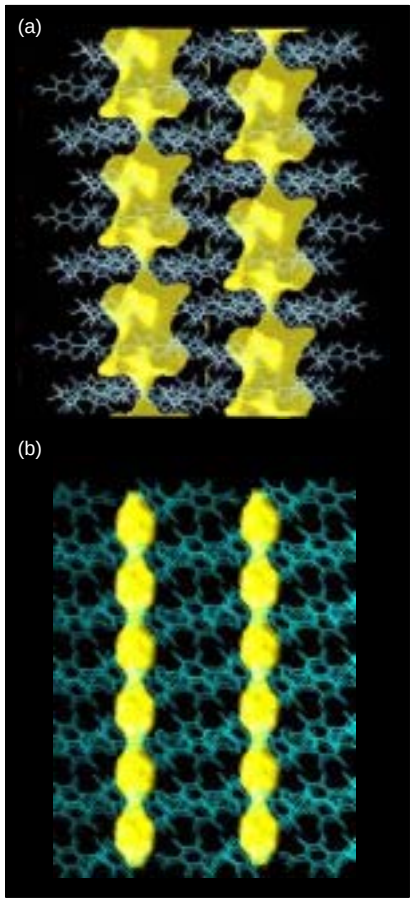


Figure 6. View of the nanochannels of (a) POROF-1 and (b) POROF-2

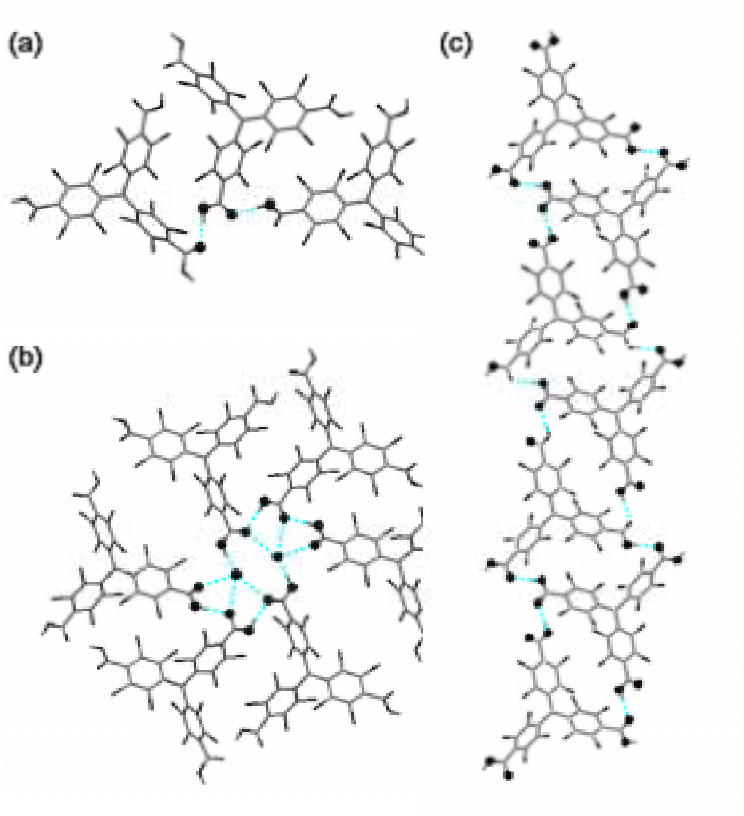


Figure 7. (a) H-bonded trimer of PTMTC radicals; (b) Hexameric motif disrupted by two water molecules; (c) One-dimensional H-bonded chain of PTMTC radicals along the *b* axis.

