Electronic Supplementary Material (ESI) for CrystEngComm.

SUPPORTING MATERIAL

Synthesis and Characterisation of New Coordination Polymers by Combining 2-Pyridyl Oximes or Alcohols with Functionalised Terephthalic Acid Analogues

Foteini Dimakopoulou,[a] Constantinos G. Efthymiou,[a] Andreas Kourtellaris,[b] Ciaran O'Malley,[a‡] Lamis Alaa Eldin Refat,[a] Anastasios Tasiopoulos,[b] Patrick McArdle,[a] and Constantina Papatriantafyllopoulou[*a]

[a.] *School of Biological and Chemical Sciences, College of Science and Engineering, University of Galway, H91 TK33 Galway, Ireland. E-mail address: constantina.papatriantafyllopo@universityofgalway.ie Tel: +353 91 493462*

[b.] *Department of Chemistry, University of Cyprus, 1678 Nicosia, Cyprus.*

[‡] *Current address: Department of Physics, Bernal Institute, University of Limerick, Limerick, Republic of Ireland.*

Table S1: Crystallographic data for **1**-**7**

Complex	**1**·3DMF	**2**·2DMF	**3**
Empirical formula	$C_{29}H_{37}N_9O_{11}Zn$	$C_{23}H_{25}N_7O_9Mn$	$C_{50}H_{42}N_{12}O_{12}Co_3$
Formula weight	753.04	598.44	1179.74
Crystal system	Triclinic	Triclinic	Triclinic
Space group	*P*$\bar{1}$	*P*$\bar{1}$	*P*$\bar{1}$
a (Å)	9.3796 (7)	9.5541(6)	11.1458(8)
b (Å)	12.5378 (8)	10.0432(6)	14.7658(8)
c (Å)	15.3451 (10)	15.8933(8)	18.7690(9)
α (°)	87.967 (5)	76.089(5)	81.504(4)
β (°)	73.076 (6)	72.979(5)	89.225(5)
γ (°)	84.839 (6)	76.732(5)	86.463(5)
V (Å^3)	1719.3 (2)	1394.49(15)	3049.2(3)
Z	2	2	2
ρ_{calc} (g cm^{-3})	1.455	1.406	1.285
Radiation, *λ* (Å)	1.54184	1.54184	1.54184
μ (mm^{-1})	1.608	4.392	6.851
Measd/independent reflns (R_{int})	11682 /6767 (0.060)	9478/ 6313 (0.0588)	21718/11529 (0.0992)
Parameters refined	483	722	694
GoF (on F^2)	1.130	1.135	1.020
R_1[a] ($I > 2\sigma(I)$)	0.0656	0.0778	0.0764
wR_2[b] ($I > 2\sigma(I)$)	0.1816	0.2130	0.2121
$(\Delta\rho)_{max}/(\Delta\rho)_{min}$ (e Å^{-3})	0.919/-0.772	0.895 / -0.929	0.913 /-1.047
Complex	**4**·DMF	**5**	**6**.2DMF
Empirical formula	$C_{23}H_{25}N_3O_9Ni$	$C_{20}H_{16}N_2O_8Zn$	$C_{26}H_{30}N_8O_9Ni$
Formula weight	546.17	461.74	657.29
Crystal system	Triclinic	Monoclinic	Monoclinic
Space group	*P*$\bar{1}$	*P2/n*	P2 1/c

a (Å)	9.6616(13)	9.49420(2)	17.2182(10)
b (Å)	10.644(2)	10.0245(3)	10.0832(6)
c (Å)	12.4656(15)	13.4633(4)	18.2479(9)
a (°)	95.832(14)	90	90
β (°)	90.191(11)	93.449(2)°	105.108(5)
γ (°)	97.496(15)	90	90
V (Å^3)	1264.2(4)	1278.75(7)	3058.6(3)
Z	2	2	4
ρ_{calc} (g cm^{-3})	1.435	1.199	1.427
Radiation, *λ* (Å)	0.71073	1.54184	0.71073
μ (mm^{-1})	0.823	1.654	0.698
Measd/independent reflns (R_{int})	8537 /2970 (0.0963)	8508/4741 (0.0332)	21202 / 5571 (0.0911)
Parameters refined	332	145	419
GoF (on F^2)	0.707	1.043	0.901
R_1[a] ($I > 2\sigma(I)$)	0.0815	0.0419	0.0812
wR_2[b] ($I > 2\sigma(I)$)	0.1818	0.1199	0.2268
$(\Delta\rho)_{max}/(\Delta\rho)_{min}$ (e Å^{-3})	1.078/ -0.429	0.361/-0.289	1.147/- 1.242

Complex	**7**·DMF
Empirical formula	$C_{72}H_{74}N_{14}O_{24}Zn_3$
Formula weight	1715.56
Crystal system	Monoclinic
Space group	*Ia*
a (Å)	18.3768(9)
b (Å)	10.3212(6)
c (Å)	45.523(2)
a (°)	90
β (°)	92.253(4)
γ (°)	90

V (Å^3)	8627.6(8)
Z	4
ρ_{calc} (g cm^{-3})	1.321
Radiation, λ (Å)	0.71073
μ (mm^{-1})	0.904
Measd/independent reflns (R_{int})	36376 / 18203 (0. 1108)
Parameters refined	985
GoF (on F^2)	0.982
R_1[a] ($I > 2\sigma(I)$)	0.1022
wR_2[b] ($I > 2\sigma(I)$)	0.2450
$(\Delta\rho)_{max}/(\Delta\rho)_{min}$ (e Å^{-3})	1.437 /-0.453

Table S2: Hydrogen bonding details for **1**·3DMF.

D – H … A	D … A (Å)	H … A (Å)	DHA (º)	Symmetry operator of A
O(8) – H(8) … O(5)	2.570	1.787	140.0	*x*, *y*, *z*
O(2) – H(2) … O(4)	2.550	1.603	165.5	*x*, *y*, *z*
O(7) – H(7) …O(3)	2.520	1.566	147.6	*x*, *y*, *z*
O(1) – H(1) … O(6)	2.549	1.584	175.8	*x*, *y*, *z*
N(3) – H(1N3) … O(11)	2.869	2.037	158.1	*x*, *y*, *z*
N(3) -H(2N3)…O(10)	2.890	2.160	148.5	*x*, *y*, *z*
N(6)-H(2N6)…O(7)	2.957	2.171	150.2	*-1+x*, *y*, *z*
N(6)-H(1N6)…O(1)	3.028	2.254	166.2	*-1+x*, *y*, *z*

A=acceptor, D=donor

Table S3: Hydrogen bonding details for **4**·DMF.

D – H … A	D … A (Å)	H … A (Å)	DHA (º)	Symmetry operator of A
O(3) – H(3A) … O(2)	2.516	1.809	143.7	*1-x*, 2-*y*, 1-*z*
O(8) – H(8) … O(1)	2.609	1.789	177.6	*x, y, z*
O(7) – H(7A) …O(5)	2.605	1.849	152.5	*x, y, z*
O(6) – H(6) … O(5)	2.583	1.867	145.2	*x, y, z*

A=acceptor, D=donor

Table S4: Hydrogen bonding details for **6**· 2DMF.

D – H … A	D … A (Å)	H … A (Å)	DHA (º)	Symmetry operator of A
O(3) – H(3A) … O(4)	2.497	2.176	103.4	*x*, *y*, *z*
N(2) – H(2B) …O(9A)	2.843	2.033	156.5	*x, y, z*
O(6) – H(6) … O(5)	2.583	1.867	145.2	*x, y, z*
N(2)-H(2A)…O(6)	2.576	2.276	100.6	*x, y, z*
N(6)-H(6A)…O(7)	2.576	2.280	100.6	*x, y, z*

A=acceptor, D=donor

Table S5: Hydrogen bonding details for **7**· DMF.

