0.09 mmol, 12.27 mg) in a 2:1 molar ratio, respectively. Elemental analysis and TG-DSC suggested the composition of a discrete complex $[(ZnCl_2)(TPT)_2]{\bullet}2(H_2O)$.

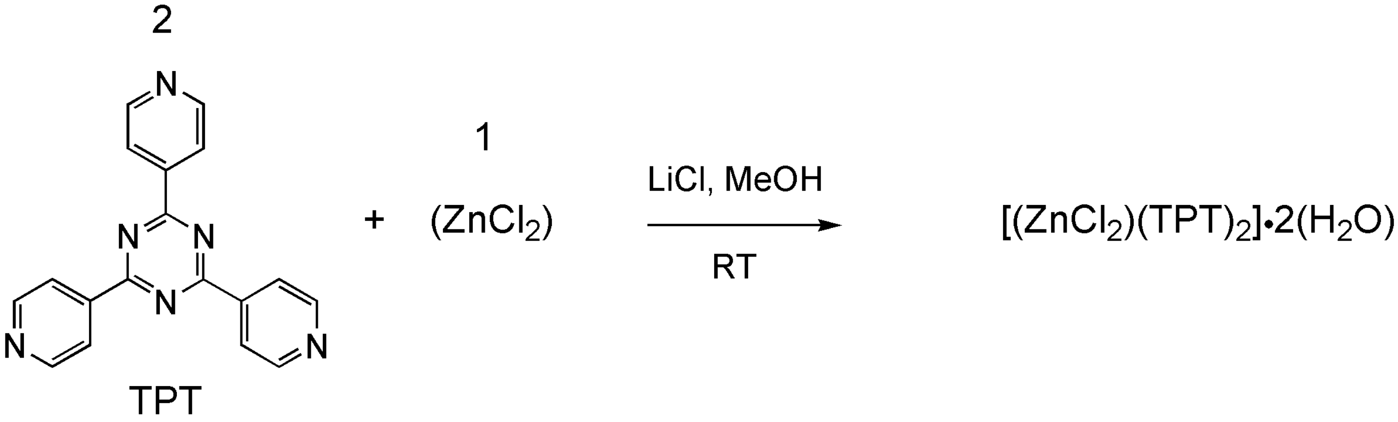

Figure S1. Synthesis of ML_2.

We also obtained as a minor product, a single crystal of **ML_2** in our attempts to obtain a different network. The layering of a methanol solution (4 mL) of $ZnCl_2$ (0.12 mmol, 16.36 mg) into a nitrobenzene/methanol (16/4 mL) solution of TPT (0.08 mmol, 25 mg) and triphenylene (0.12, 27.36 mg) at 298 K for a week resulted as a minor product in single crystal of **ML_2**. The single crystal data also shows the same molecular arrangement and the simulated powder X-ray diffraction is the same as the experimental one. The monoclinic unit cell parameters are: a = 43.862(10) Å, b = 3.8289(9) Å, c = 21.287(5) Å; β = 109.309(2)°. The space group is $C2/c$.

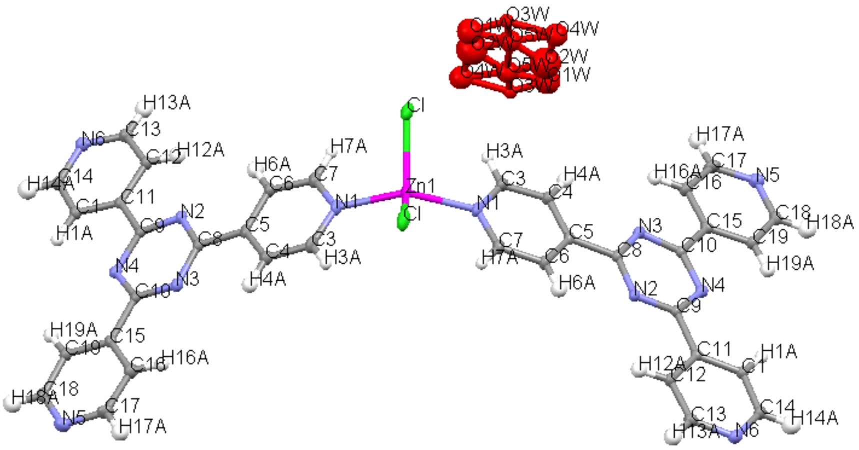

Figure S2. Asymmetric unit of **ML$_2$** :[$(ZnCl_2)(TPT)_2$]•2(H_2O).

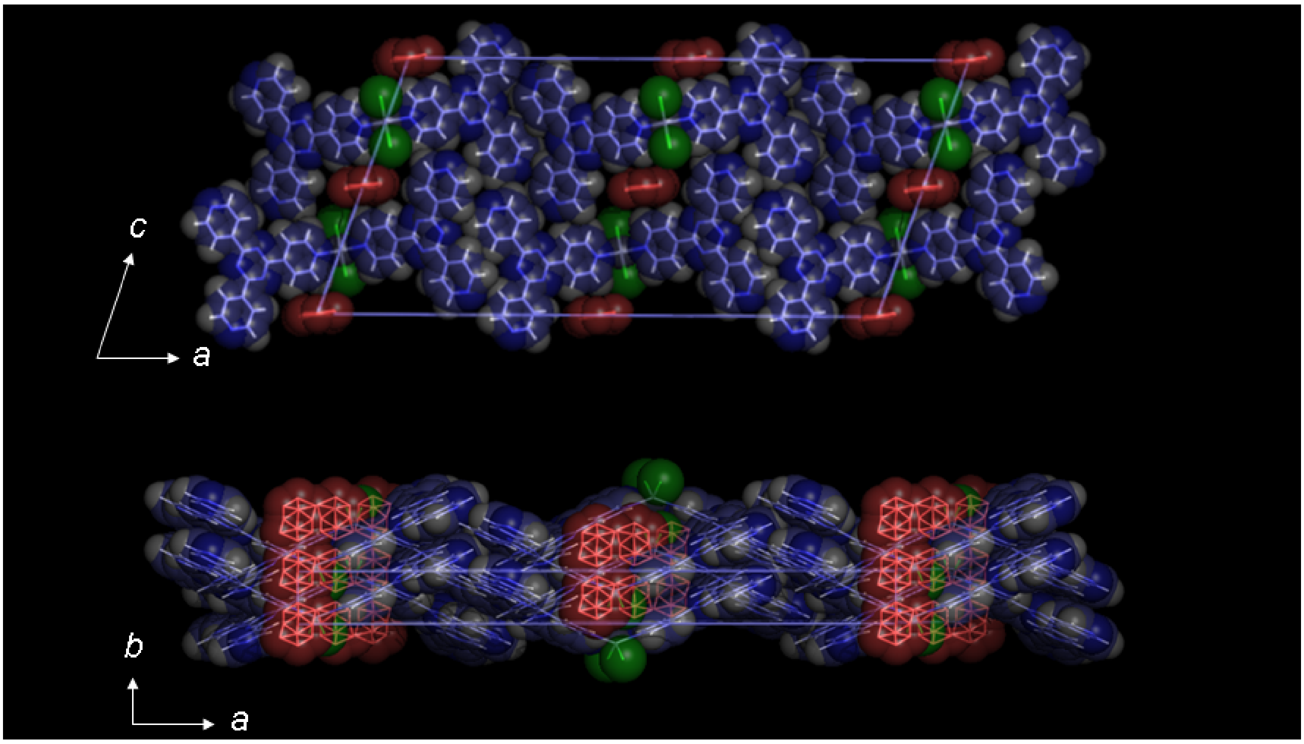

Figure S3. Crystal structure of **ML$_2$**. Top: viewed along the *b* axis. Disordered water molecules (red) are included in the channels formed between **ML$_2$**. Bottom: viewed along the *c* axis showing the *π*-*π* stacking between the **ML$_2$**. Color code: blue, carbon; dark blue, nitrogen; grey, hydrogen; green, chlorine; red, oxygen.