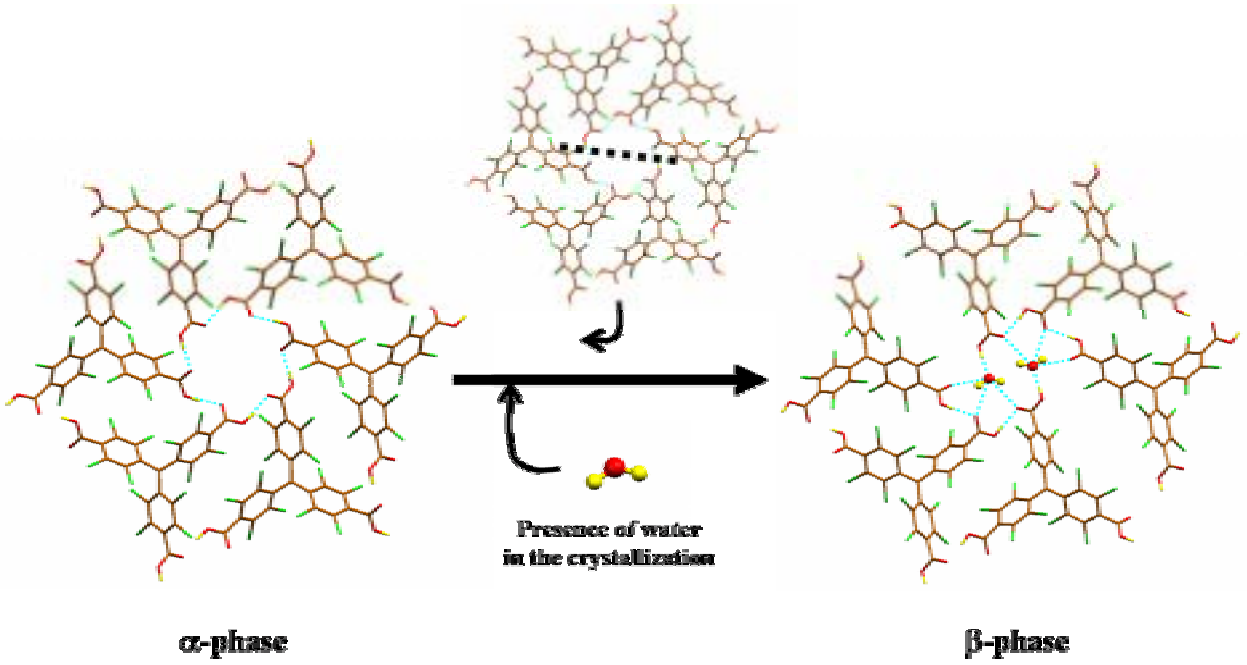


Figure 8. Schematic view of the disruption of the hexameric motif in η-phase due to the presence of water molecules.

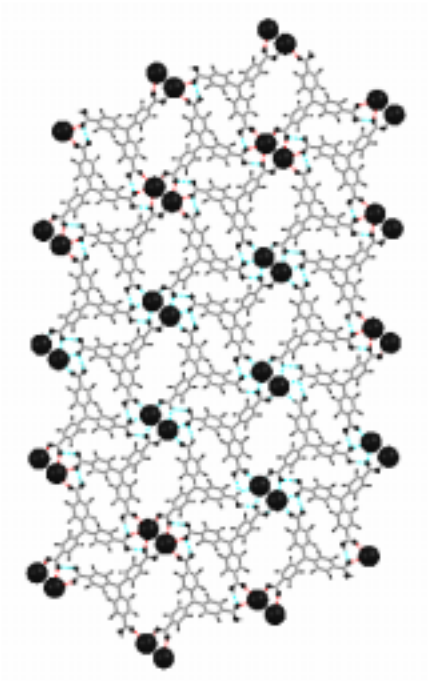


Figure 9. One-dimensional H-bonded chains connected to each other by water molecules along the *bc* plane.

