Supplementary Material (ESI) for Green Chemistry
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ELECTRONIC SUPPLEMENTARY INFORMATION

Direct Use of Waste PET as Unfailing Source of Organic Reagents in the Synthesis of Intrinsic White/Yellow Luminescent Nanoporous Zincophosphates

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Contents

Synthesis method

NTHU-3-TA·EG were obtained by heating a reaction mixture containing one mmol of $Zn(NO_3)_2 \cdot 6H_2O$, 4 mmol of $C_6N_4H_{18}$ (trisaminoethylamine, tren), two mmol of TA, 6 mmol of H_3PO_4, 5 mL of EG and 5 mL of H_2O in a 23 mL Teflon-lined autoclave at 160 °C for 3 days. It resulted in muti-phased product containg transparent hexagonal plates of **NTHU-3-TA·EG**. The formula was determined from single crystal X-ray diffraction methods as $(H_3tren)_2[Zn_3(PO_4)_4]$ (TA)(EG)$_2$.

NTHU-3-TA·H$_2$O were obtained by heating a reaction mixture containing one mmol of $ZnCl_2$, 0.3 g scraps of waste PET bottle, 4 mmol of $C_6N_4H_{18}$ (tren), 6 mmol of H_3PO_4, 10 mL of H_2O in a 23 mL Teflon-lined autoclave at 160 °C for 3 days. Transpaent hexagonal plate-like sizable crystals of **NTHU-3-TA·H$_2$O** up to 0.25 x1.48 x 1.60 mm^3 were produced as a single-phased product with yield ~86.5% (based on Zn). Consumption of PET was 100%. The formula was determined from single crystal X-ray diffraction methods as $(H_3tren)_2[Zn_3(PO_4)_4] \cdot (TA \cdot 2H_2O)$.

Compound **1** were obtained by heating a reaction mixture containing one mmol of $ZnCl_2$, 0.5 g scraps of waste PET bottle, 6 mmol of H_3PO_4, 6.4 mmol of tmdp, 5 mL of H_2O in a 23 mL Teflon-lined autoclave at 160 °C for 3 days.The light brown crystals of **1** with a size up to 0.23 x 0.5 x 1.2 mm^3 were produced with yield~90% (based on Zn) plus a side product of co-crystal (TA·tmdp). The formula was determined from single crystal X-ray diffraction methods as $(H_2tmdp)[Zn_2(HPO_4)_2(BDC)]$.

Compound **2** were prepared from the reaction mixture containing one mmol of $Zn(NO_3)_2 \cdot 6H_2O$, 1.2 mmol of TA, 6 mmol of H_3PO_4, 6.4 mmol of tmdp, 5 mL of EG and 5 mL of H_2O in a 100 mL Teflon autoclave and heated in microwave oven (START D, Milestone, maximum power of 400 W) at 160 ^oC for 40 minutes. Light brown crystals **2** were obtained in a yield of 34.2% (based on Zn). The formula was determined from single crystal X-ray diffraction methods as $(H_2tmdp)[Zn_2(HPO_4)_2(BDC)]$.

Compound **3** were prepared from the reaction mixture containing one mmol of $ZnCl_2$, 1.2 mmol of TA, 6 mmol of H_3PO_4, 6.4 mmol of tmdpp, 0.5 mmole of D(+)-glutamic acid, 5 mL of EG and 5 mL of H_2O. This mixture was then microwaved in the same way as aforementioned. Transparent crystals of **3** were obtained in ~40.8% yield (based on Zn). Formula for the crystal was confirmed as $(H_2tmdpp)[Zn_2(HPO_4)_2(BDC)]$ via single crystal X-ray diffraction.