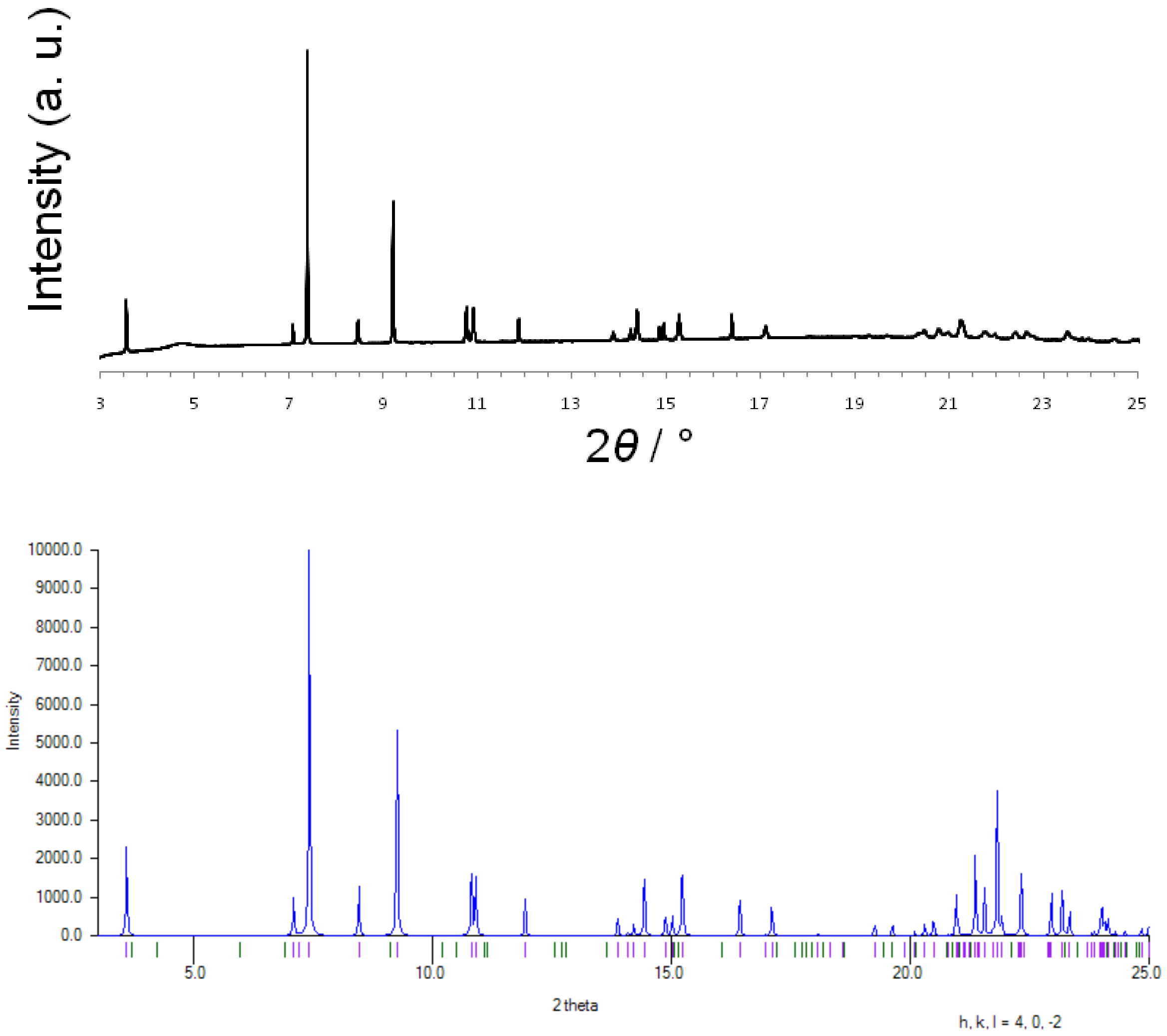

Figure S4. Experimental synchrotron PXRD pattern corresponding to **ML$_2$** (top) and simulated from single crystal data (bottom). Wavelength: 1.3 Å.

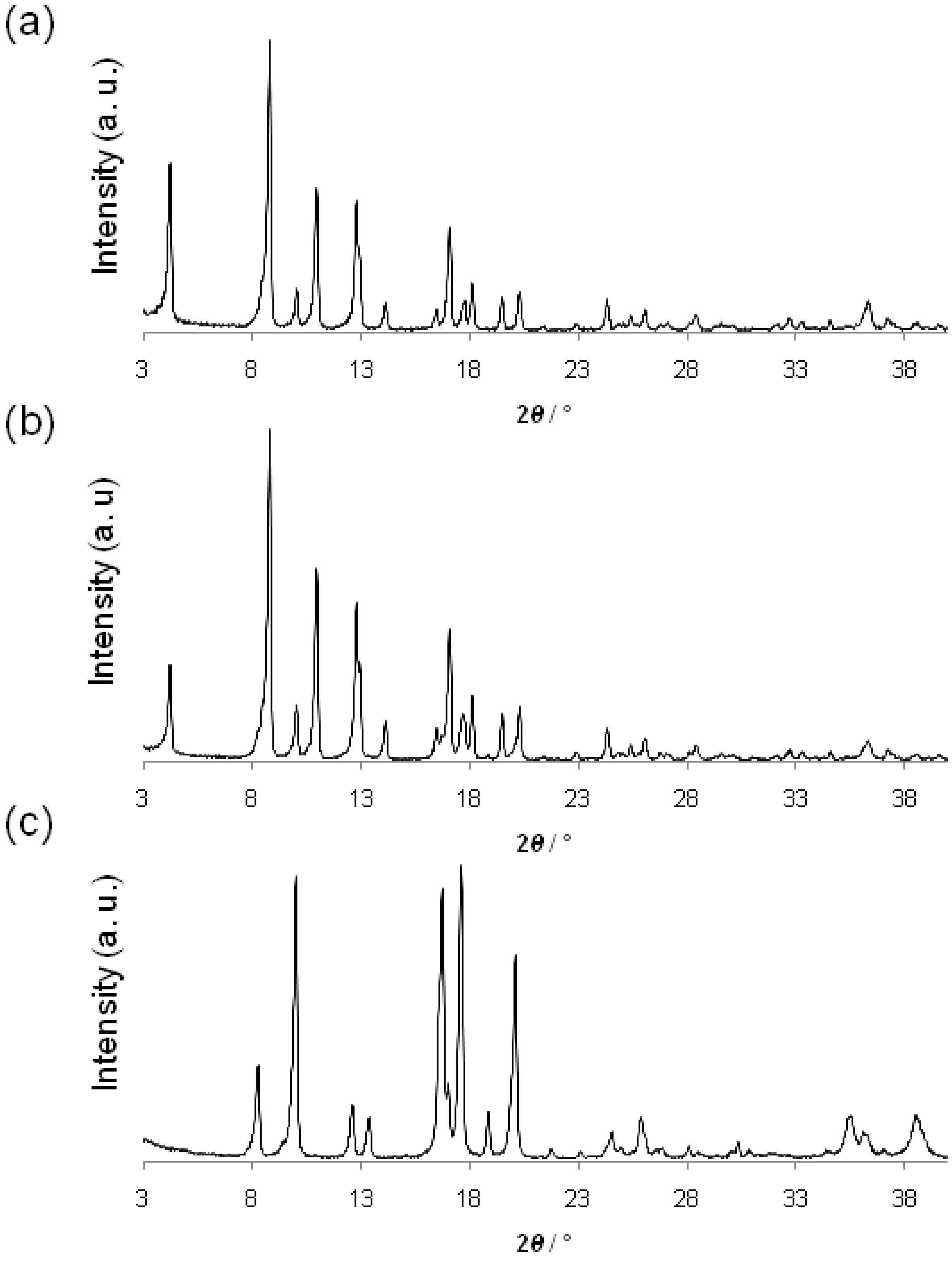

Figure S5. Solubility of $\mathbf{ML_2}$ in methanol: (a) PXRD diffractogram of $\mathbf{ML_2}$ before being immersed in methanol, and (b) after 18 hours in methanol. Clearly the crystal structure of $\mathbf{ML_2}$ is the same after exposure with methanol. Moreover, we observed little change in sample weight before and after immersion in methanol. This shows that $\mathbf{ML_2}$ is not dissolved and transformed into TPT (c) and therefore the reaction takes place in the solid-liquid interface. Wavelength: 1.54056 Å.

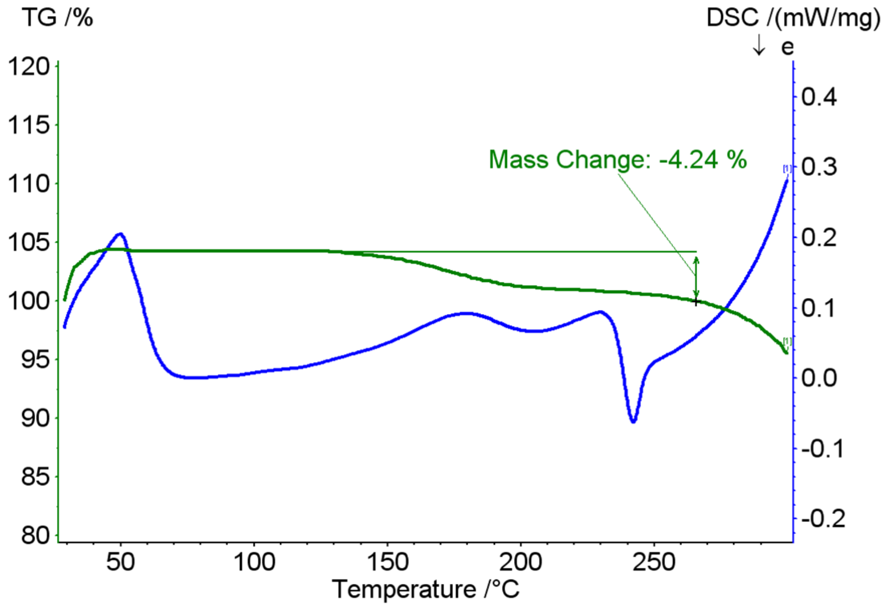

Figure S6. TG/DSC corresponding to **ML_2** recorded at a heating rate 5 K/min under N_2 atmosphere (gas flow rate 80 mL/min). Weight loss values corresponding to two water molecules. Calculated (4.5 %) and experimental (4.24 %).

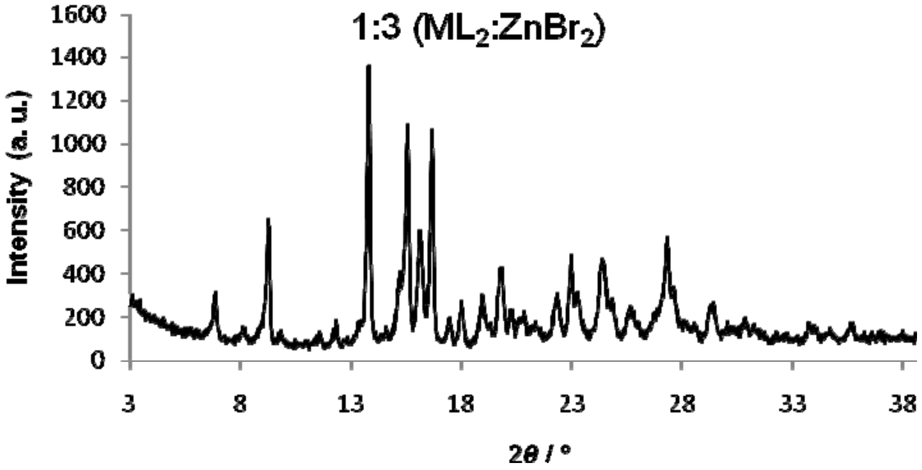

Figure S7. PXRD pattern corresponding to the complexation of **ML_2** and $ZnBr_2$ using the ratio 1:3 (ML_2 : $ZnBr_2$) at 275 K. Wavelength: 1.54056 Å.