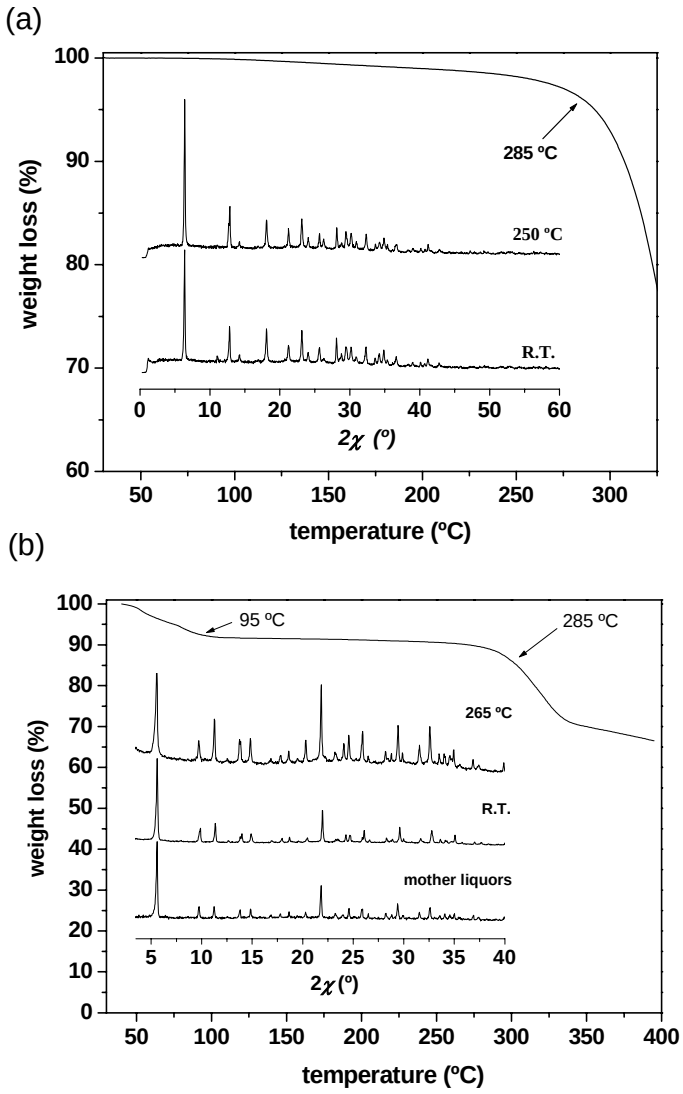


Figure 10. Thermal gravimetric study of a few single crystals of as-synthesized (a) POROF-2 and (b) POROF-1. Inset. Powder X-Ray diffractions of POROF-1 and POROF-2 at different temperatures.

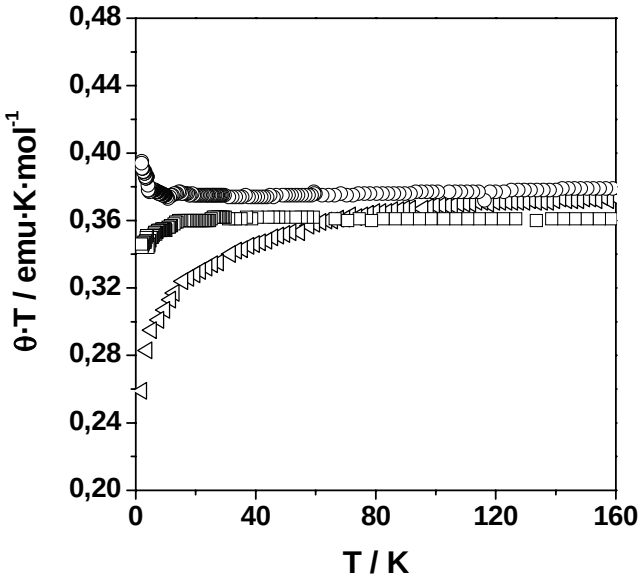


Figure 11. Temperature dependence of the magnetic susceptibility of POROF-1 (l>), POROF-2 (o) and η-phase PTMTC (Ĭ).

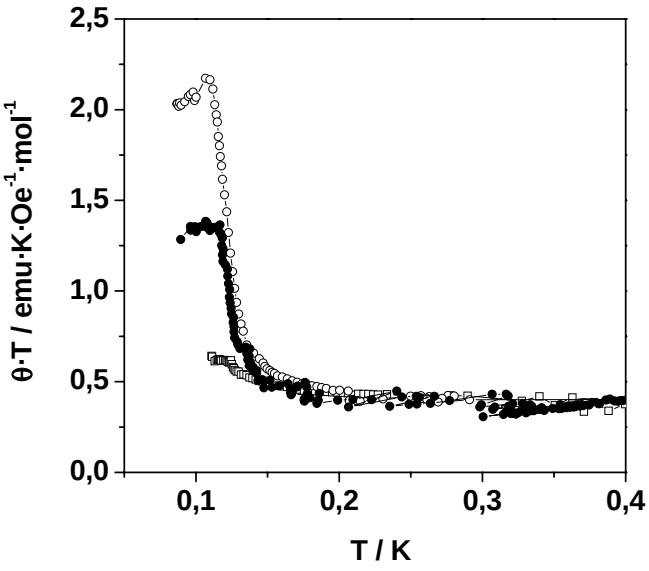


Figure 12. Temperature dependence of the magnetic susceptibility of POROF-2 at lower temperatures at an external magnetic field of 200 (o), 500 (ŏ) and 1000 (Ĭ) Oe.