Table S1. Crystallographic Data

Compound	**NTHU-3-TA·EG**	**NTHU-3-TA·H₂O**	**1**	**2**	**3**
Empirical formula	$C_{24}H_{60}N_8O_{24}P_4Zn_3$	$C_{20}H_{52}N_8O_{22}P_4Zn_3$	$C_{21}H_{22}N_2O_{12}P_2Zn_2$	$C_{21}H_{22}N_2O_{12}P_2Zn_2$	$C_{21}H_{34}N_2O_{12}P_2Zn_2$
Formula Mass	1164.79	1076.69	687.09	687.09	699.18
Crystal system	monoclinic	monoclinic	monoclinic	orthorhombic	monoclinic
a /Å	14.919(1)	15.0025(5)	27.621(1)	9.9740(5)	10.8928(2)
b /Å	8.4607(8)	8.6854(3)	9.1189(4)	9.1804(5)	8.79170(10)
c /Å	34.445(3)	30.545(1)	9.9954(5)	27.539 (2)	27.7665(4)
β/°	102.271(2)°	99.181(1)°	92.211(1)°	-	101.0510(10)°
Unit cell volume/ Å³	4248.5(7)	3948.9(2)	2515.7(2)	2521.6(2)	2609.79(7)
Temperature/K	296(2)	296(2)	295(2)	295(2)	296(2)
Space group	*C2/c*	*C2/c*	$P2_1/c$	$Pna2_1$	$P2_1/c$
Z	4	4	4	4	4
D_{cacl}, g/cm^{-3}	1.821	1.811	1.814	1.810	1.779
μ, mm^{-1}	1.927	2.062	2.103	2.098	2.028
*R*1	0.0573	0.0342	0.0513	0.0537	0.0360
*wR*2	0.1422	0.0673	0.1324	0.1146	0.0785
CCDC number	768399	768400	-	804562	790337

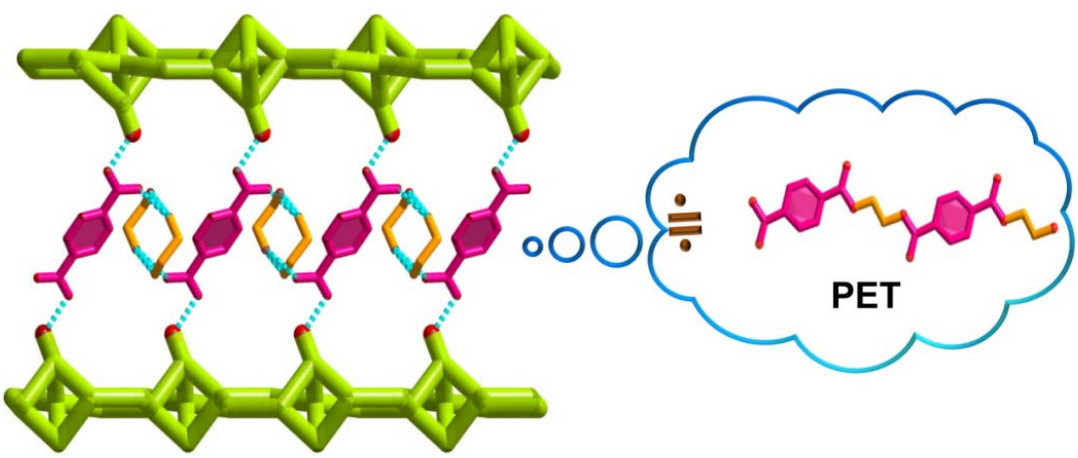

Fig. S1 The structure of **NTHU-3-TA·EG**: infinite supramolecular chains of $_\infty${TA·2EG} consisting of TA (in pink) and EG (in orange) molecules are residing between zincophosphate layers (in green). The infinite chain was associated with the polymer chain of PET in thinking