D – H … A	D … A (Å)	H … A (Å)	DHA (º)	Symmetry operator of A
O(7) – H(7) … O(2)	2.537	1.863	138.6	*x*, *y*, *z*
O(5) -H(5B) … O(3)	2.655	2.255	110.3	*x, y, z*
O(10) – H(10B) …O(11)	2.597	3.151	41.8	*x, y, z*
O(15) – H(15A) … O(18)	2.512	1.751	153.4	*x, y, z*
O(19) – H(19B) … O(21)	2.562	1.860	142.9	*x, y, z*
O(14)-H(14A)…O(9)	2.519	1.778	149.3	*x, y, z*
O(6)-H(6)…O(3)	2.634	1.890	150.1	*0.5+x, 2-y, z*
O(13)-H(13A)…O(12)	2.556	1.755	164.3	*0.5+x, 1-y, z*
O(16)-H(16)…O(20)	2.503	1.685	175.2	*-0.5+x, -y, z*

A=acceptor, D=Donor

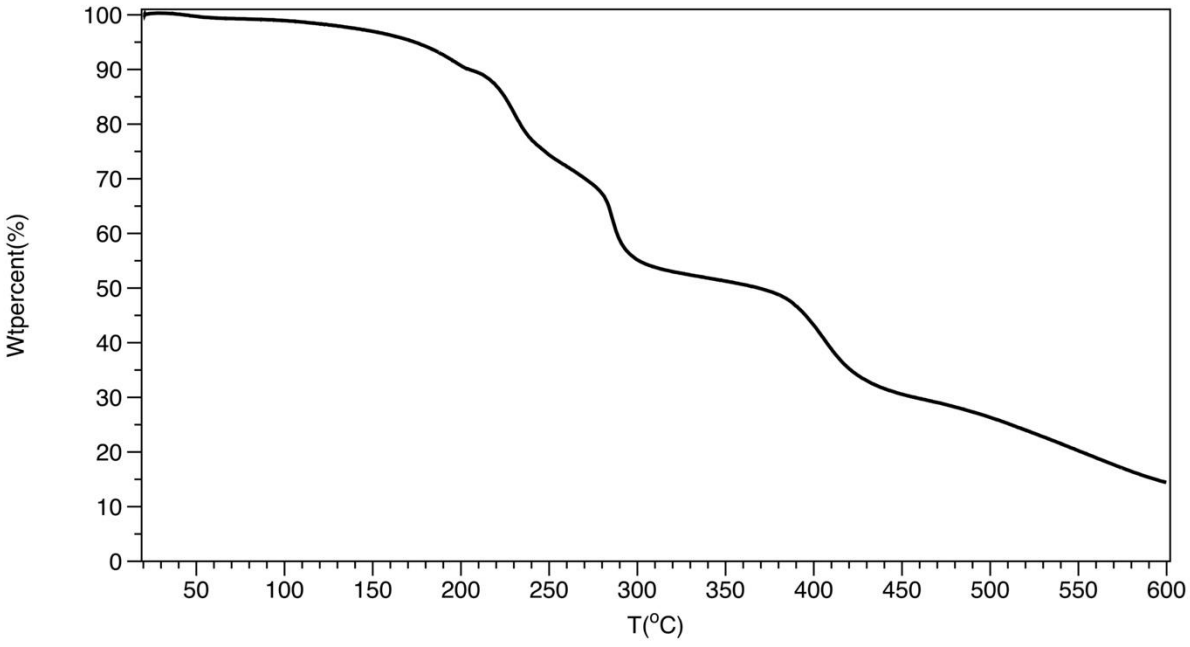

Fig. S1: TGA plot for **4**•DMF.

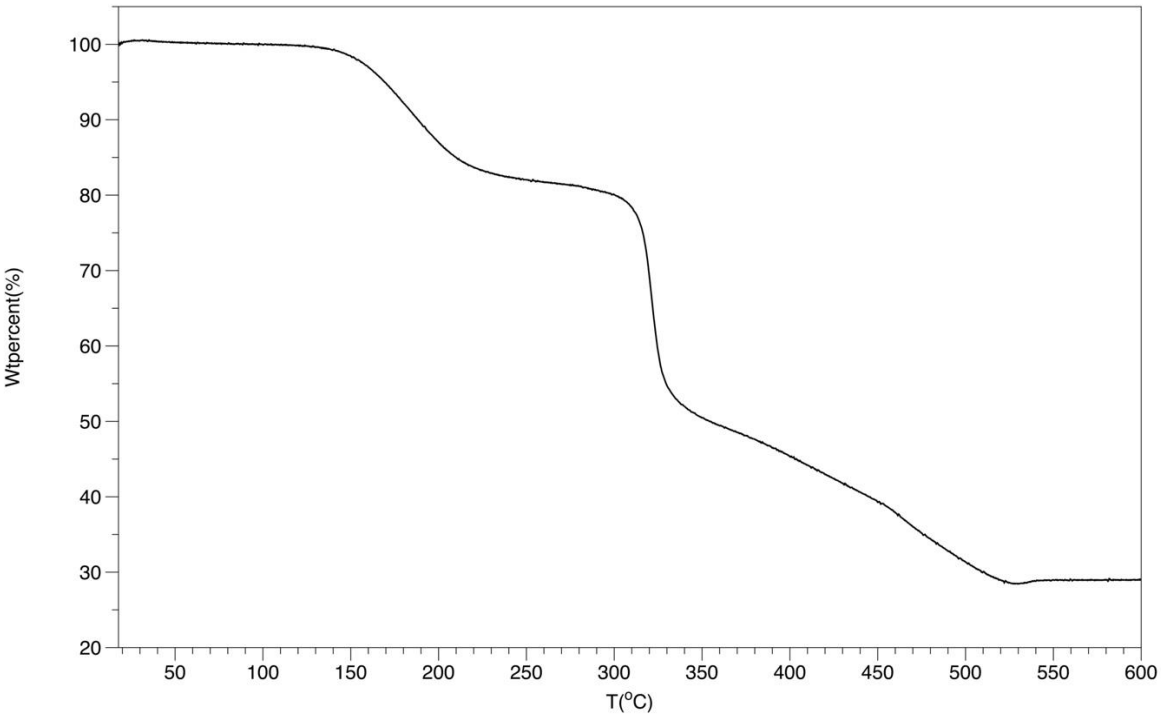

Fig. S2: TGA plot for **6**•2DMF.

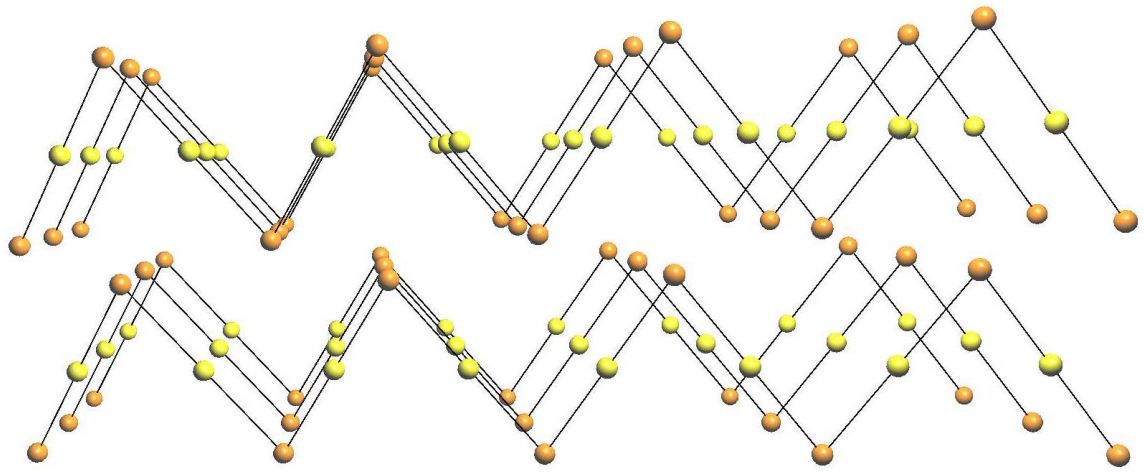

Fig. S3: The 2-c network of **1** along [100] plane ($\{Zn(Hhmp)_2\}^{2+}$:orange and H_2DHBDC:yellow node).

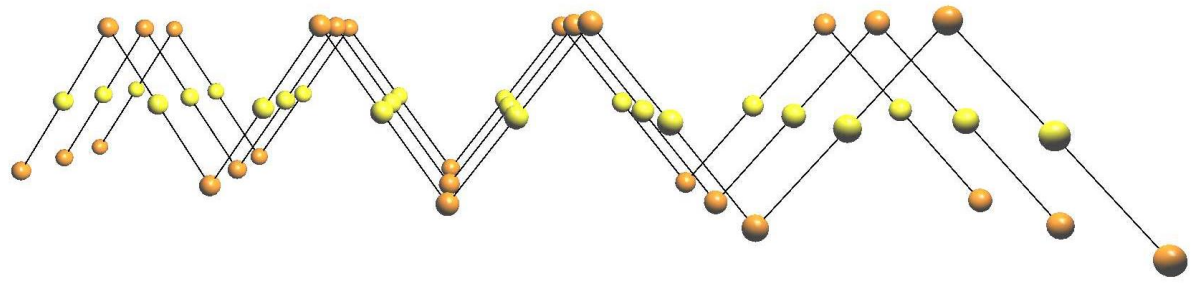

Fig. S4: The 2-c network of **5** along [100] plane ($\{Zn(H_2pyaox)_2\}^{2+}$:orange and H_2DHBDC:yellow node).