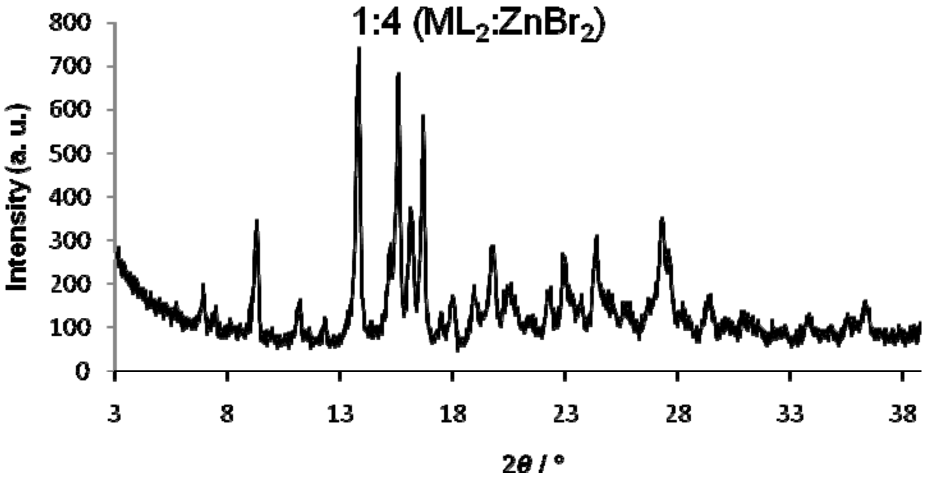

Figure S8. PXRD pattern corresponding to the complexation of **ML_2** and $ZnBr_2$ using the ratio 1:4 (ML_2 : $ZnBr_2$) at 275 K. Wavelength: 1.54056 Å.

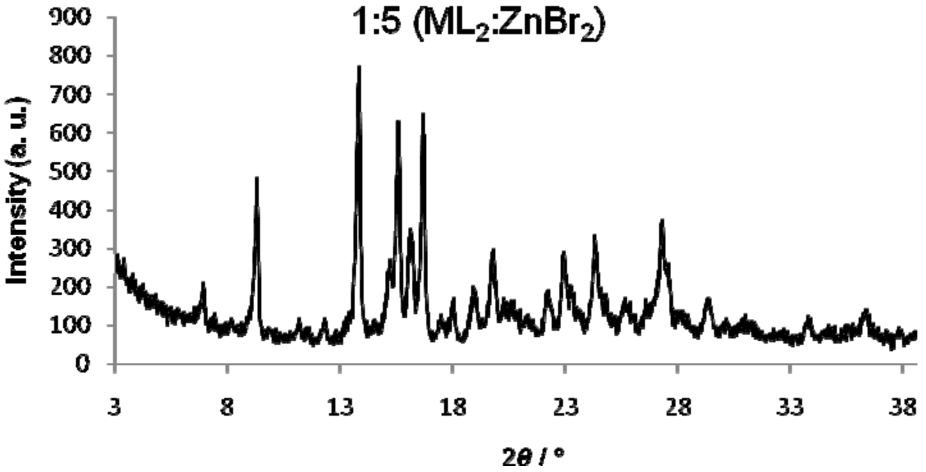

Figure S9. PXRD pattern corresponding to the complexation of **ML_2** and $ZnBr_2$ using the ratio 1:5 (ML_2 : $ZnBr_2$) at 275 K. Wavelength: 1.54056 Å.

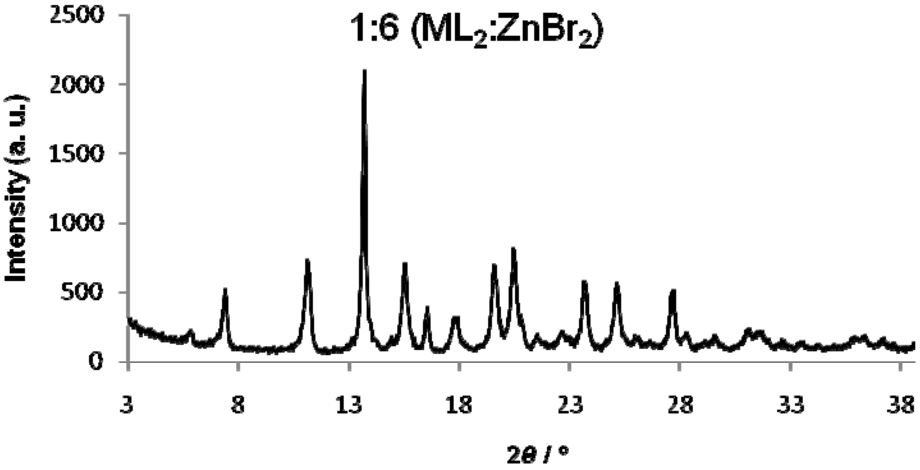

Figure S10. PXRD pattern corresponding to the complexation of **ML_2** and $ZnBr_2$ using the ratio 1:6 (ML_2 : $ZnBr_2$) at 275 K. Wavelength: 1.54056 Å.

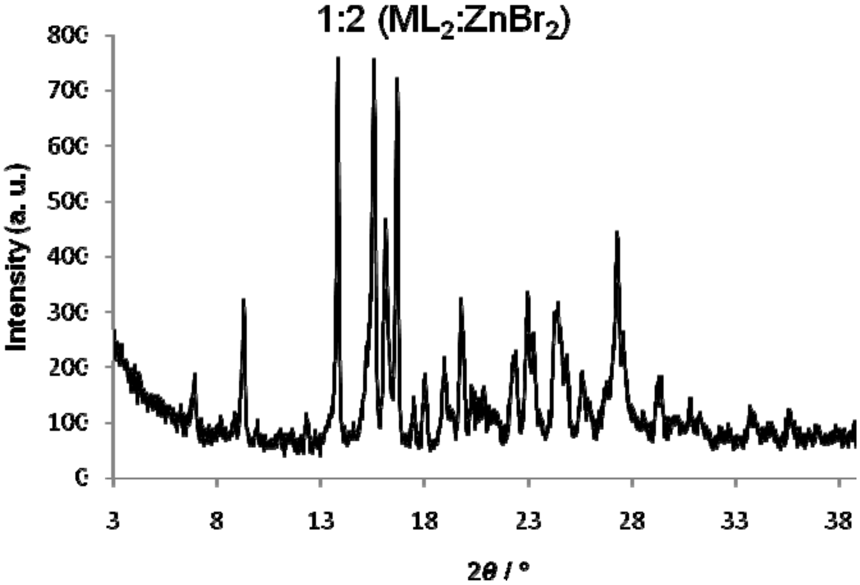

Figure S11. PXRD pattern corresponding to the complexation of **ML_2** and $ZnBr_2$ using the ratio 1:2 (ML_2 : $ZnBr_2$) at 300 K. Wavelength: 1.54056 Å.

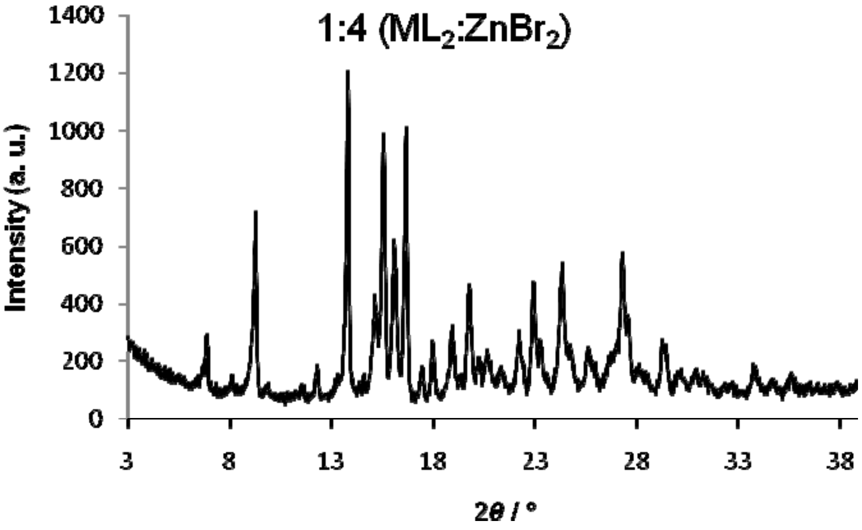

Figure S12. PXRD pattern corresponding to the complexation of **ML_2** and $ZnBr_2$ using the ratio 1:4 (ML_2 : $ZnBr_2$) at 300 K. Wavelength: 1.54056 Å.