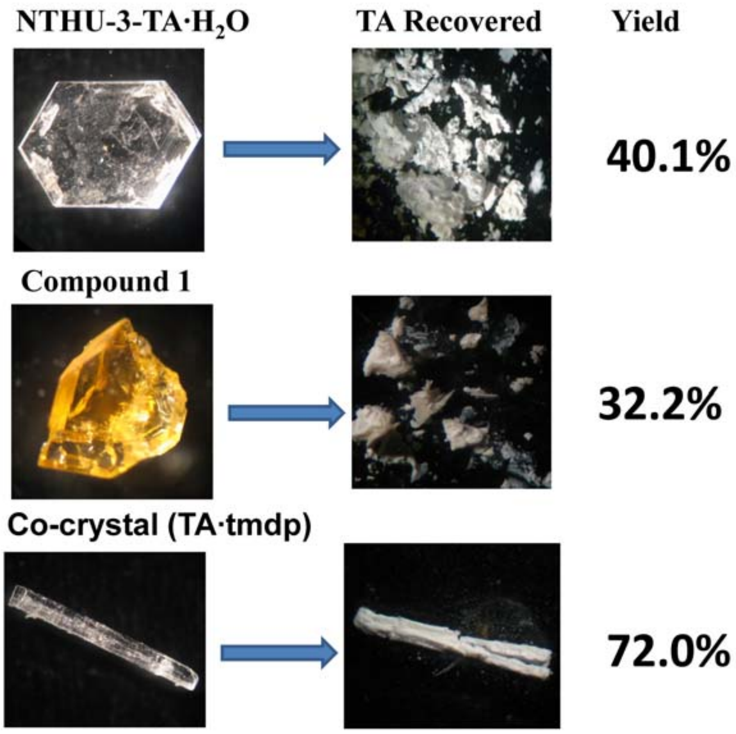

Fig. S2. Photos showing TA were recovered from **NTHU-3-TA·H$_2$O**, compound **1** and (TA. tmdp). TA solids remained in solution after the inorganic part was dissolved in 3M HCl solution

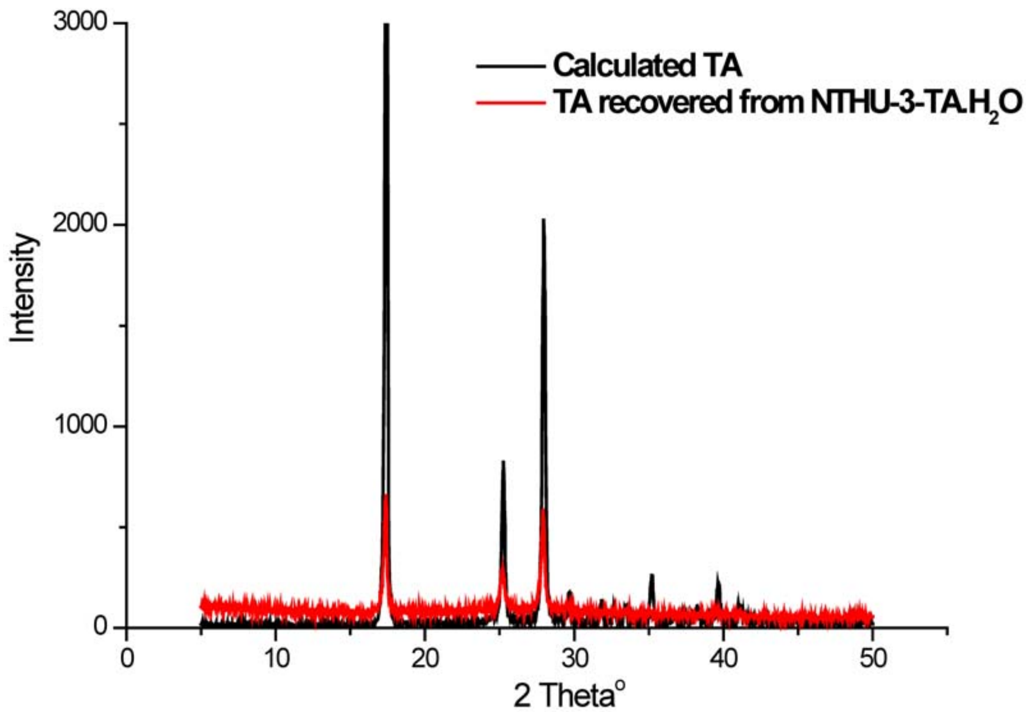

Fig. S3. PXRD patterns of TA recovered from **NTHU-3-TA·H$_2$O**.