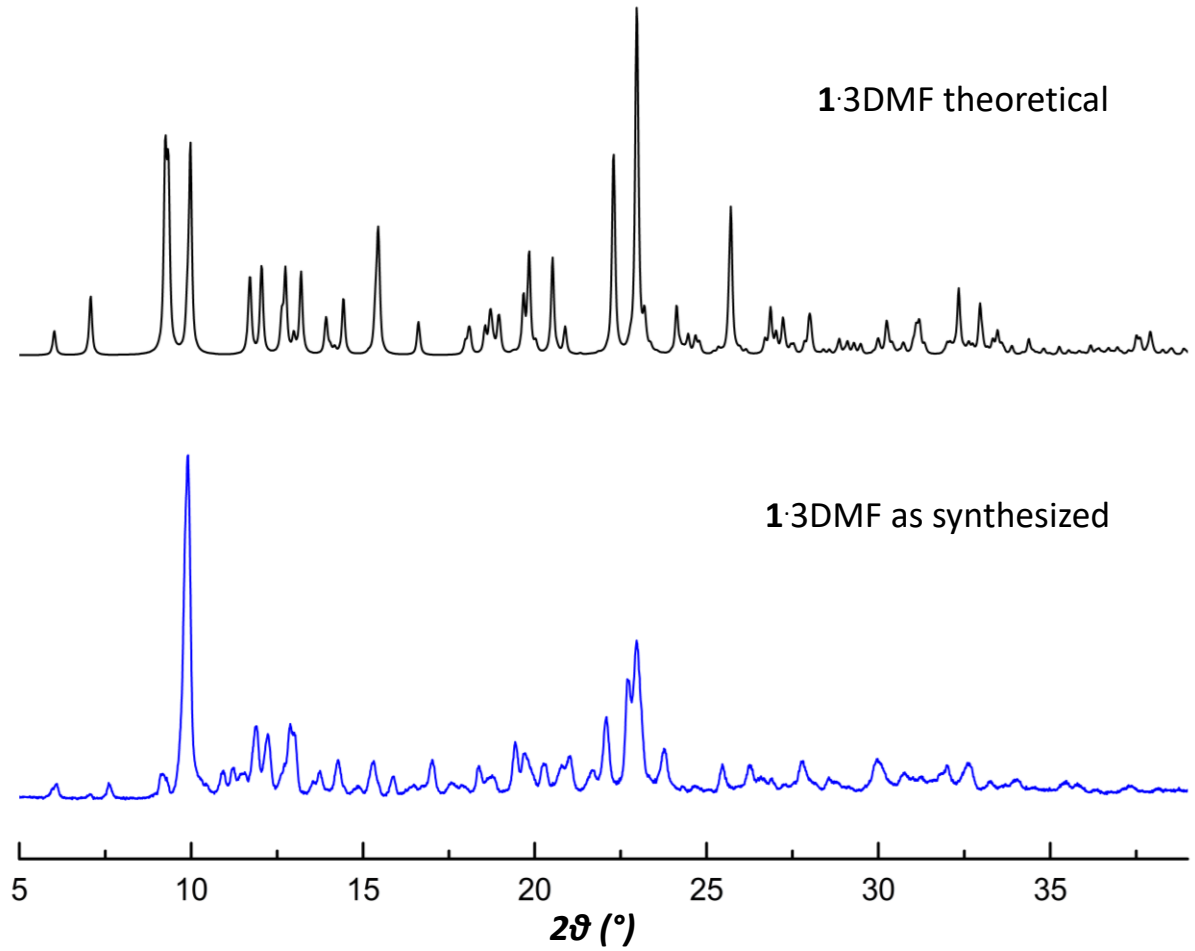

Fig. S5: The PXRD patterns of **1**·3DMF as synthesized (below) and theoretical (above).

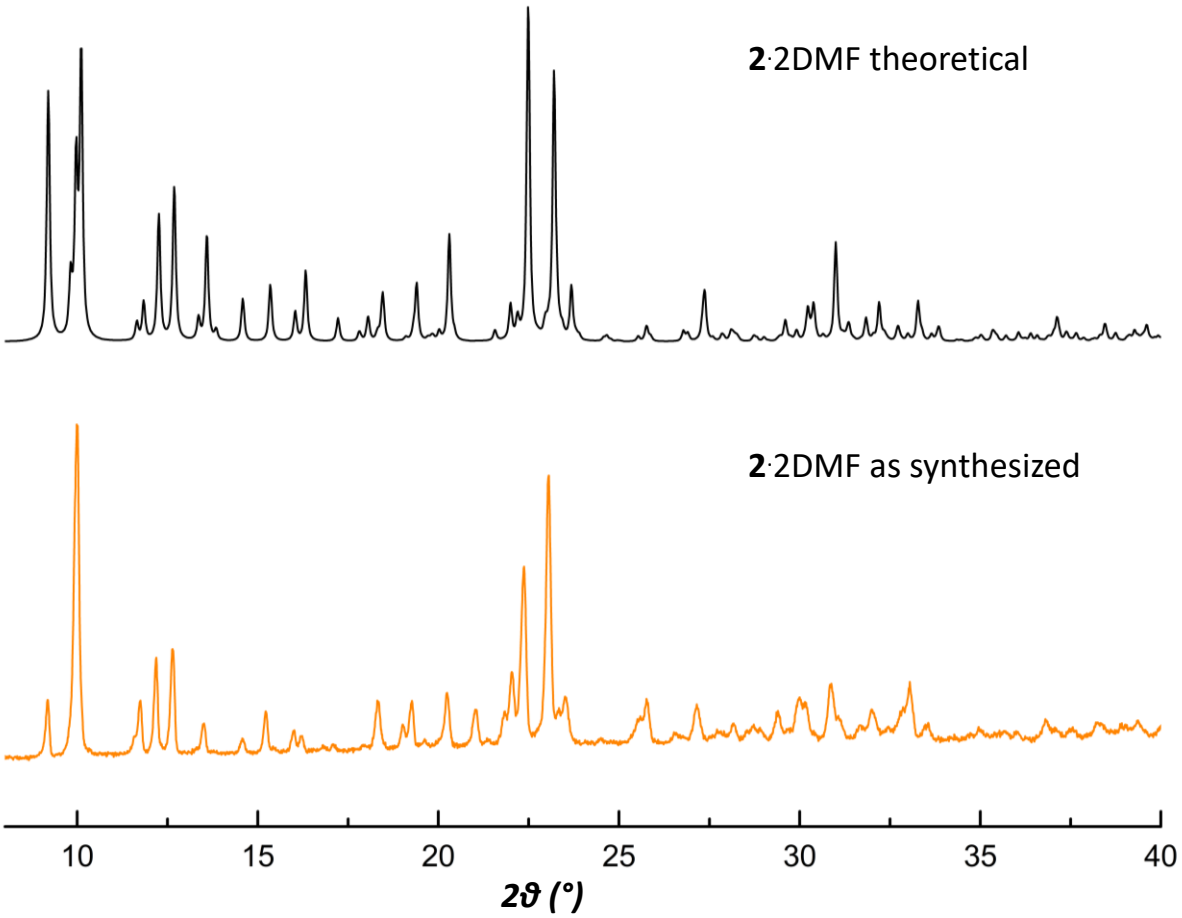

Fig. S6: The PXRD patterns of **2**·2DMF as synthesized (below) and theoretical (above).

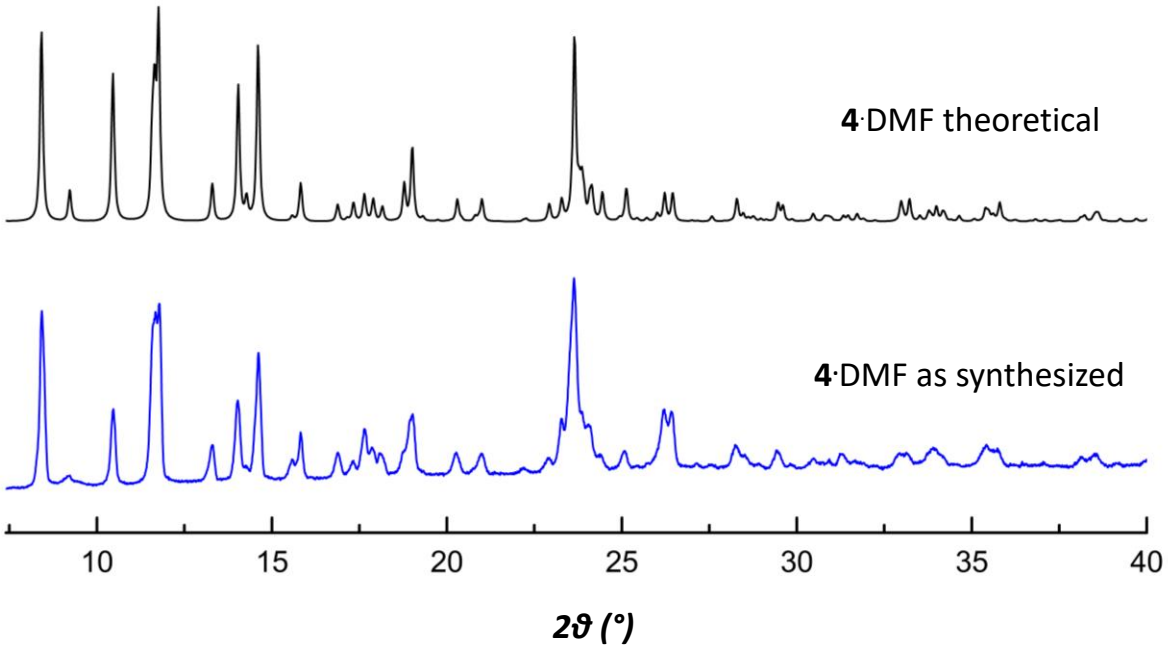

Fig. S7: The PXRD patterns of **4**·DMF as synthesized (below) and theoretical (above).