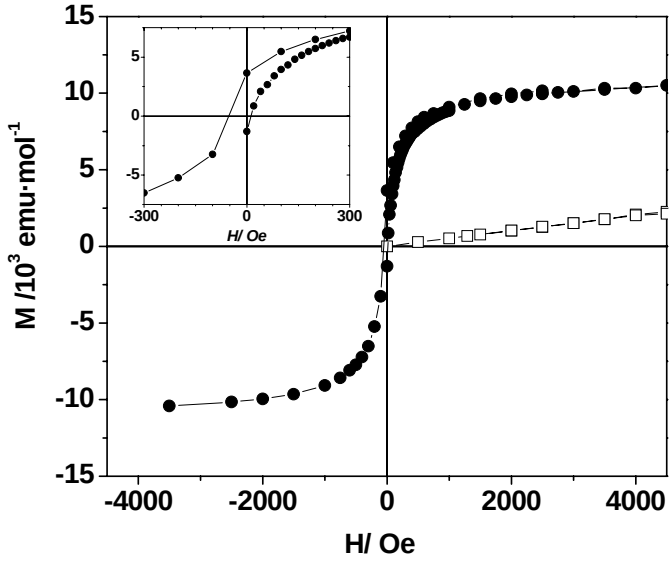
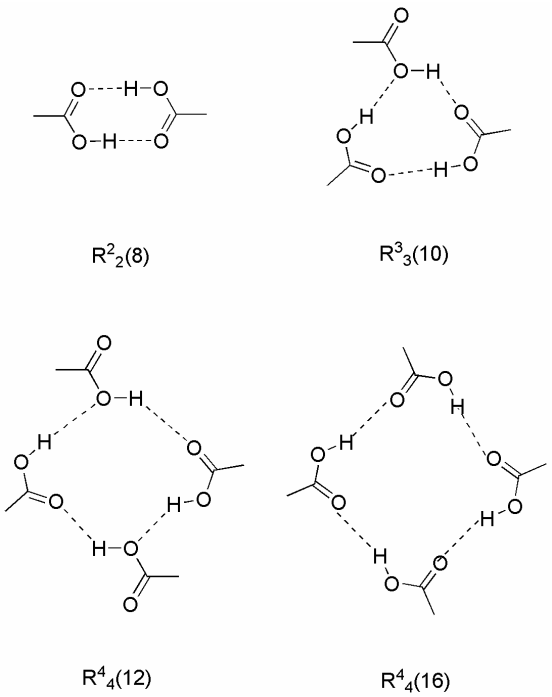


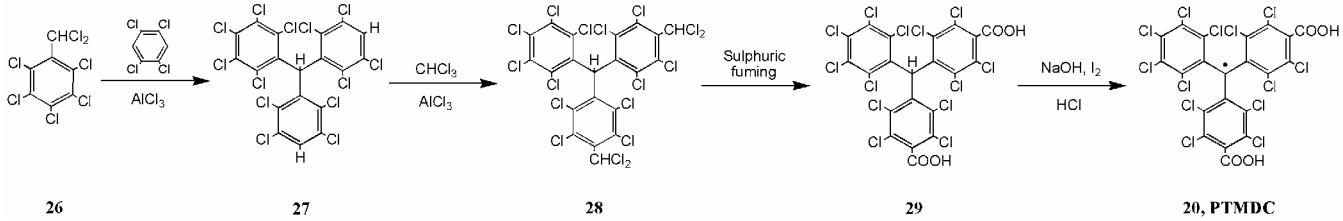
Figure 12. Magnetization curves of POROF-2 at 1350 (Ĭ) and 80 (ŏ) mK. Inset. Hysteresis curve at 80 mK.