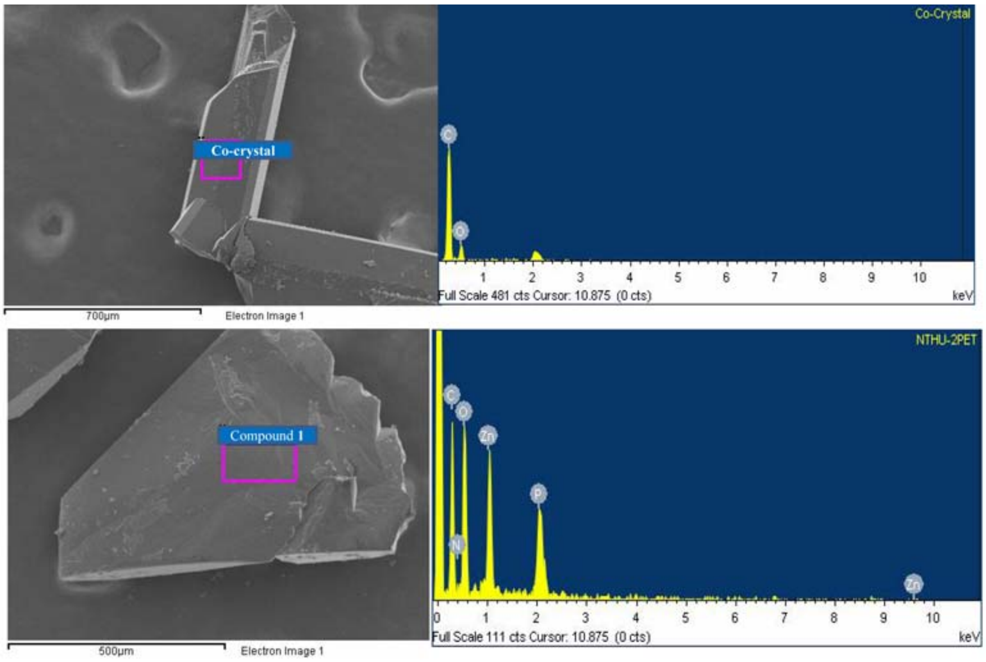

Fig. S4. SEM images and EDX spectra for the co-crystals of (TA·tmdp) and compound **1**. Pink rectangles mark the scanned range of electron beam confirming the existing element of Zn, P, O, N, C without impurity elements