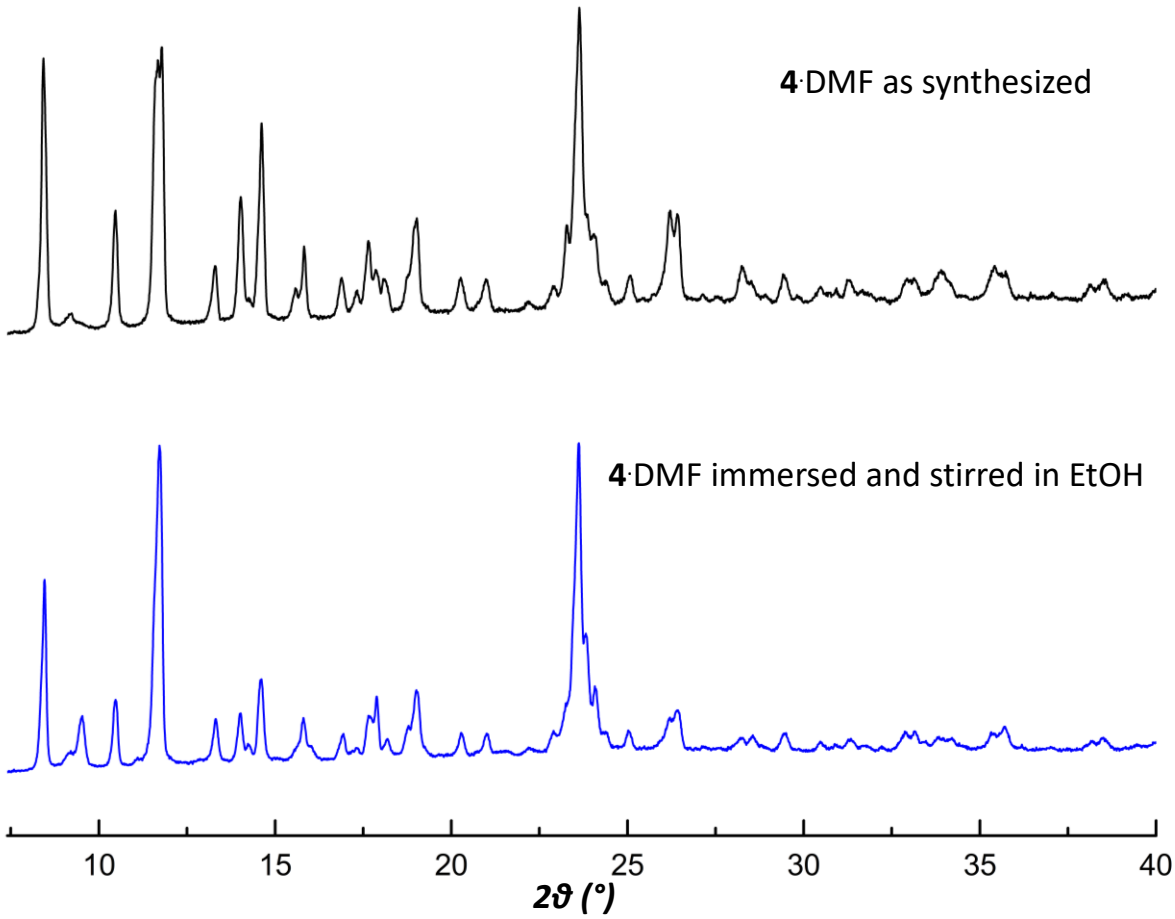

Fig. S8: The PXRD patterns of **4**·DMF as synthesized (above) and after being immersed and stirred in EtOH for 100 h (below).

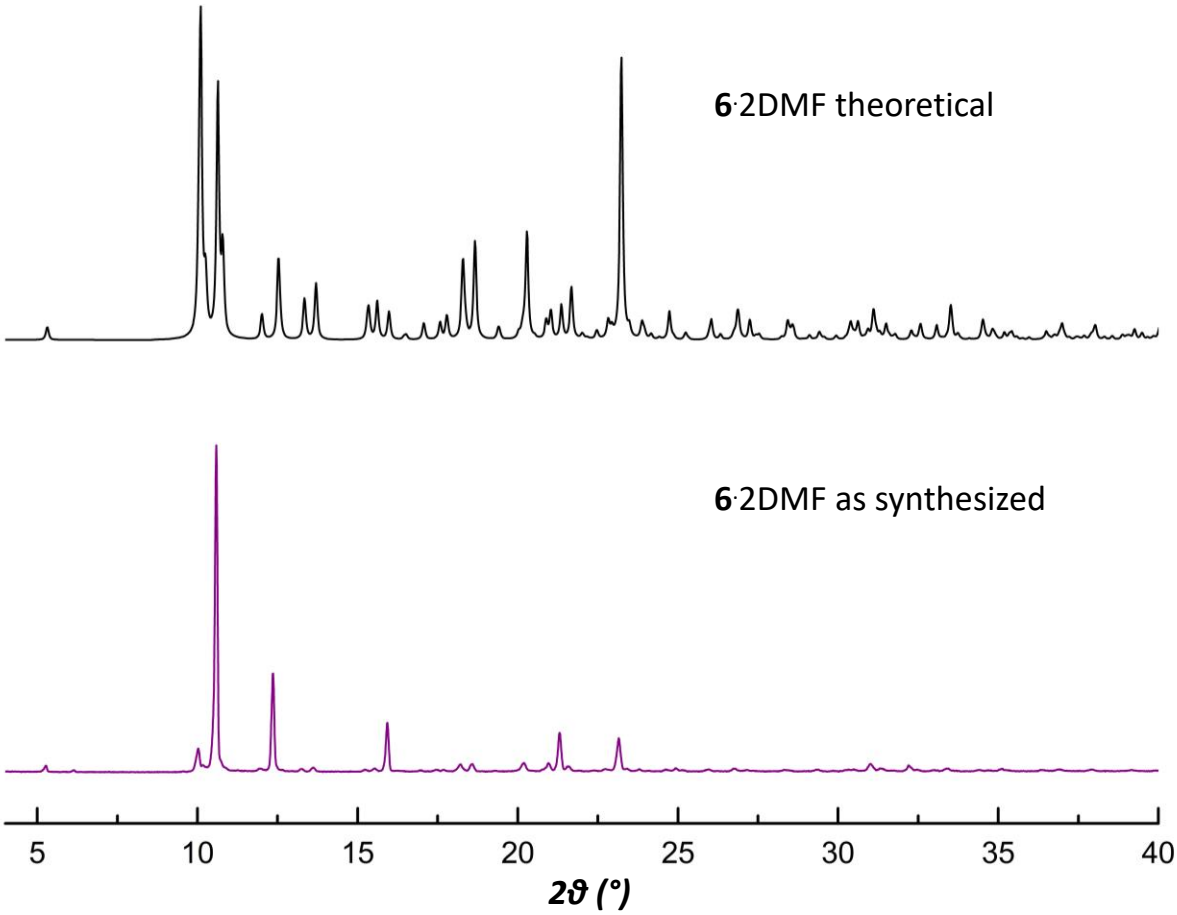

Fig. S9: The PXRD patterns of **6**·2DMF as synthesized (below) and theoretical (above).