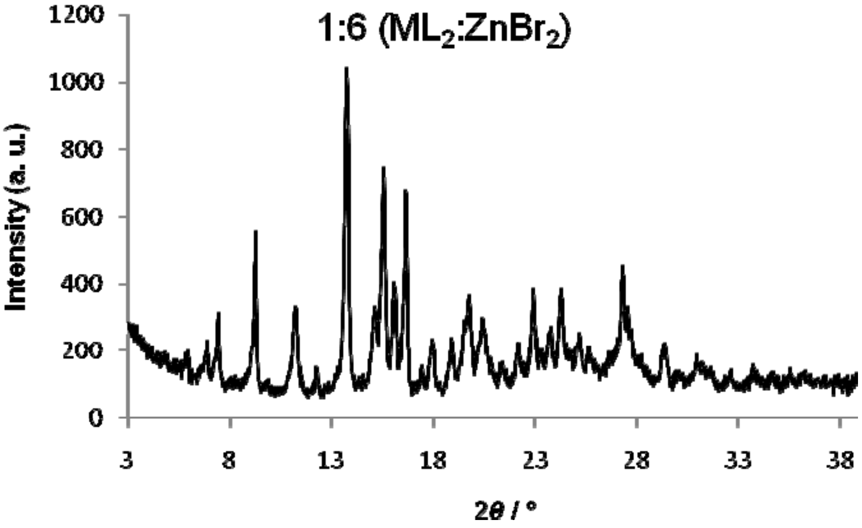

Figure S13. PXRD pattern corresponding to the complexation of **ML_2** and $ZnBr_2$ using the ratio 1:6 (ML_2 : $ZnBr_2$) at 300 K. Wavelength: 1.54056 Å.

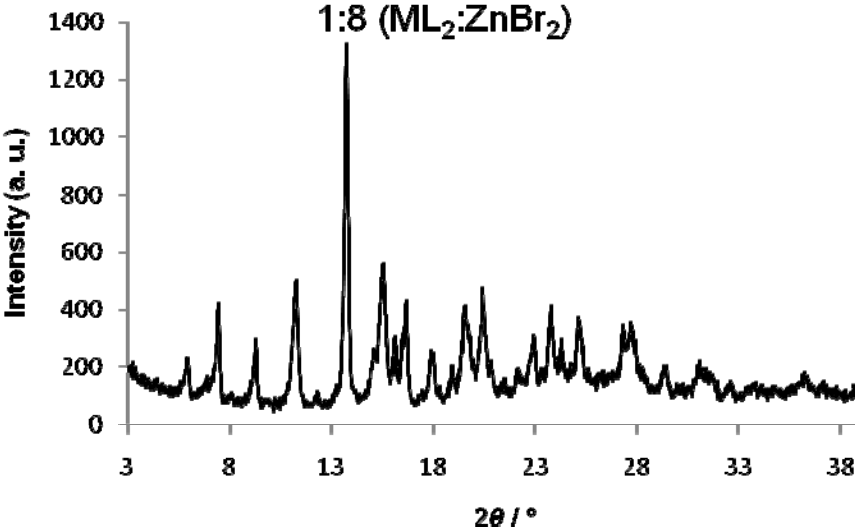

Figure S14. PXRD pattern corresponding to the complexation of **ML$_2$** and ZnBr$_2$ using the ratio 1:8 (ML$_2$: ZnBr$_2$) at 300 K. Wavelength: 1.54056 Å.

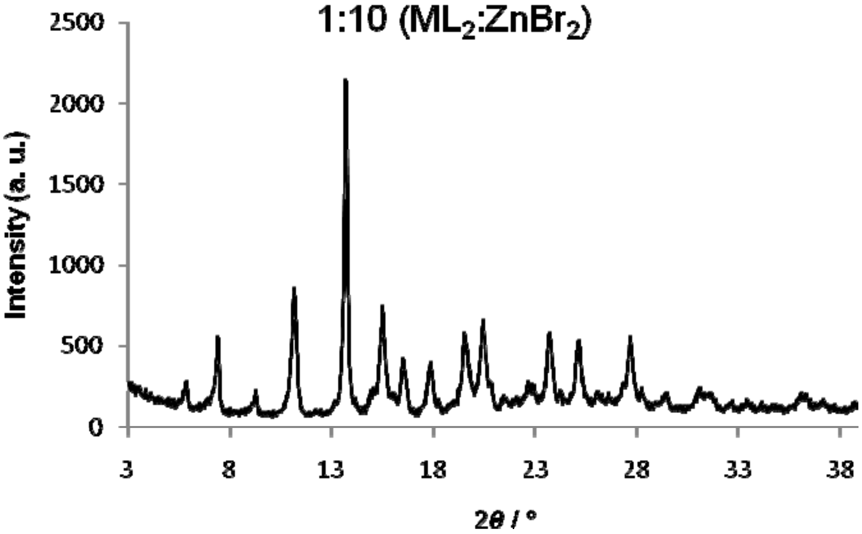

Figure S15. PXRD pattern corresponding to the complexation of **ML$_2$** and ZnBr$_2$ using the ratio 1:10 (ML$_2$: ZnBr$_2$) at 300 K. Wavelength: 1.54056 Å.

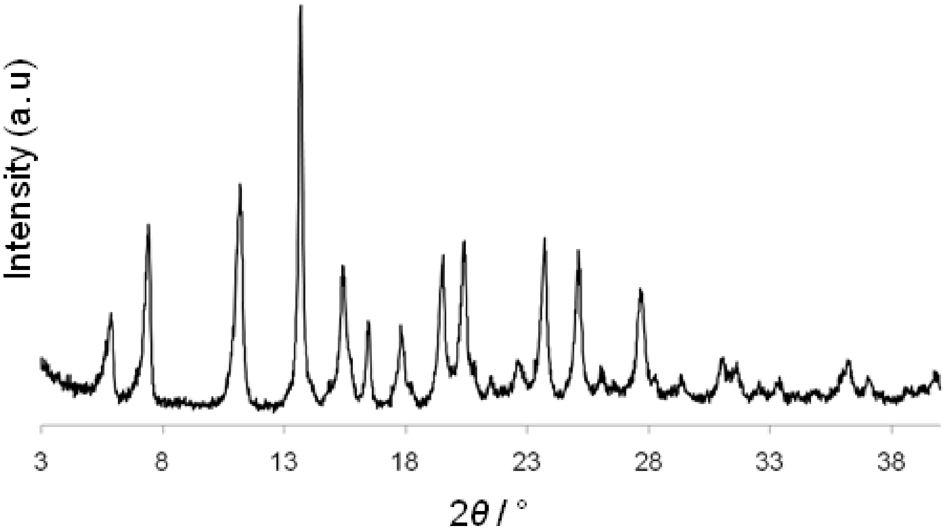

Figure S16. PXRD pattern corresponding to the kinetic product **1** obtained using the ratio 1:7 (ML_2 : $ZnBr_2$) at 275 K and kept in the solid-state (i.e. outside the mother solution). Wavelength: 1.54056 Å.

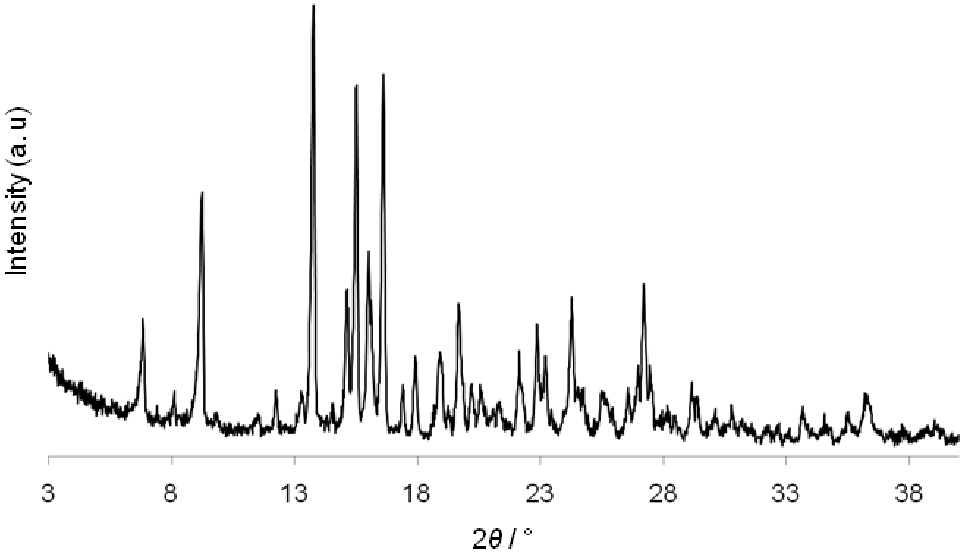

Figure S17. PXRD pattern of phase **I** obtained after keeping **1** during 18 hours in the mother solution after the solid-liquid interface synthesis. Wavelength: 1.54056 Å.

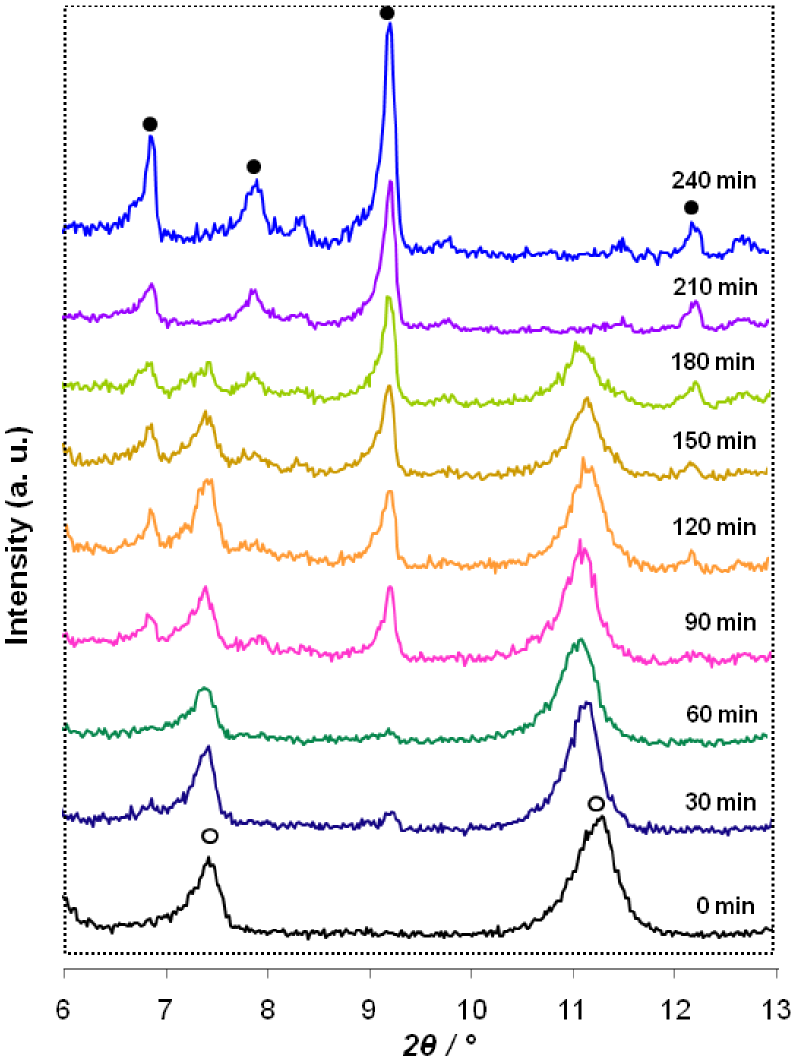

Figure S18. PXRD time-dependent transformation of **1** (open circles) to phase **I** (solid circles) in methanol measured at 298 K. Complete transformation of **1** occurs after 3.5 hours. Wavelength: 1.54056 Å.

