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Excimer Formation In Crystalline and Nanostructured Coordination Polymers

Jing Chen[1]*, Antonia Neels*[2] *and Katharina M. Fromm*[1]***

1) Department of Chemistry, University of Fribourg
Chemin du Musée 9, CH-1700 Fribourg, Switzerland
Fax: (+) 41 263009738
E-mail: *katharina.fromm@unifr.ch*

2) CSEM, CH-2002 Neuchatel, Switzerland

1.) Supplementary Structural Information

Ligand L1

The structure of ligand L1 was first determined by single crystal x-ray diffraction, however on bad crystal quality (see table below). Details on powder determination is given below.

Table S1. Crystallographic Data and Structure Refinement Summary for ligand **L1**, complexes **1** and **2**.

Compond	**L1**	**1**	**2**
Empirical formula	$C_{28}H_{20}N_2O_4$	$Ag_3C_{84}H_{64}N_9O_{23}$	$AgC_{28}H_{20}N_3O_7$
Formula weight	448.46	1891.05	618.34
Crystal system	Monoclinic	Triclinic	Monoclinic
Space group	$P2_1/c$	P-1	$P2_1/c$
a (Å)	4.0224(8)	9.6132(19)	14.988(3)
b (Å)	19.576(4)	12.664(3)	12.305(3)
c (Å)	13.525(3)	16.763(3)	13.071(3)
α/°	90.00	74.32(3)	90.00
β/°	93.77(3)	87.31(3)	92.45(3)
γ /°	90.00	73.91(3)	90.00
V (Å^3)	1062.7(4)	1887.0(7)	2408.4(9)
Z	2	1	4
μ (Mo Kα, mm^{-1})	0.095	0.859	0.894
F(000)	468	956	1248
θ rang (degree)	1.83-25.61	3.16 - 24.60	1.36 - 25.62
h (range)	-4 to 4	-11 to 11	-18 to 18
k (range)	-23 to 23	-14 to 14	-14 to 14
l (range)	-16 to 16	-19 to 19	-15 to 15
reflns collected/unique	9269/1926	47427 / 6307	81220 / 4524
reflns obsd [$I > 2\sigma(I)$]	1314	5516	4318
GOF	1.401	1.122	1.129
R1, Rint	0.2098, 0.1732	0.0508, 0.0593	0.0279, 0.0296
wR1 , wR2	0.3722, 0.3933	0.1247, 0.1297	0.0689, 0.0698

Table S2. Hydrogen bonds for Complex **1**. [distances (Å) and angles (º)]

D-H···A	***d* (D-H)**	***d* (H···A)**	***d* (D···A)**	**Angle D-H···A**
C1-H1···O12	0.9500(0)	2.5900(0)	3.280(13)	129.697(44)
C2-H2···O13A	0.9500(0)	2.5700(0)	3.250(12)	128.274(38)
C5-H5···O7$^{\#1}$	0.9500(0)	2.5500(0)	3.072(8)	114.636(45)
C7-H7B···O2	0.9900(0)	2.3600(0)	2.726(7)	101.0(0)
C10-H10···O1	0.9500(0)	2.5500(0)	3.034(6)	112.0(0)
C22-H22A···O4	0.9900(0)	2.3000(0)	2.729(7)	105.0(0)
C25-H25···O8$^{\#2}$	0.9500(0)	2.3200(0)	3.071(10)	135.443(43)
C27-H27···O9$^{\#3}$	0.9500(0)	2.5800(0)	3.340(8)	136.717(37)
C28-H28···O6$^{\#4}$	0.9500(0)	2.5200(0)	3.183(8)	127.358(44)
C29-H29···O11$^{\#5}$	0.9500(0)	2.5013(6)	3.2606(7)	136.942(31)
C30-H30···O9$^{\#5}$	0.9500(0)	2.4400(0)	3.208(8)	137.887(49)
C32-H32···O11	0.9500(0)	2.5002(6)	3.2476(7)	135.584(42)
C35-H35A···O6	0.9900(0)	2.2900(0)	2.690(9)	103.0(0)
C38-H38···O5	0.9500(0)	2.4700(0)	2.997(6)	115.0(0)

[a] Symmetry transformations used to generate equivalent atoms : #1 3-x, -y, 1-z ; #2 x, y, -1+z ; #3 -1+x, y, -1+z ; #4 –x. 1-y, -z ; #5 1-x, 1-y, 1-z.

Table S3. Hydrogen bonds for Complex **2**. [distances (Å) and angles (º)]

D-H···A	***d* (D-H)**	***d* (H···A)**	***d* (D···A)**	**Angle D-H···A**
C1-H1···O6	0.9500(0)	2.4700(0)	3.200(3)	134.0(0)
C4-H4···O3$^{\#1}$	0.9500(0)	2.5761(1)	3.4295(10)	149.640(22)
C5-H5···O5$^{\#2}$	0.9500(0)	2.5300(0)	3.286(3)	136.863(21)
C7-H7A···O7$^{\#3}$	0.9900(0)	2.4200(0)	3.036(3)	119.547(18)
C20-H20···O2	0.9500(0)	2.4900(0)	2.998(3)	113.0(0)
C22-H22A···O2$^{\#4}$	0.9900(0)	2.5700(0)	3.506(3)	157.528(11)
C25-H25···O1$^{\#5}$	0.9500(0)	2.3000(0)	3.170(3)	151.773(22)
C27-H27···O5$^{\#6}$	0.9500(0)	2.5500(0)	3.284(3)	133.734(18)

[a] Symmetry transformations used to generate equivalent atoms: # 1; 1+x, y, z ; #2 1–x, 1-y, -1-z ; #3 x, y, 1+z ; #4–x, 1-y, -z ; #5 -1+x, y, z ; #6 –x, 1-y, 1-z.