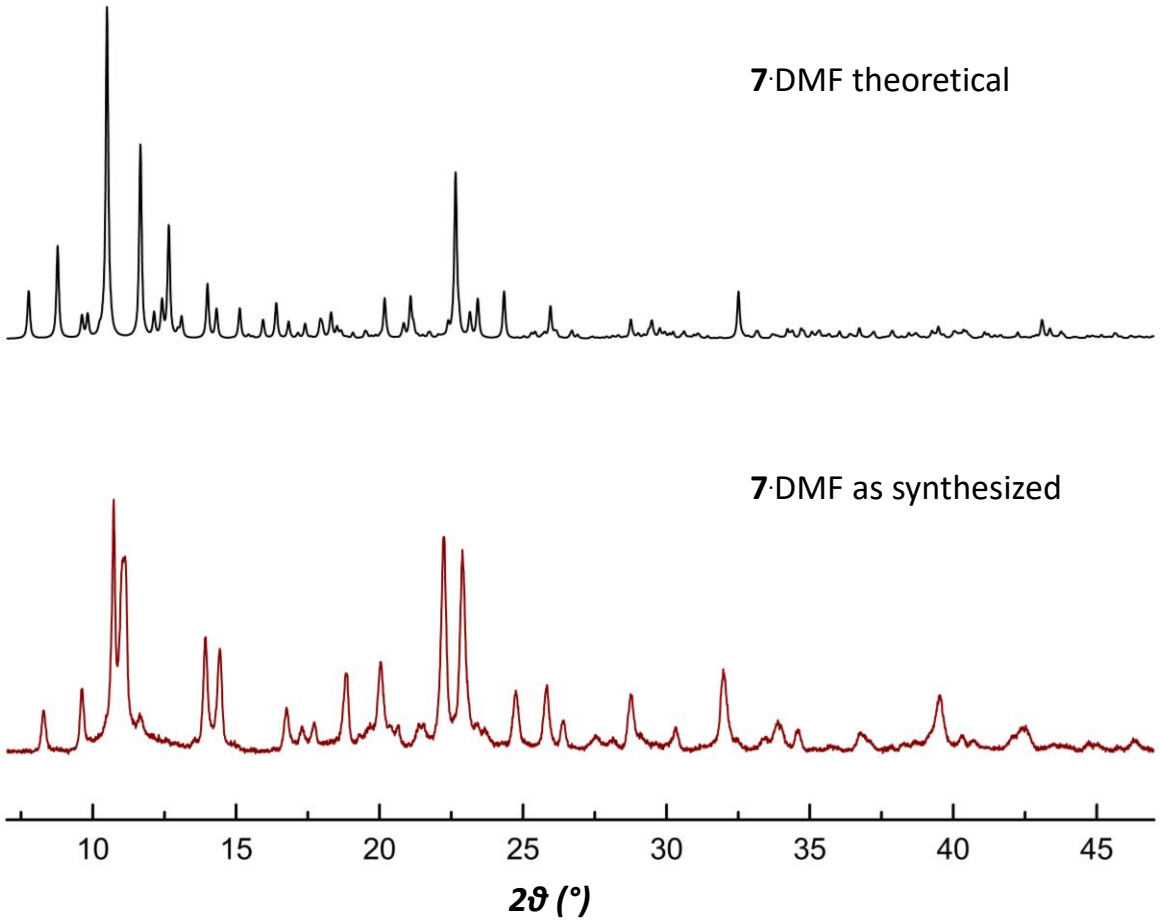

Fig. S10: The PXRD patterns of **7**·DMF as synthesized (below) and theoretical (above).