SCHEMES

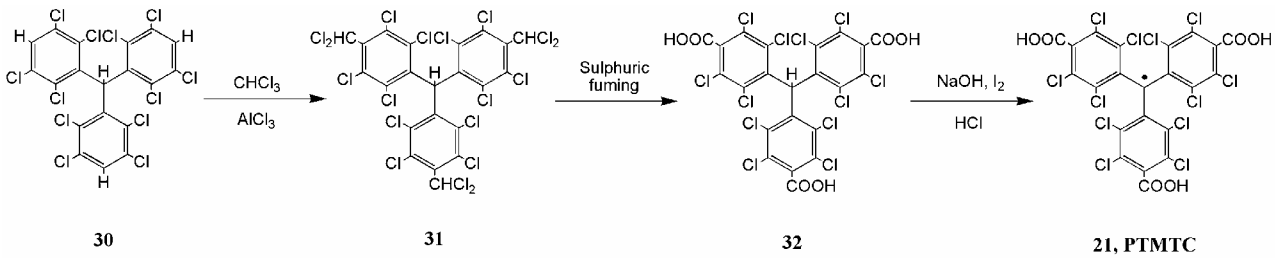
Scheme 1. Cyclic H-Bonded synthons of carboxylic groups.



Scheme 2. Schematic synthesis of PTMDC radical.

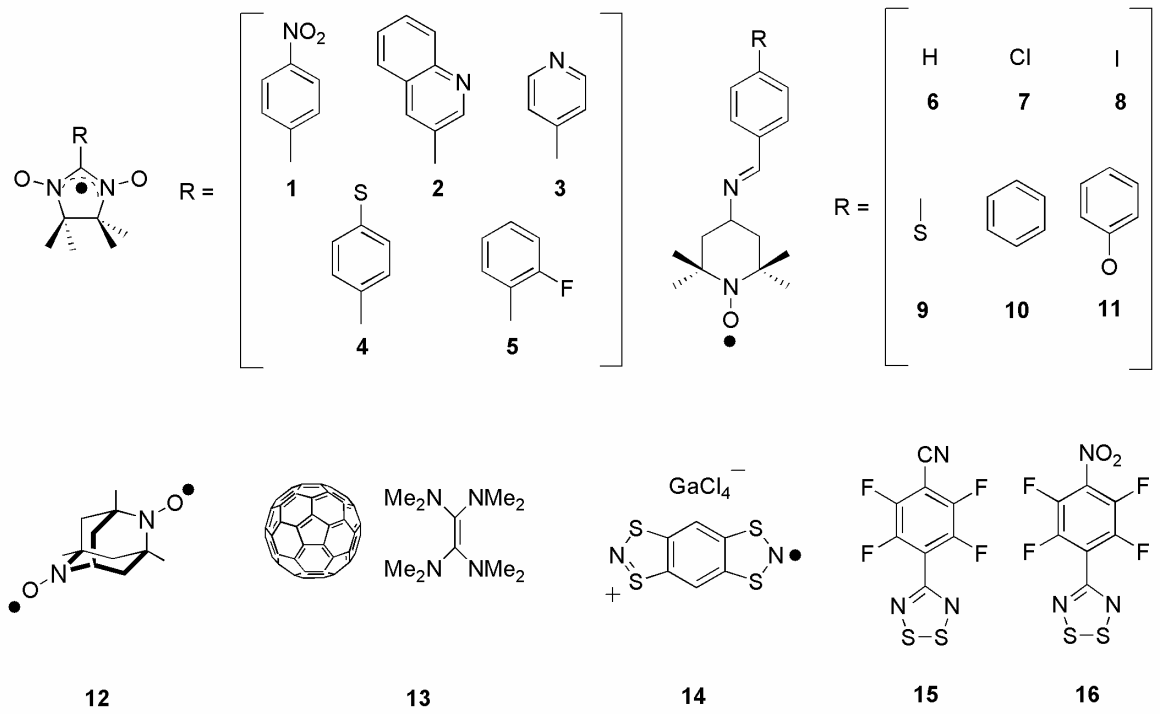


Scheme 3. Schematic synthesis of PTMTC radical.

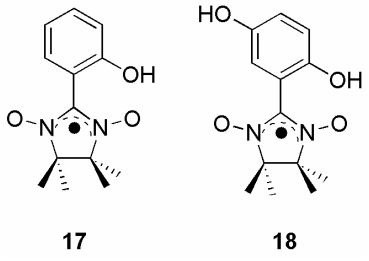


SCHARTS.