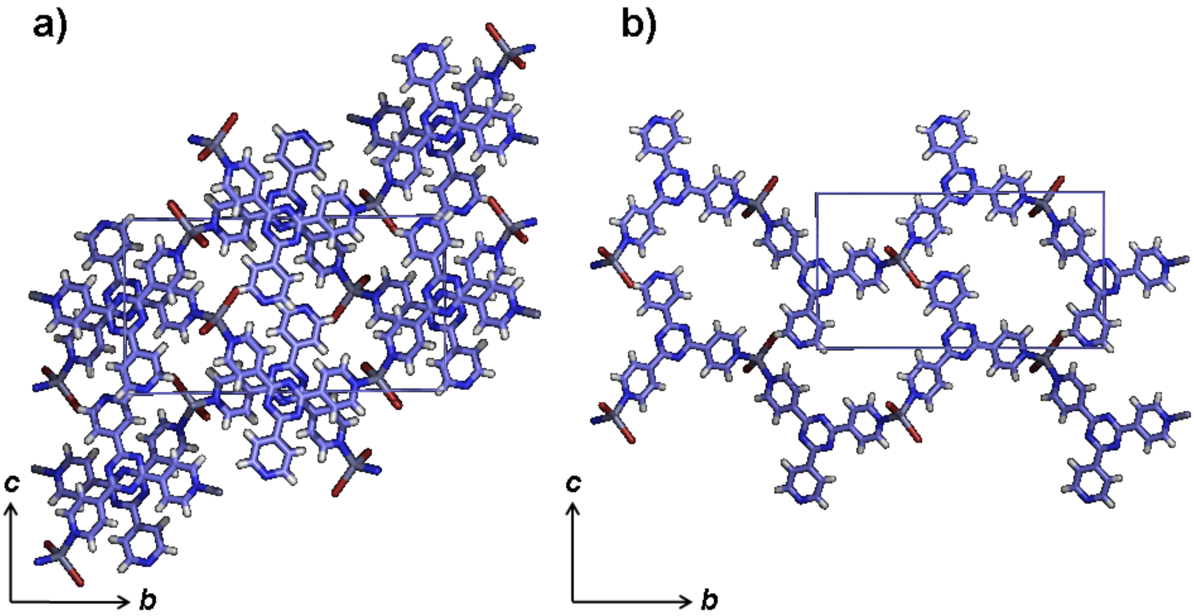

Figure S19. Crystal structure of **2** obtained from single crystal data. Compound **2** is non porous (a) and forms 1D chains along the *b* crystallographic direction (b).

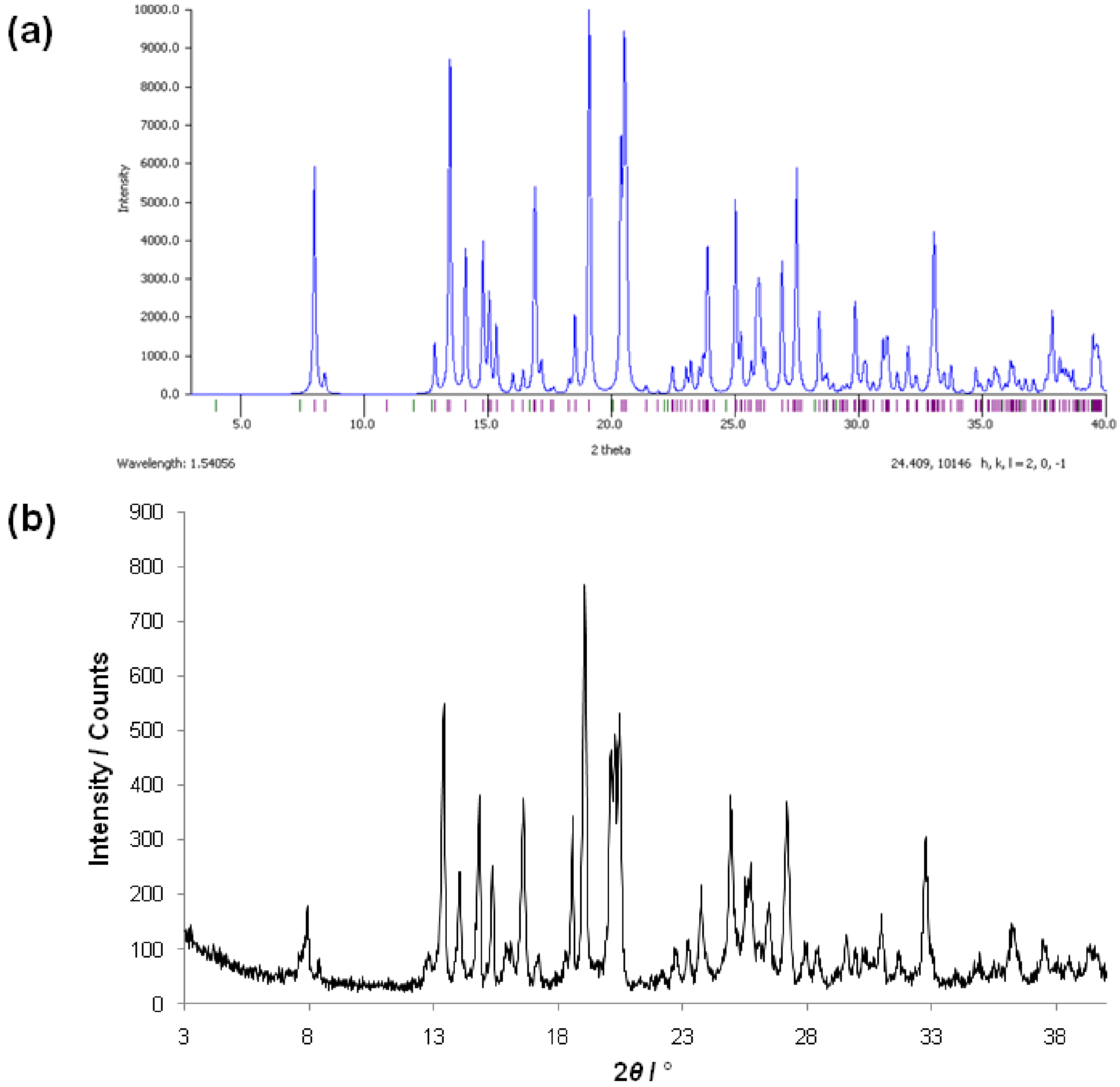

Figure S20. a) Simulated PXRD pattern of **2** from single crystal. b) Experimental PXRD obtained from bulk crystals of **2**.

Ab Initio **crystal structure determination of [(ZnCl$_2$)(ZnBr$_2$)$_2$(TPT)$_2$] (1).**

High quality powder X-ray diffraction pattern of compound **1** was recorded at 298 K in transmission mode [0.3 mm capillary; synchrotron radiation λ = 1.3 Å; 2θ range, -1.042 to 60.872°; step width, 0.003°; data collection time, 45 sec] on a diffractometer equipped with a white imaging plate detector at SPring-8 BL15XU beam line.

The PXRD pattern of **1** was indexed using the program DICVOL (Boultif, A.; Louër, D. *J. Appl. Crystallogr.* **1991**, *24*, 987-993) to give a orthorhombic unit cell (a = 29.958 Å, b = 12.907 Å, c = 12.769 Å) with good figures of merit. The space group was assigned from systematic absences as *Pccn*. Unit cell and profile refinement were carried out using the Pawley method, led to excellent fit (R_{wp} = 20.35, χ^2 = 4.22) for this lattice parameters and space group. Structure solution was carried out by the simulated annealing method with the program DASH (David, W. I. F.; Shankland, K; van de Streek, J; Pidcock, E; Motherwell, W. D. S.; Cole, J. C, *J. Appl. Crystallogr.,* **2006**, *39*, 910-915). One rigid group of [(ZnBr$_2$)(TPT)(ZnCl$_2$)$_{0.5}$] in which Zn-N$_{\text{pyridyl}}$ bonds were allowed to rotate, in the asymmetric unit and Z = 8 for space group *Pccn* were introduced by using a constrained Z-matrix description. 20 runs of 6×10^6 Monte Carlo moves each were performed. The best structure obtained (Profile χ^2 = 151.13) was taken as the starting structural model for Rietveld refinement.