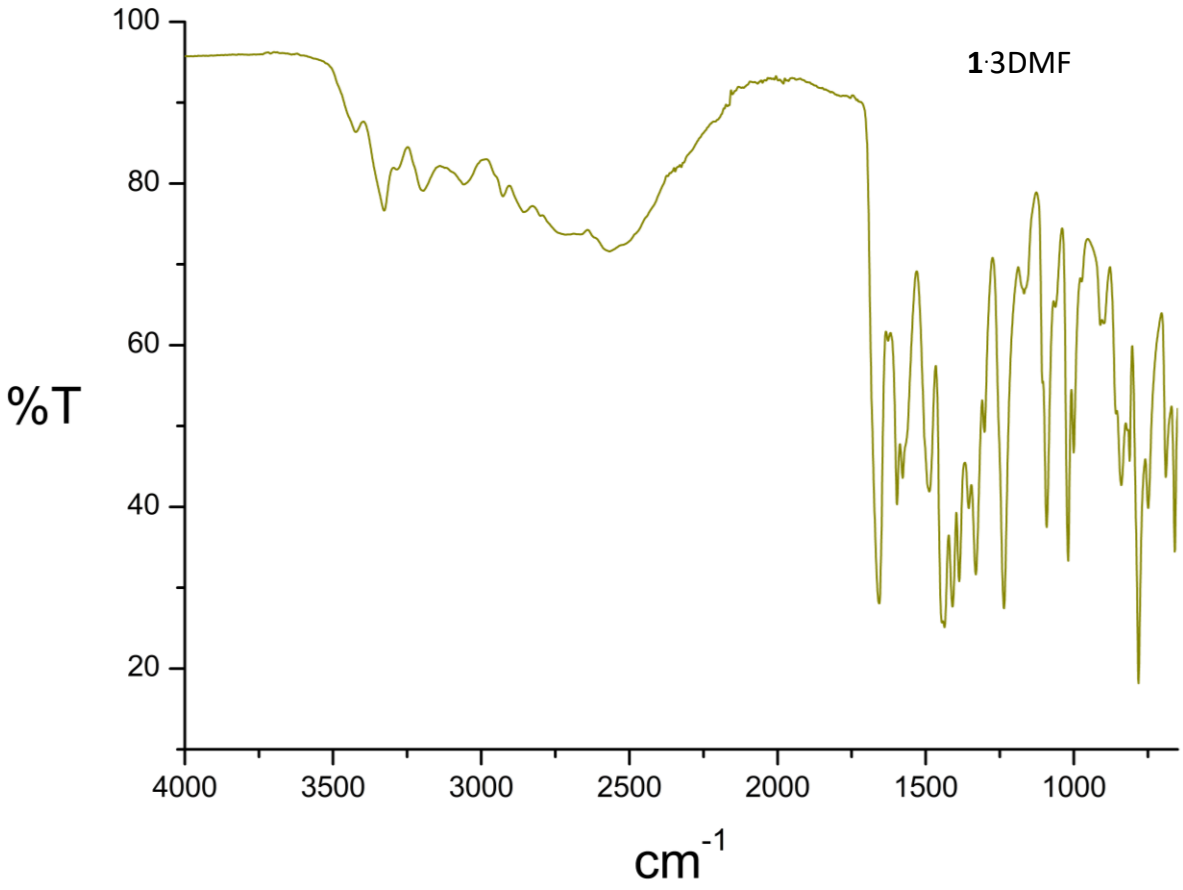

Fig. S11: IR spectrum of **1**•3DMF

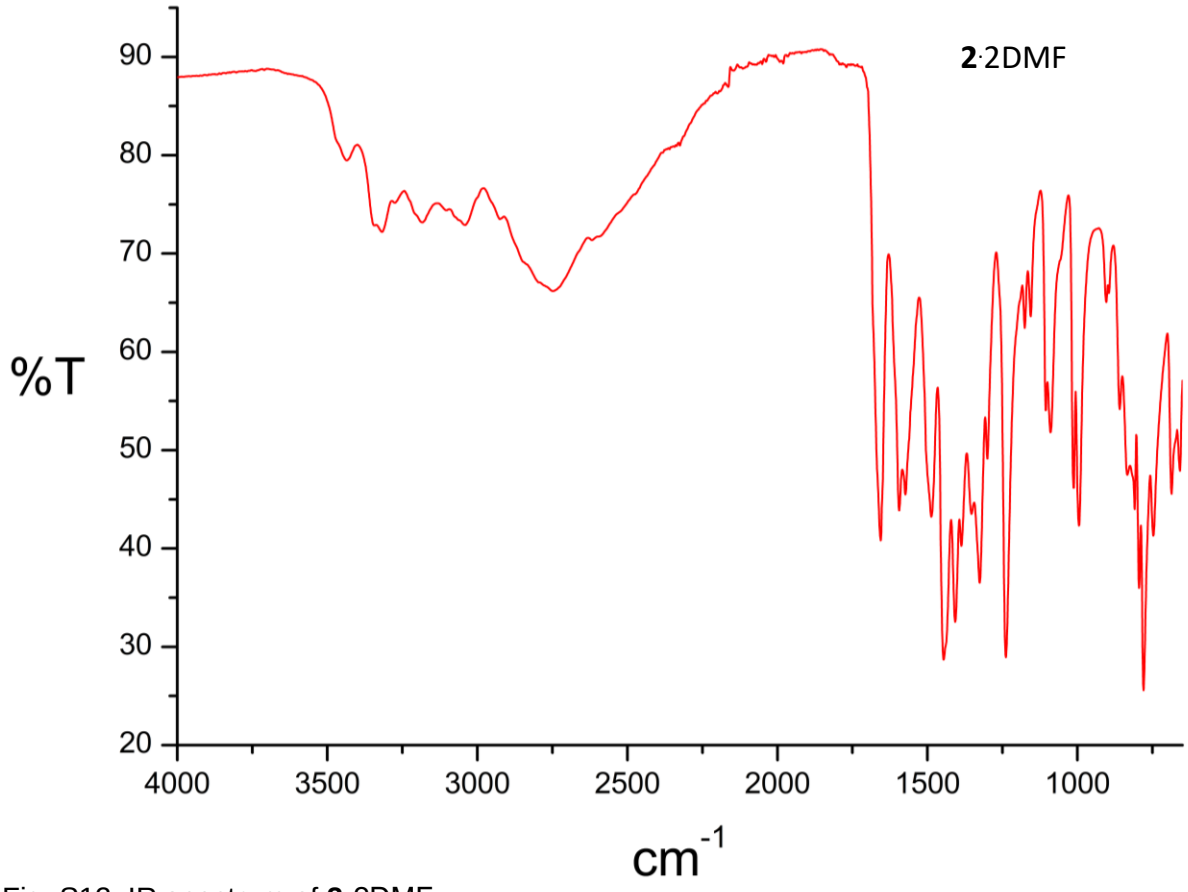

Fig. S12: IR spectrum of **2**•2DMF

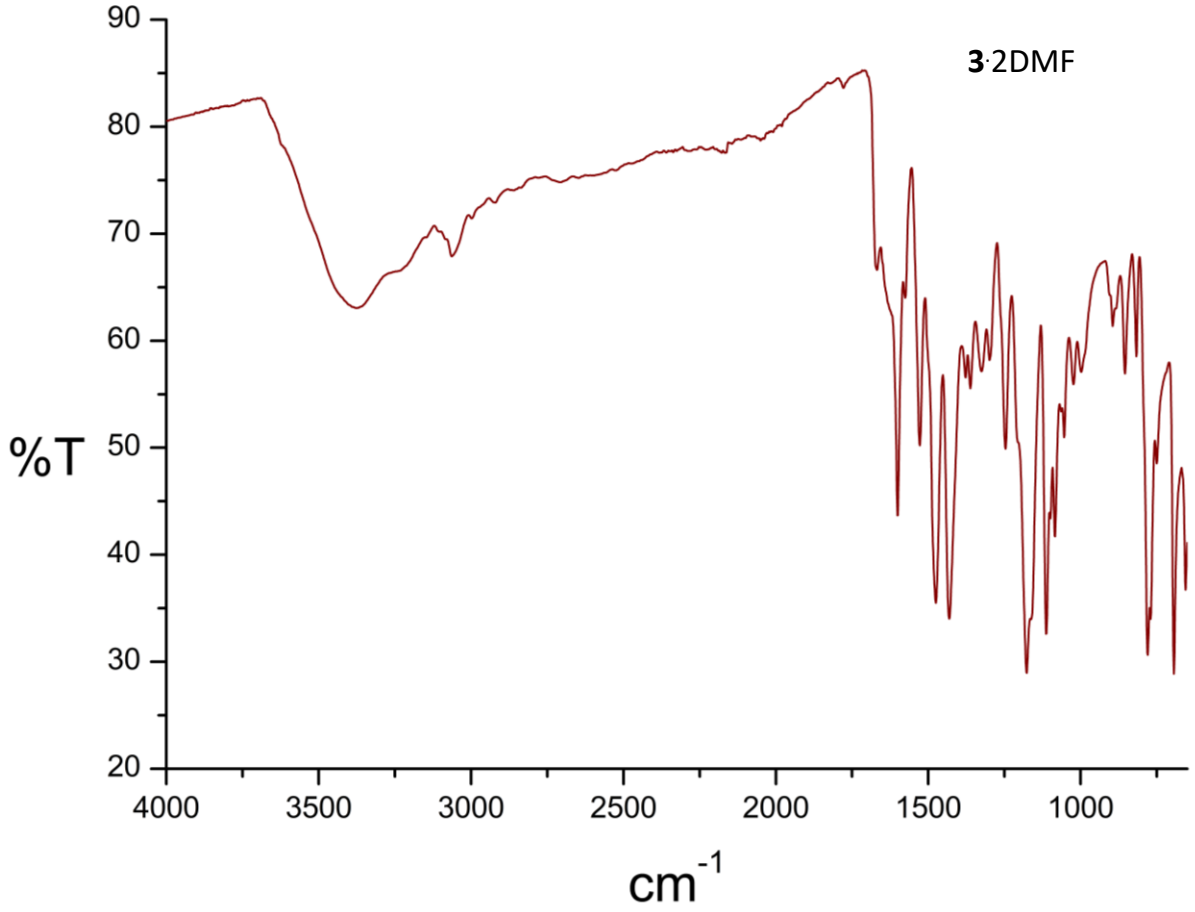

Fig. S13: IR spectrum of **3**•2DMF

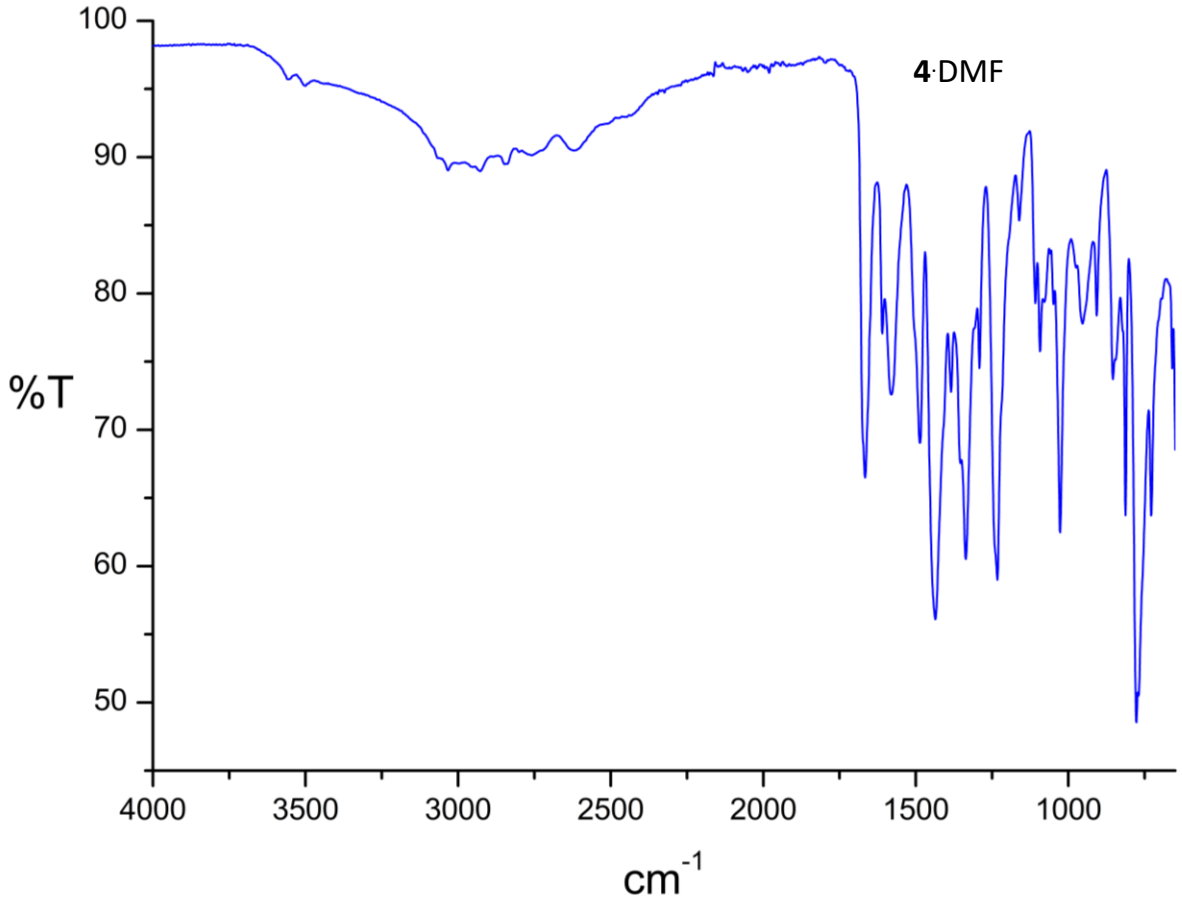

Fig. S14: IR spectrum of **4**•DMF

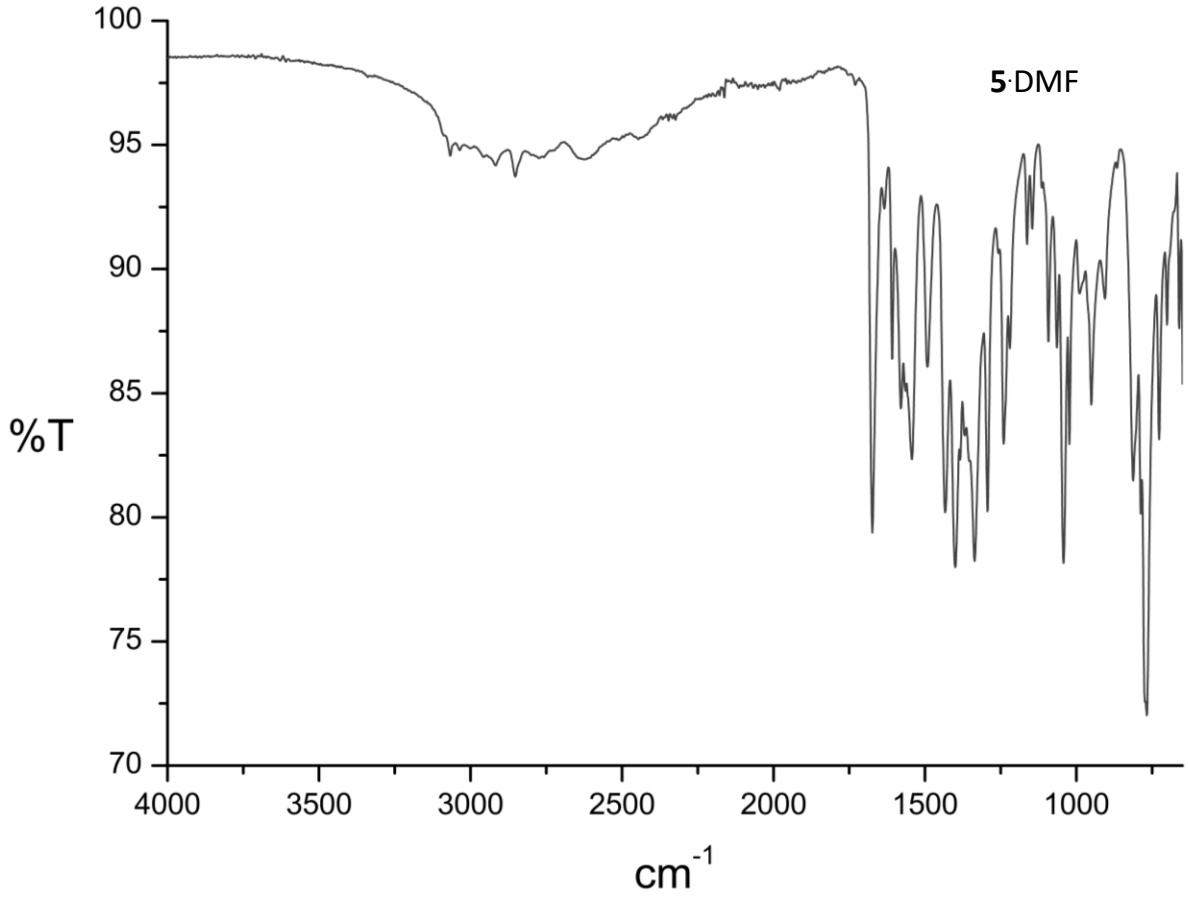