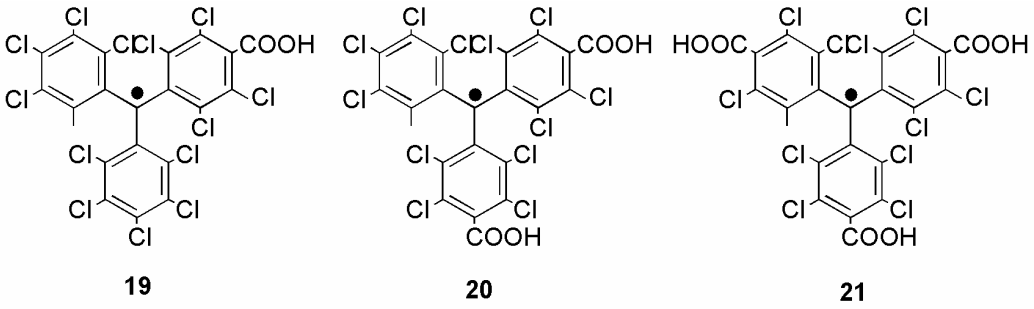
Schart 1



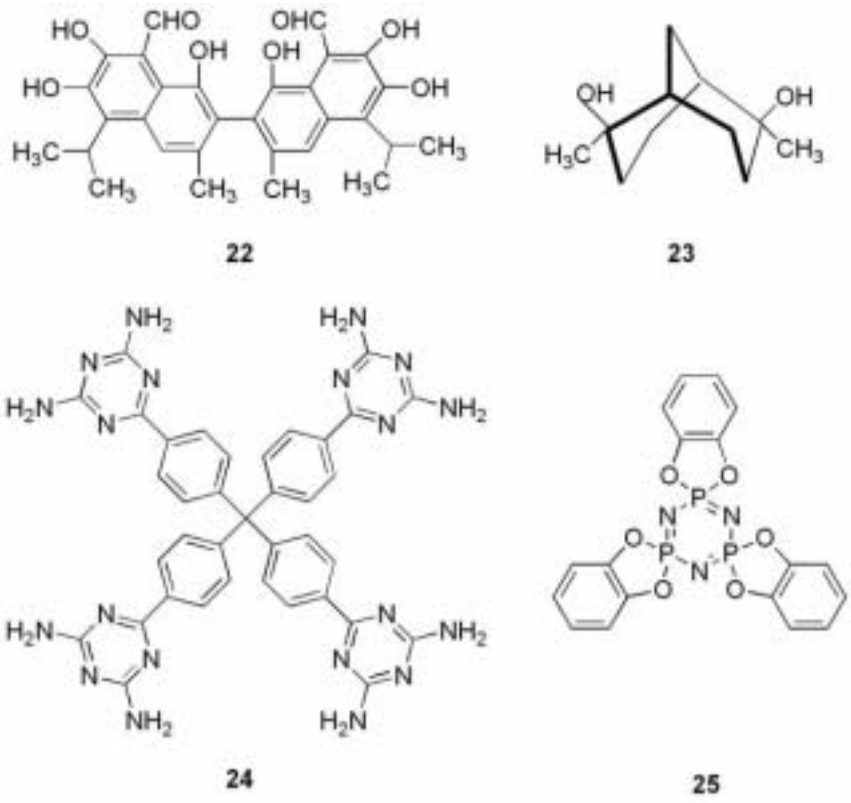
Schart 2



Schart 3



Schart 4



TABLES.

Table 1. Crystallographic Data for POROF-1, POROF-2 and η-phase PTMTC.

	POROF-1	POROF-2	η-phase PTMTC
formula	$C_{27}H_{16}Cl_{13}O_4$	$C_{22}H_3Cl_{12}O_6$	$C_{23}H_6Cl_{15}O_7$
fw	865.25	788.64	926.03
cryst syst.	trigonal	trigonal	triclinic
space group	R-3	P-3c1	P-1
a (Å)	31.4651(6)	15.9283(7)	8.7828(6)
b (Å)	31.4651(7)	15.9283(7)	13.4459(8)
c (Å)	18.8447(7)	13.8886(11)	14.172(1)
ζ (º)	90.00	90.00	83.978(4)
η (º)	90.00	90.00	87.636(4)
ν (º)	120.00	120.00	88.648(4)
V(Å^3)	16157.6(8)	3051.6(3)	1662.64(19)
Z	18	4	2
Temp (K)	233(2)	233(2)	223(2)
R_1	0.0461	0.0585	0.0427
wR_2	0.1183	0.1418	0.0949
GOF	1.025	1.133	1.049

Table 2. Dihedral angles (º) between the phenyl groups (Ar) and the reference plane and angle between carboxyl group and phenyl rings.