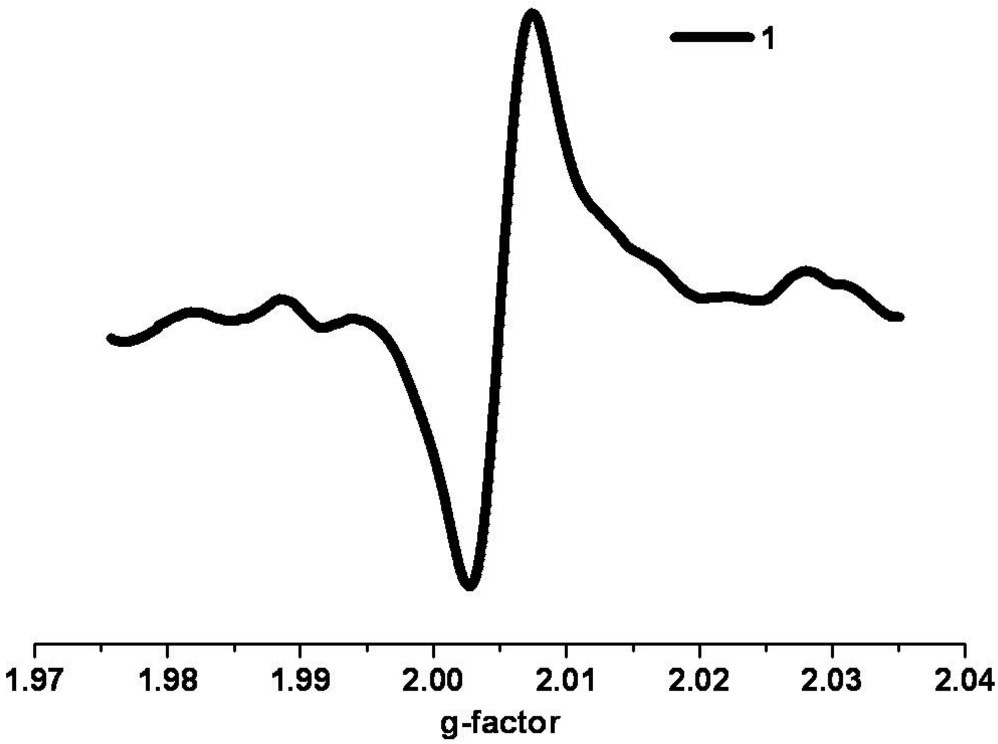

Fig. S5. EPR spectrum of compound **1** measured at 298K.

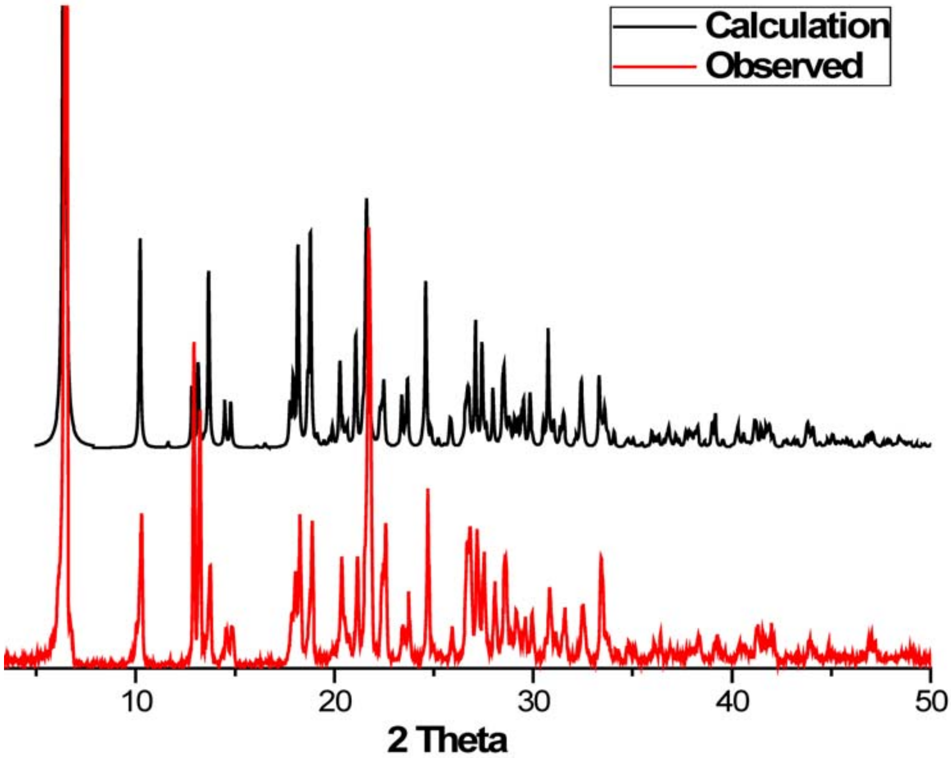

Fig. S6. Powder XRD patterns for compound **1**.