Fig. S15: IR spectrum of **5**•DMF

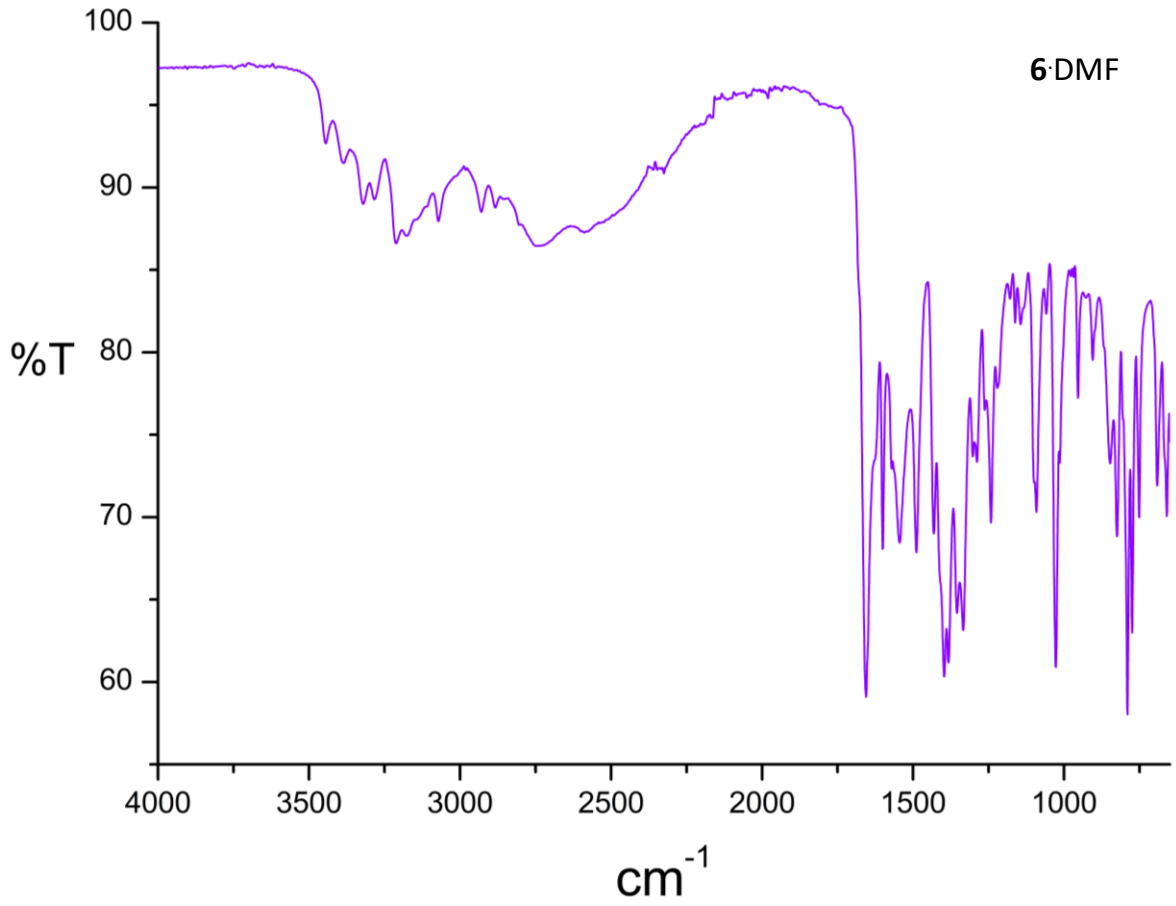

Fig. S16: IR spectrum of **6**•DMF

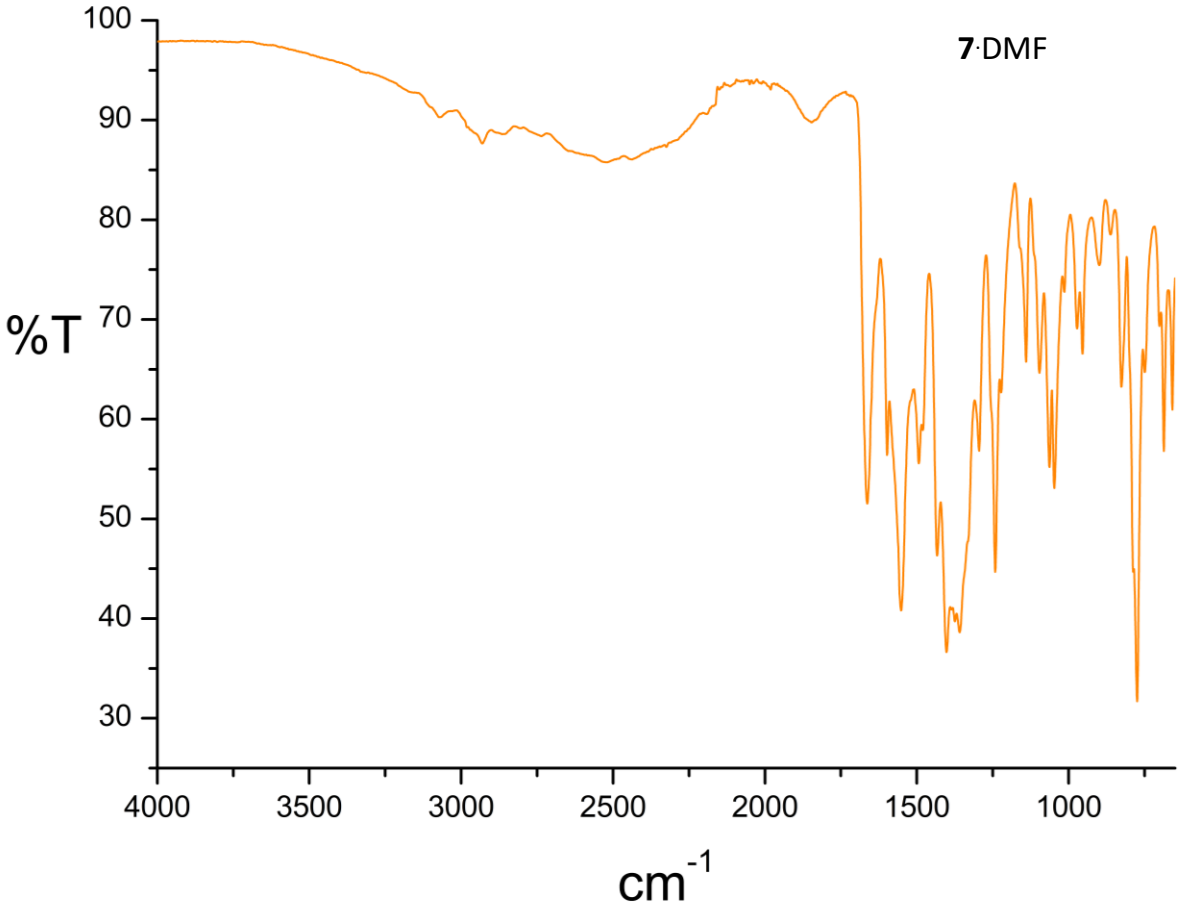

Fig. S17: IR spectrum of **7**•DMF

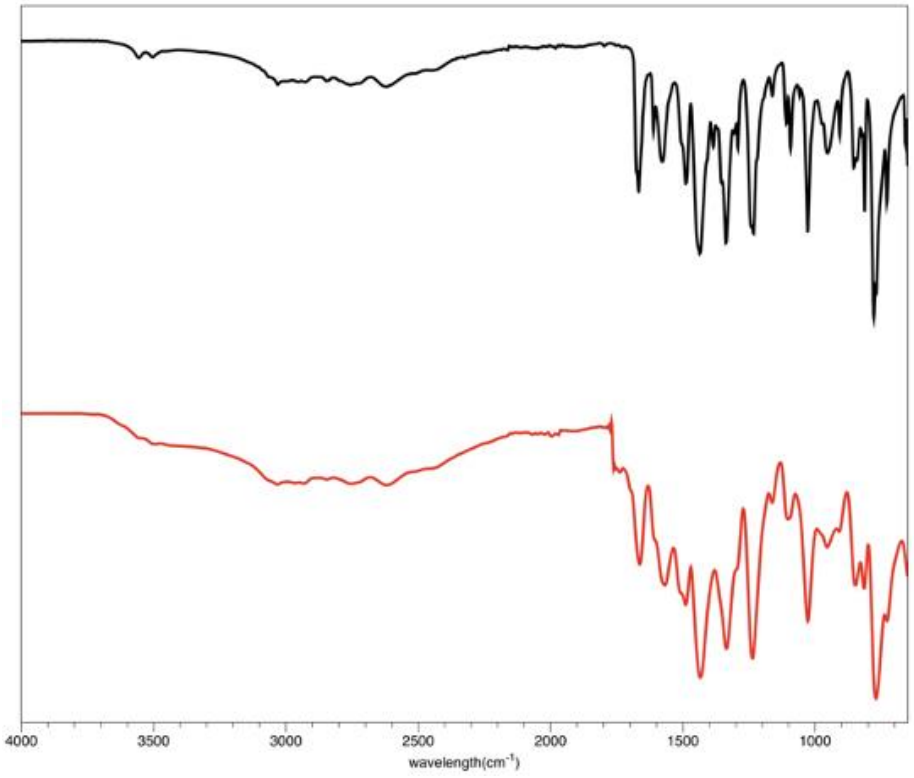

Fig. S18: IR spectrum of **4**•DMF before (top) and after (bottom) being stirred in EtOH for 100 h.