Compound	Ar	Angle (º)	Carboxyl	Angle (º)
PTMDC (POROF-1)	C3-C8	45.2	O1-C1-O2	81
	C10-C15	49.0	O3-C2-O4	90
	C16-C21	43.7		
PTMTC (POROF-2)	C2-C7	49.7	O1-C1-O2	87
PTMTC (η-phase)	C5-C10	51.7	O1-C1-O2	88
	C11-C16	49.4	O3-C2-O4	79
	C17-C22	40.6	O5-C3-O6	81

Table 3. Supramolecular interactions in PTMMC, POROF-1, POROF-2 and η-PTMTC.

	PTMMC	**POROF-1**	**POROF-2**	**η-phase**
Primary structure	Discrete H-bonded dimers	2-D H-bonded sheets	2-D H-bonded sheets	1-D H-bonded chains H-bonded through water molecules
H-bonded synthon	$[R^2_2(8)]$	$[R^2_2(8)]$ and $[R^6_6(24)]$	$[R^6_6(24)]$	$[R^4_4(12)]$ and $[R^3_3(8)]$
D····A H-bonding dist (Å)	O1····O2 = 2.676	O3····O4 = 2.677 O3····$Cl11_p$ = 3.092 O1····O2 = 2.692	O1····O2 = 2.657	O2····O3 = 2.655 O4····O5 = 2.749 O1····$O7_{(water)}$ = 2.534 O2····$O7_{(water)}$ = 3.015 O4····$O7_{(water)}$ = 2.991 O6····$O7_{(water)}$ = 2.908
Cl····Cl contact dist (Å)		$Cl1_m$····$Cl4_m$ = 3.48 $Cl2_o$····$Cl4_m$ = 3.32 $Cl5_o$····$Cl12_m$ = 3.45	$Cl2_o$····$Cl3_o$ = 3.44	$Cl6_o$····$Cl12_m$ = 3.45
Secondary structure	H-bonded chains connected by Cl····Cl contacts.	Sheets connected by H-bondings and Cl····Cl contacts.	Sheets connected by Cl····Cl contacts.	Sheets connected by H-bondings and Cl····Cl contacts.
D····A H-bonding dist (Å)	O2····$Cl12_p$ = 3.263	O4····$Cl9_o$ = 3.23		O3····$Cl6_o$ = 3.27
Cl····Cl contact dist (Å)	$Cl1_m$····$Cl9_o$ = 3.35 $Cl2_o$····$Cl8_m$ = 3.33 $Cl3_o$····$Cl11_m$ = 3.22 $Cl4_m$····$Cl7_p$ = 3.46 $Cl5_o$····$Cl5_o$ = 3.22 $Cl10_o$····$Cl13_m$ = 3.40	$Cl1_m$····$Cl7_m$ = 3.32 $Cl2_o$····$Cl7_m$ = 3.39 $Cl3_o$····$Cl6_m$ = 3.49	$Cl2_o$····$Cl4_m$ = 3.33	$Cl4_m$····$Cl10_o$ = 3.38 $Cl5_m$····$Cl7_o$ = 3.33

Table 4. Elemental analysis of POROF-1 and POROF-2

Compound	Formula	Calculated	Found
POROF-2 (R.T.)	$C_{22}Cl_{12}O_6H_3$	33.50%C, 0.38%H	33.65%C, 0.32%H
POROF-2 (265ºC)	$C_{22}Cl_{12}O_6H_3$	33.50%C, 0.38%H	33.80%C, 0.52%H
POROF-1 (R.T.)	$C_{21}Cl_{13}O_4H_2$·Hexan	36.54%C, 1.56%H	36.10%C, 1.08%H
POROF-1 (250ºC)	$\hat{C}_{21}Cl_{13}O_4H_2$·	32.40%C, 0.25%H	32.93%C, 0.42%H

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