The Rietveld refinement of **1** was performed with the program RIETAN-FP (Izumi, F.; Momma, K. *Solid State Phenom*., **2007**, *130*, 15-20) and VESTA (Momma, K.; Izumi, F. *J. Appl. Crystallogr*., **2008**, *41*, 653-658). Restraints but no constraints for all bond lengths were employed to maintain the molecular geometry. Thermal temperature factors were refined isotropically and uniform values were applied to the framework and solvent atoms.

Final Rietveld refinement: a = 29.902(3) Å, b = 12.891(1) Å, c = 12.747(1) Å, R_{wp} = 1.83 % (R_{e} = 31.41 %), R_{p} = 1.36 %, R_{B} = 2.53 %, R_{F} = 1.45 %; 14498 profile points; 195 refined variables.

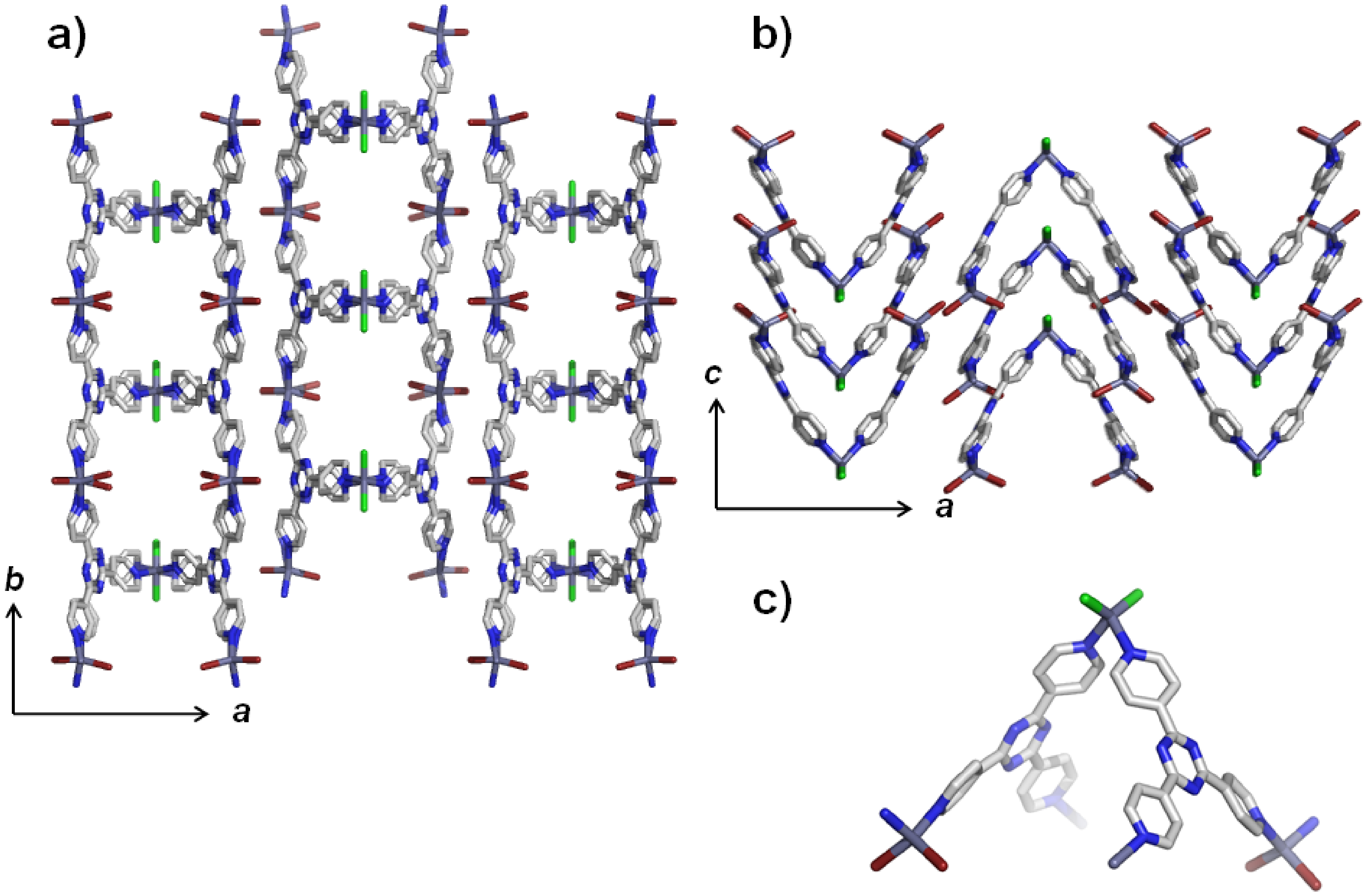

Figure S21. Crystal structure of **1** viewed along the *c* axis (a) and *b* axis (b). In (c) the asymmetric unit is shown and the slightly distorted saddle unit indicates the metastable nature of **1**. Color code: Grey: carbon; dark grey: zinc; dark blue: nitrogen; grey: hydrogen; green: chlorine; brown: bromide.

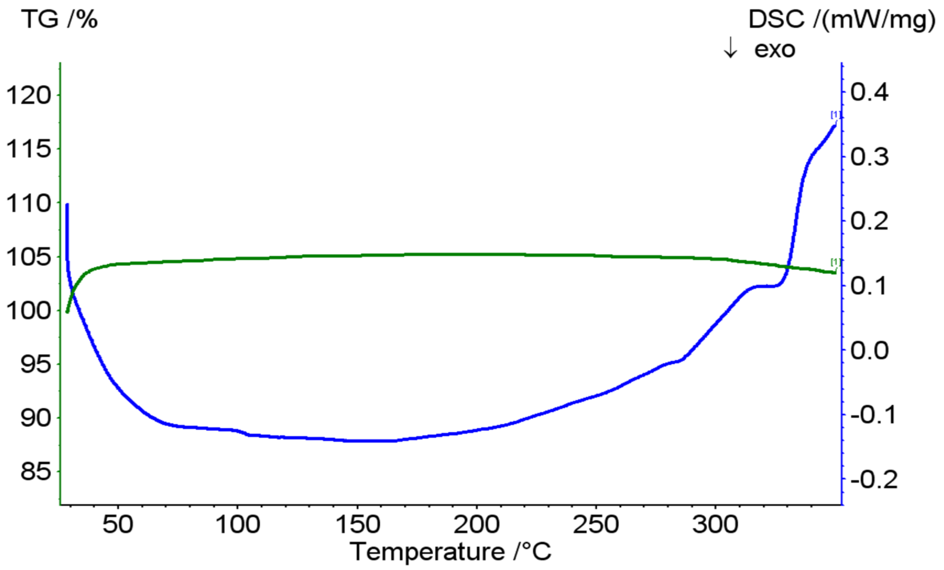

Figure S22. TG/DSC corresponding to **1** recorded at a heating rate 5 K/min under N_2 atmosphere (gas flow rate 80 mL/min).

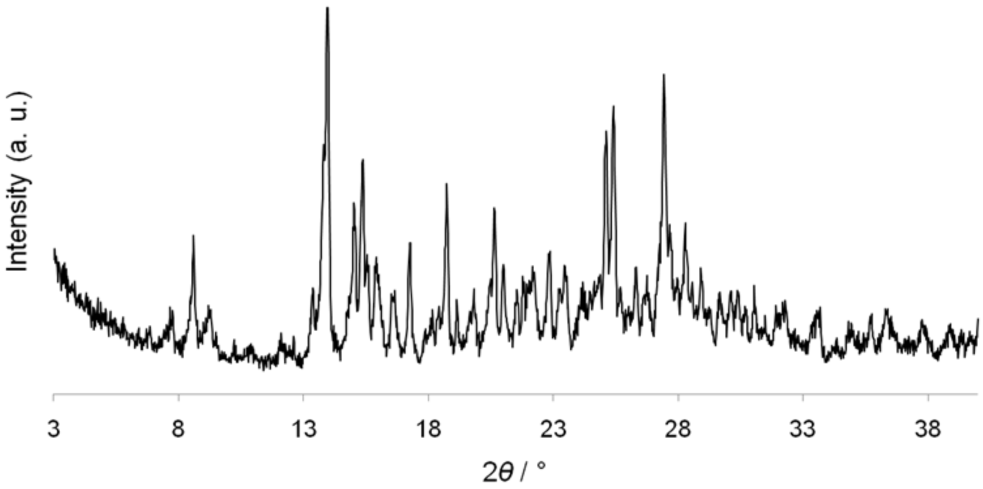

Figure S23. PXRD diffraction of **1** after being annealed during 48 hours at 573 K. Wavelength: 1.54056 Å.

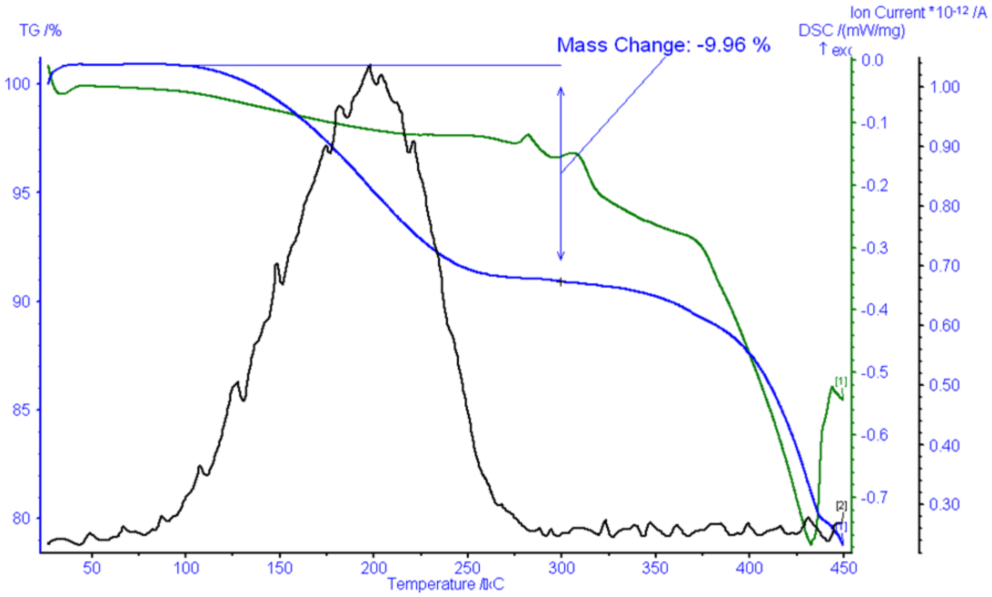

Figure S24. TG/DSC corresponding to **1•G$_1$** recorded at a heating rate 5 K/min under N_2 atmosphere (gas flow rate 80 mL/min). TG curve (blue), DSC curve (green), MS signal of nitrobenzene (m/z/ = 77, black). Heating rate 5 K/min, N_2 atmosphere (gas flow rate 80 mL/min). Guest molecules, weight loss obsd (calcd), are as follows: nitrobenzene, 9.96 (%) (9.3 %).