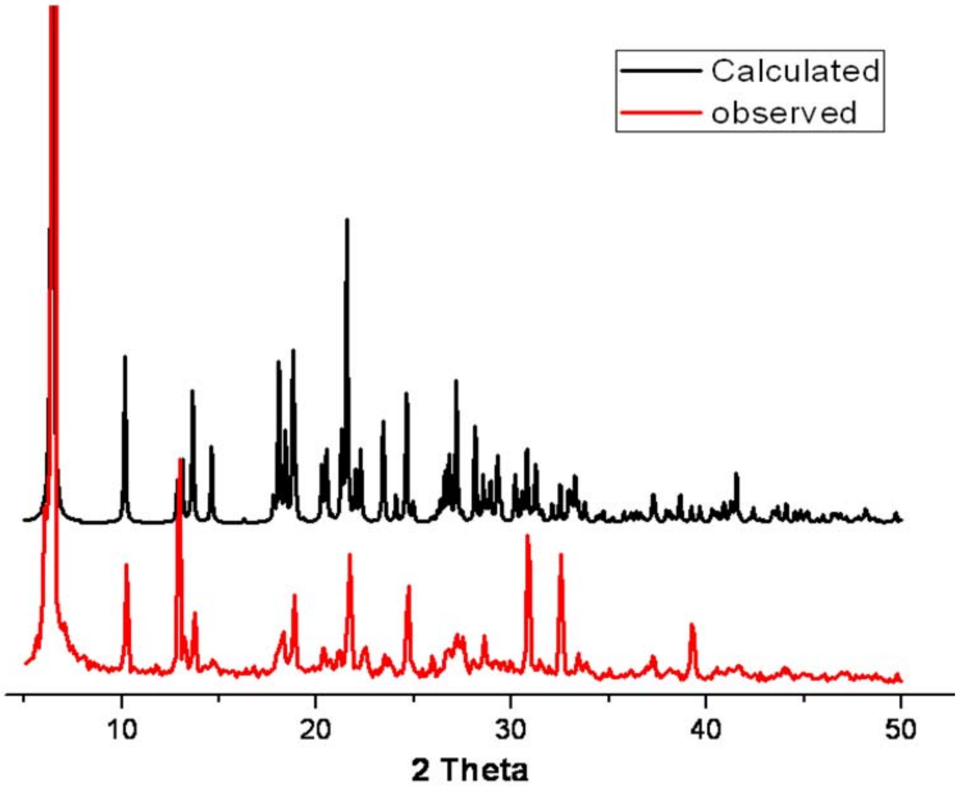

Fig. S7. Powder XRD patterns for compound **2**.

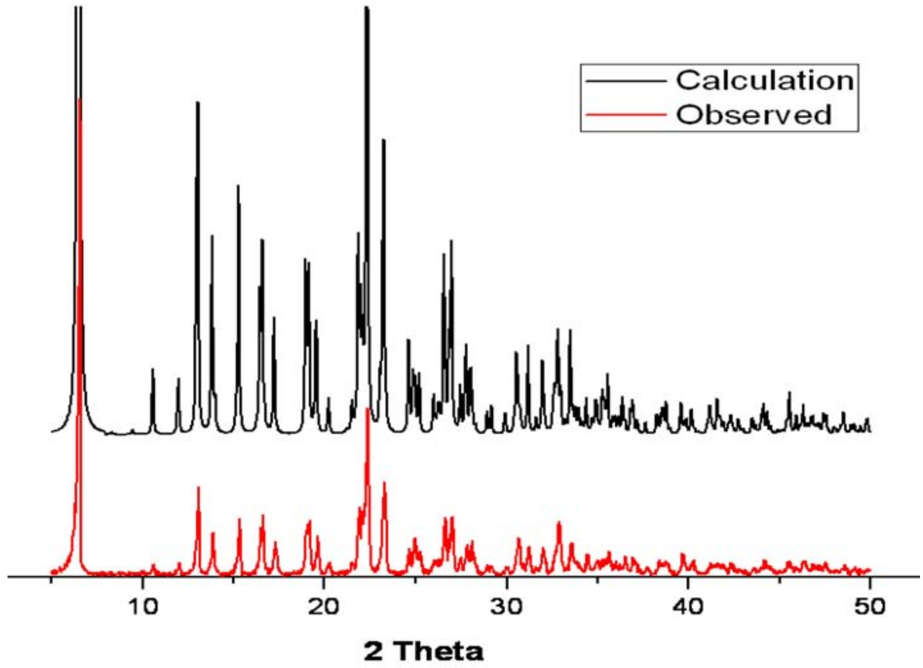

Fig. S8. Powder XRD patterns for compound **3**.