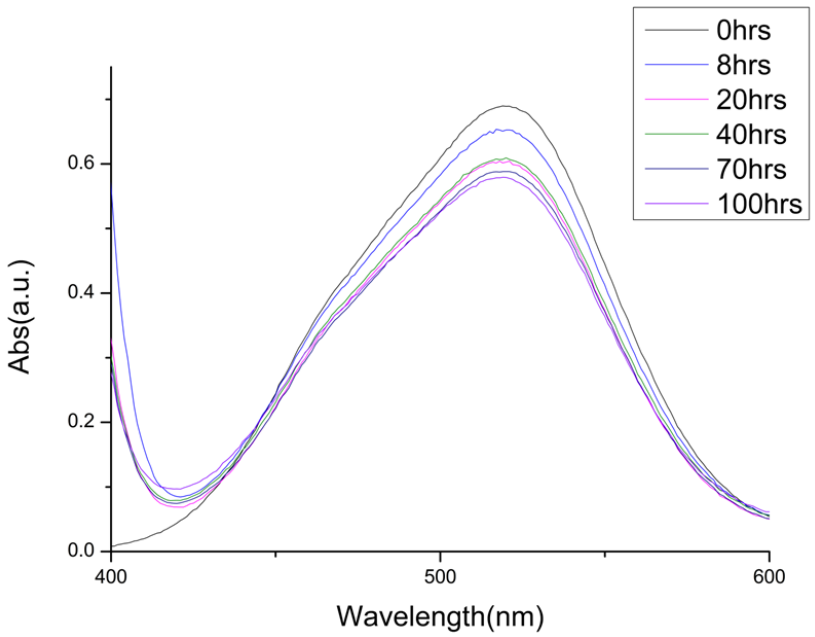

Fig. S19: UV-vis plots for Co@**4** encapsulation.

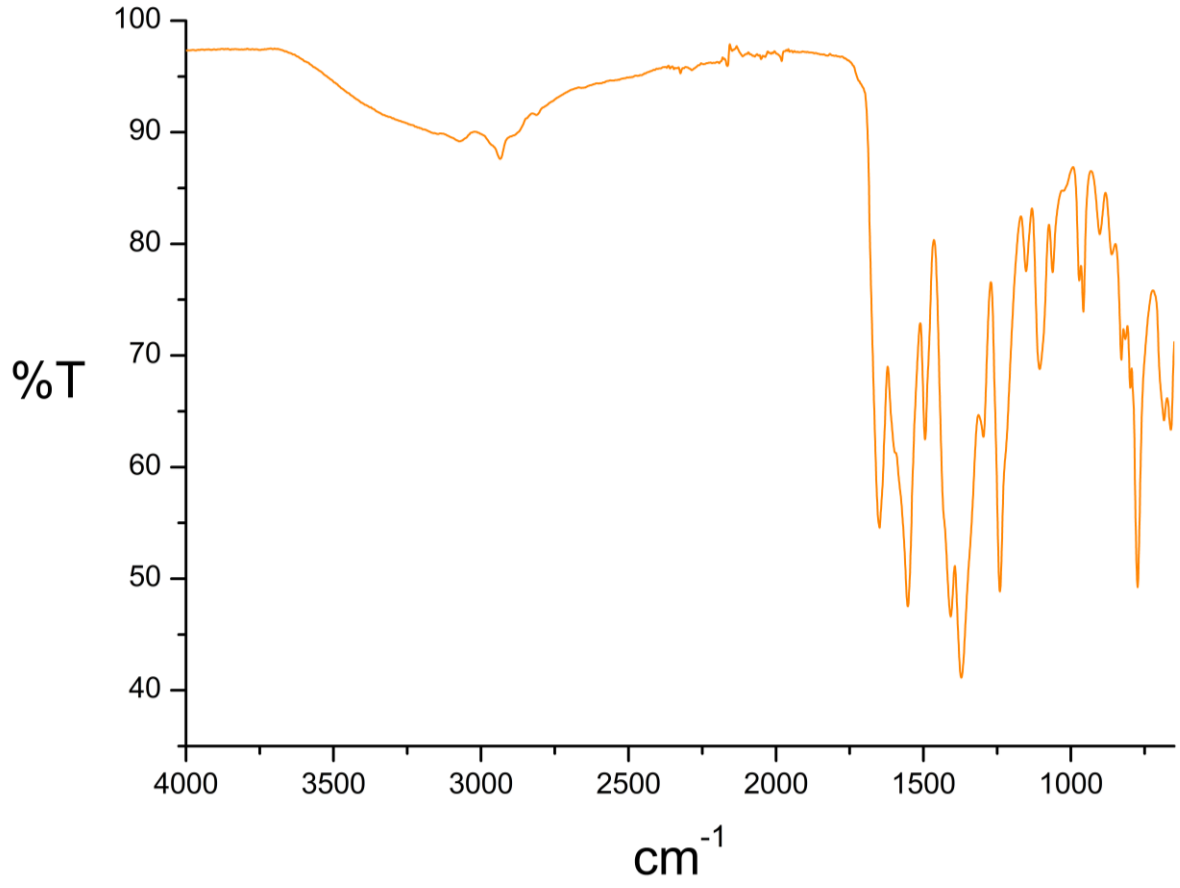

Fig. S20: IR spectrum of the product which has been derived by the reaction blend Hmpko:H_3MHBDC: $Zn(CH_3CO_2)_2.2H_2O$ in molar ratio 2:4:1. (excess of dicarboxylate).The product contains only the dicarboxylic linker.