Ab Initio crystal structure determination of [$(ZnCl_2)(ZnBr_2)_2(TPT)_2$] (**1•G$_1$**) ($G_1$ = nitrobenzene).

High quality powder X-ray diffraction pattern of compound **1•G$_1$** was recorded at 298 K in transmission mode [0.3 mm capillary; synchrotron radiation $\lambda = 1.0$ Å; 2θ range, -1.045 to 60.869°; step width, 0.003°; data collection time, 120 sec] on a diffractometer equipped with a white imaging plate detector at SPring-8 BL15XU beam line.

The PXRD pattern of **1•G$_1$** was indexed using the program DICVOL (Boultif, A.; Louër, D. *J. Appl. Crystallogr.* **1991**, *24*, 987-993) to give a monoclinic unit cell (a = 12.96433 Å, b = 32.09033 Å, c = 6.10989 Å, β = 97.458 °) with good figures of merit. The space group was assigned from systematic absences as $P2_1$. Unit cell and profile refinement were carried out using the Pawley method, led to excellent fit (R_{wp} = 20.27, χ^2 = 11.687) for this lattice parameters and space group. Structure solution was carried out by the simulated annealing method with the program DASH (David, W. I. F.; Shankland, K; van de Streek, J; Pidcock, E; Motherwell, W. D. S.; Cole, J. C, *J. Appl. Crystallogr.,* **2006**, *39*, 910-915). One rigid group of [$(ZnBr_2)(TPT)(ZnCl_2)(TPT)(ZnBr_2)$] in which Zn-N$_{\text{pyridyl}}$ bonds were allowed to rotate and two rigid groups of nitrobenzene in the asymmetric unit and $Z = 2$ for space group $P2_1$ were introduced by using a constrained Z-matrix description. 20 runs of 6×10^6 Monte Carlo moves each were performed. The best structure obtained (Profile χ^2 = 39.34) was taken as the starting structural model for Rietveld refinement.

The Rietveld refinement of **1•G$_1$** was performed with the program RIETAN-FP (Izumi, F.; Momma, K. *Solid State Phenom*., **2007**, *130*, 15-20) and VESTA (Momma, K.; Izumi, F. *J. Appl. Crystallogr*., **2008**, *41*, 653-658). Restraints but no constraints for all bond lengths were employed to maintain the molecular geometry. Thermal temperature factors were refined isotropically and uniform values were applied to the framework and solvent atoms.

Final Rietveld refinement: a = 12.941 (1) Å, b = 32.046 (2) Å, c = 6.1025 (4) Å, β = 97.429 (4) R_{wp} = 3.17 % (R_{e} = 31.23 %), R_{p} = 2.47 %, R_{B} = 3.79 %, R_{F} = 2.07 %; 11640 profile points; 284 refined variables.

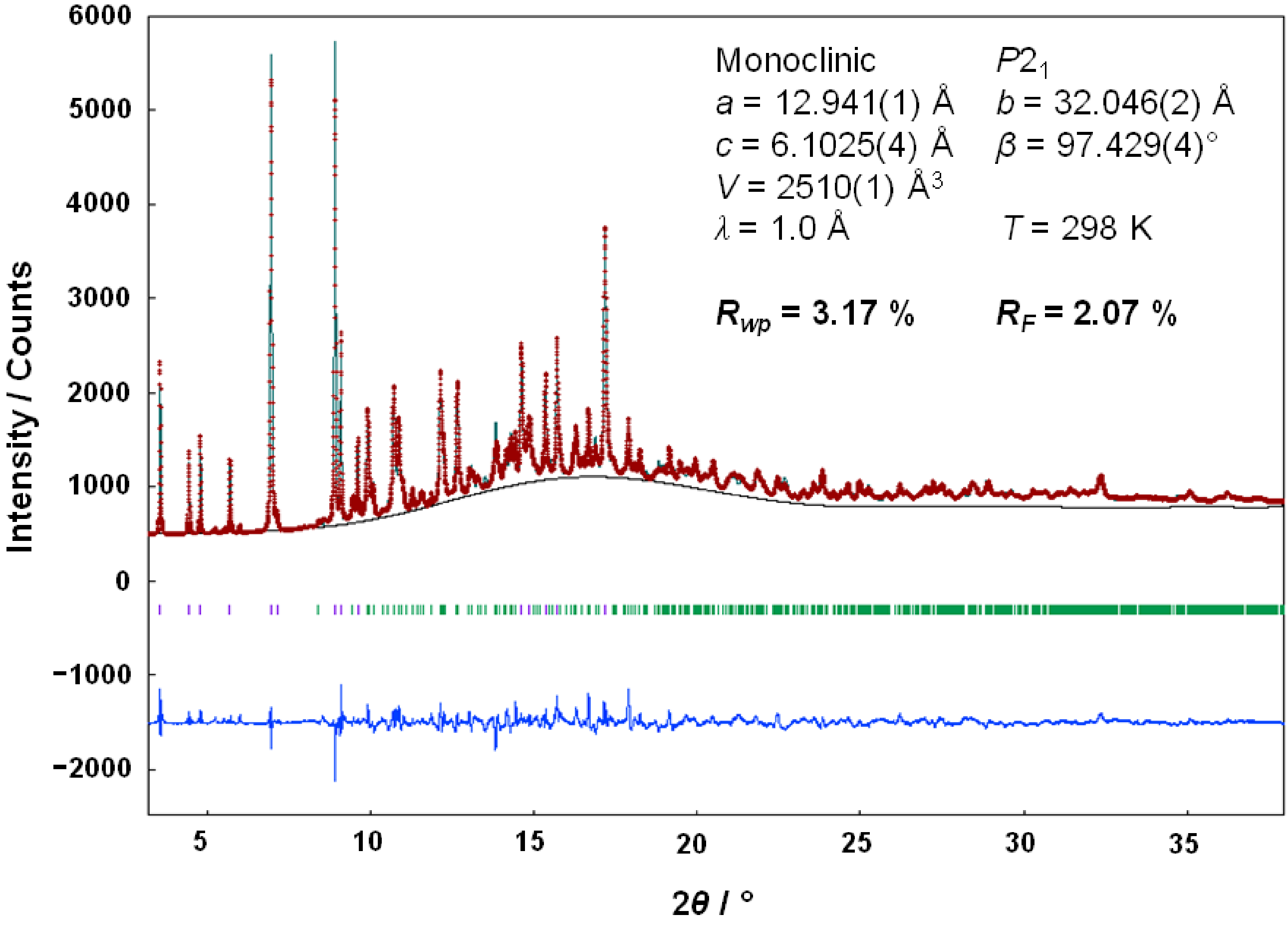

Figure S25. Final Rietveld refinement of **1•G$_1$**. Experimental (red), calculated (pale-blue), and difference (dark-blue) PXRD profiles.