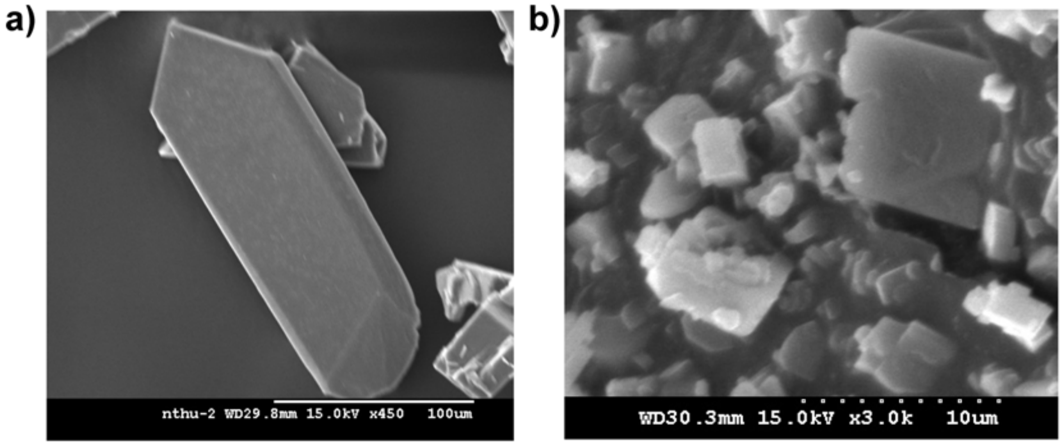

Fig. S9. SEM images of sizable crystals from microwave synthesis for **2** (a) and **3** (b).