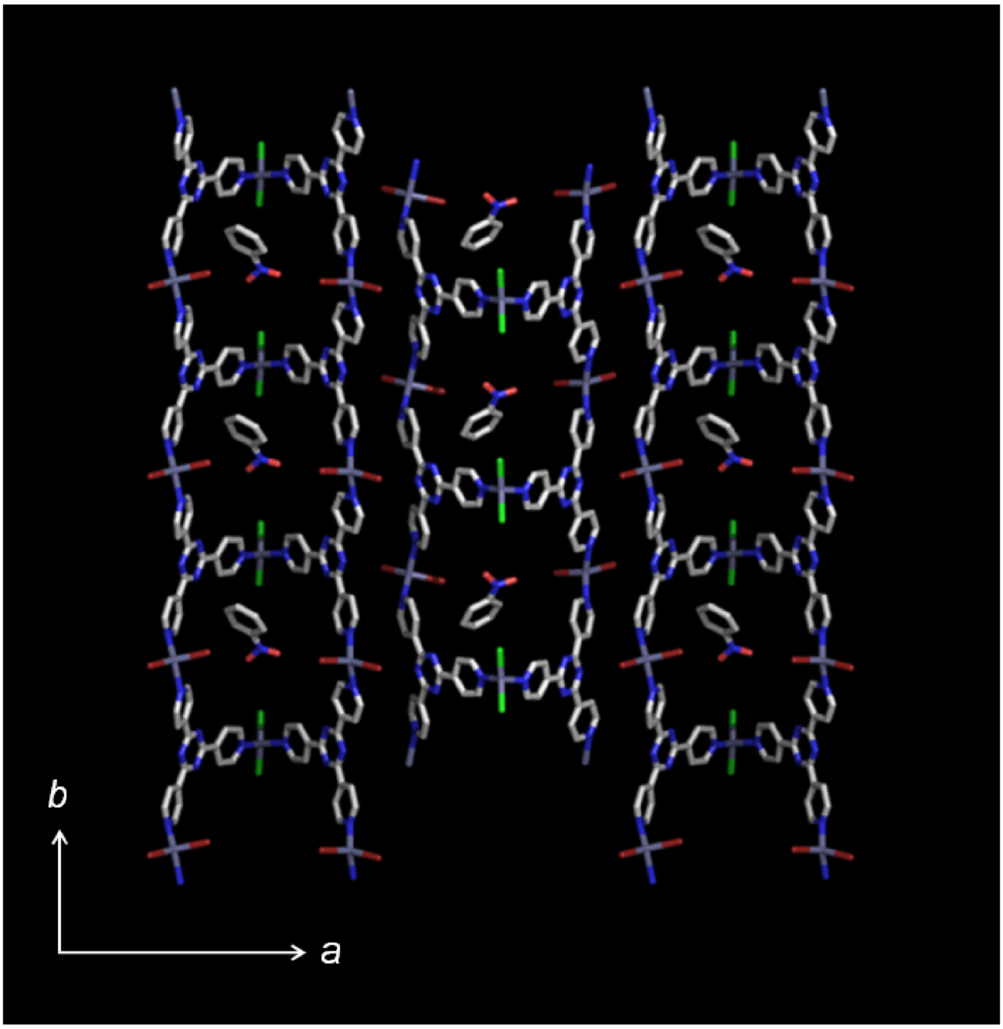

Figure S26. Crystal structure of **1•G$_1$** viewed along the *c* axis (a). Color code: grey, carbon; dark grey, zinc; dark blue, nitrogen; grey, hydrogen; green, chlorine; brown, bromide. Nitrobenzene molecules are included in the pore.

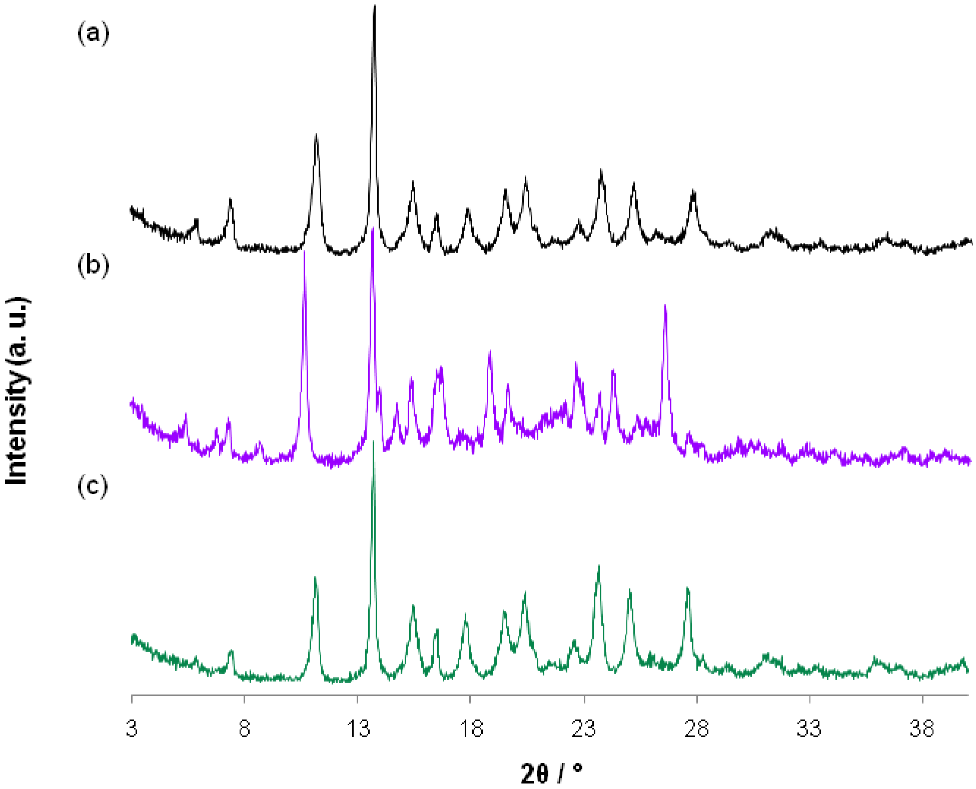

Figure S27. PXRD diffraction patterns of: (a) **1** (black) and (b) **1•G$_1$** (purple) showing the change in the diffraction pattern after the inclusion of nitrobenzene. (c) The porous structure **1** is restored after heating **1•G$_1$** up to 493 K (green). Wavelength: 1.54056 Å

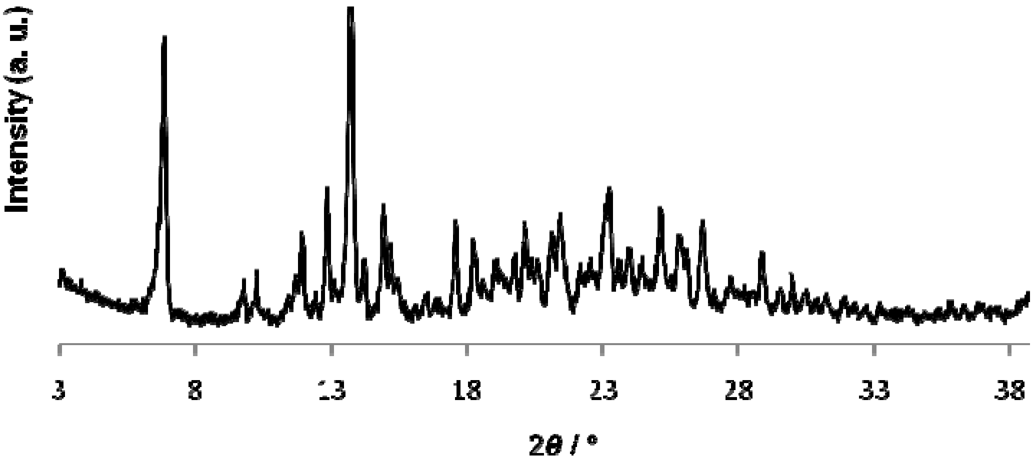

Figure S28. PXRD pattern corresponding to the product obtained after complexation of ML_2 with $ZnBr_2$ 1:6 (ML_2 : $ZnBr_2$) dissolved in nitrobenzene/methanol solution at 275 K. Recorded at 300 K. This PXRD pattern agrees with that of $[(ZnBr_2)_3(TPT)_2]_n$•5(nitrobenzene)(H_2O) reported in ref. 7. This fact means that solution phase reactions give totally different products from solid-liquid interface reactions.

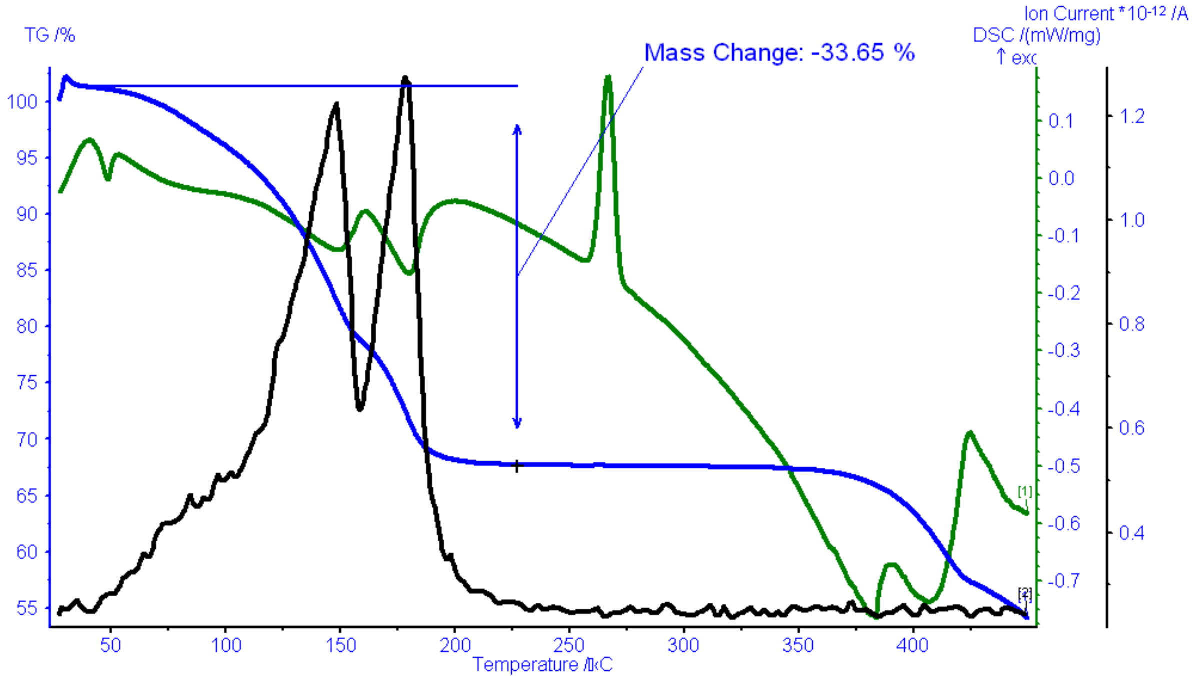

Figure S29. TG/DSC corresponding to the product obtained after complexation of ML_2 with $ZnBr_2$ 1:6 (ML_2 : $ZnBr_2$) dissolved in nitrobenzene/methanol solution at 275 K, recorded at a heating rate 5 K/min under N_2 atmosphere (gas flow rate 80 mL/min). Calculated (calcd) and observed (obsd) value corresponding to the weight loss of 5 nitrobenzene molecules are: calcd: 33.67 % ; obsd: 33.65 %.