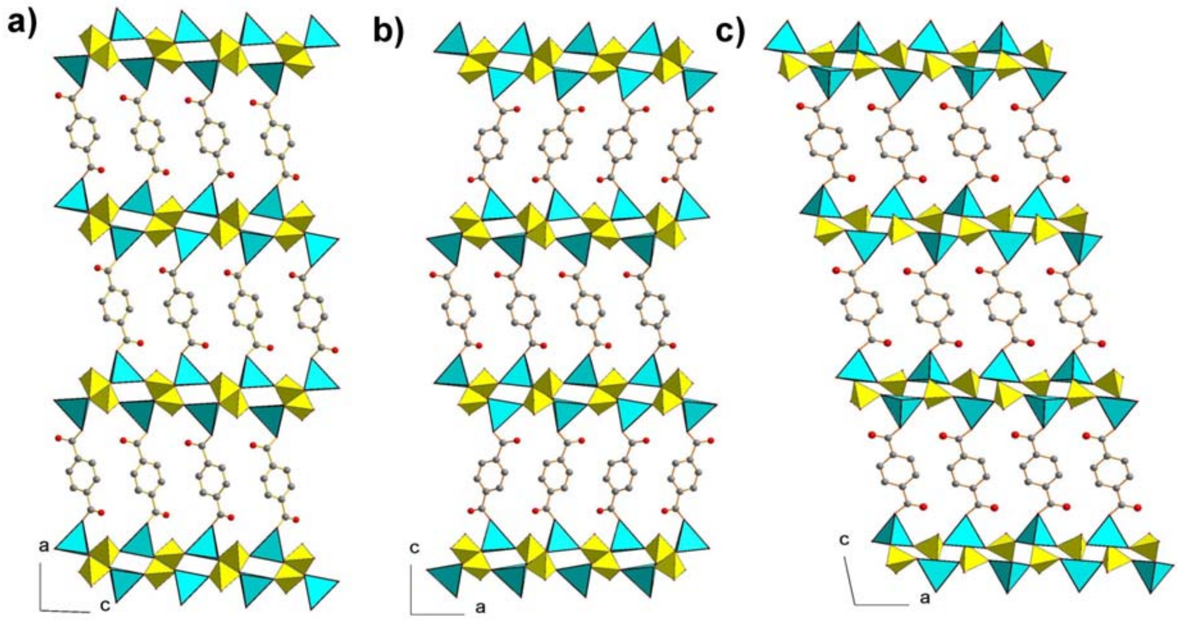

Fig. S10. Structure plots showing pillaring BDC ligands arrangements on ac plane: in consecutive layers they are all parallel in **1** (a) and **3** (c) but pointing toward opposite directions in **2** (b)

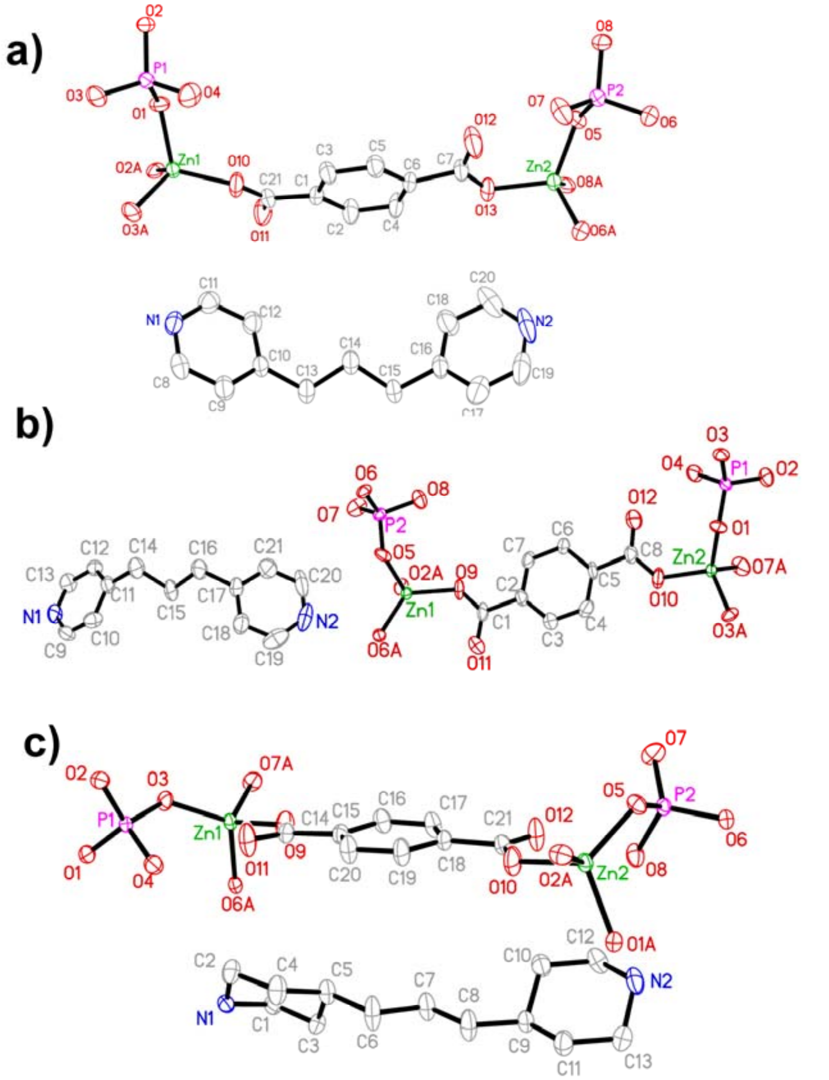

Fig. S11 ORTEP plots of the asymmetric units showing tmdp in **1** (a) and **2** (b); and tmdpp in **3** (c).