X-ray powder diffraction studies for L1

The small amount of the powder sample was measured between X-ray transparent foils and the X-ray powder data were collected on a computer controlled STOE-STADIP focusing powder diffractometer (Wolfel, 1981) equipped with a curved Ge(111) monochromator, where the $CuK_{\alpha}1$-line could be well separated (λ=1.5404Å). A STOE linear position sensitive detector (Wolfel, 1983) was used. The compound was measured in the range of 2° ≤ 2θ ≤ 90° using a step width of 0.01°. The indexing procedure was performed using ITO (Visser, 1969) in the program WinXPow (Stoe & Cie GmbH, Darmstadt, Germany (1997). The structural model obtained from a very poor single crystal structure was used for Rietveld refinement in GSAS/EXPGUI (Larson, Von Dreele, 2000; Toby, 2001). After the initial refinement of the scale, and unit cell constants, the atomic positions were refined using soft constraints defining the geometry of the molecule within some allowable errors (Internation Tables for X-ray Crystallography, Vol. C, 1999). Subsequent Rietveld refinement was carried out using gradually relaxing bond restraints. All non-hydrogen atoms were refined isotropically applying an overall temperature factor for all carbon atoms and all nitrogen and oxygen atoms. The temperature factor of the H-atoms was fixed. In the final cycles of refinement, the shifts in all parameters were less than their estimated standard deviations. Neutral atom scattering factors were used for all atoms. No corrections were made for anomalous dispersion or absorption effects.

References:

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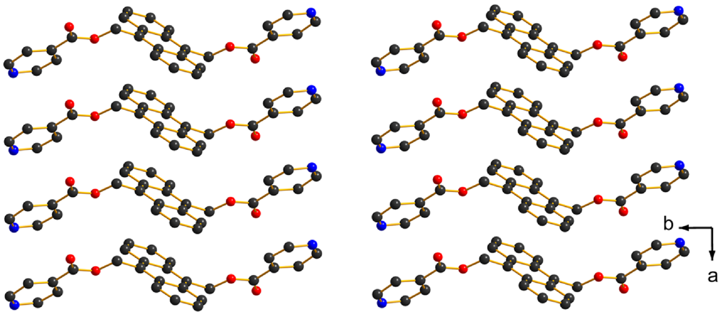
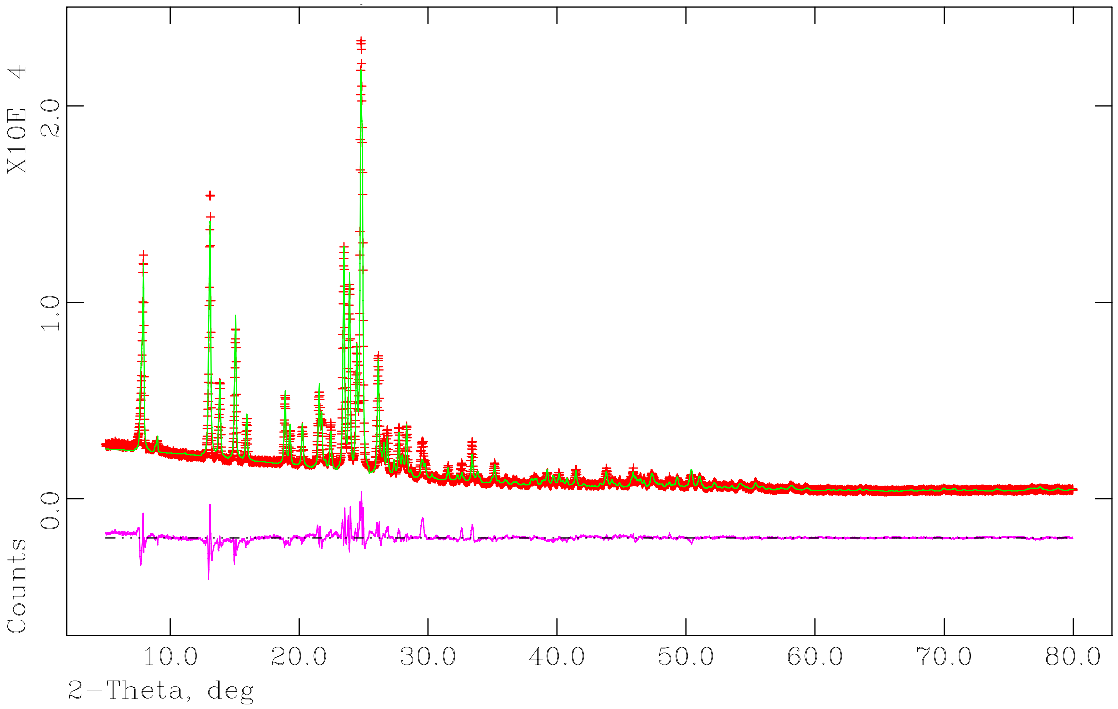
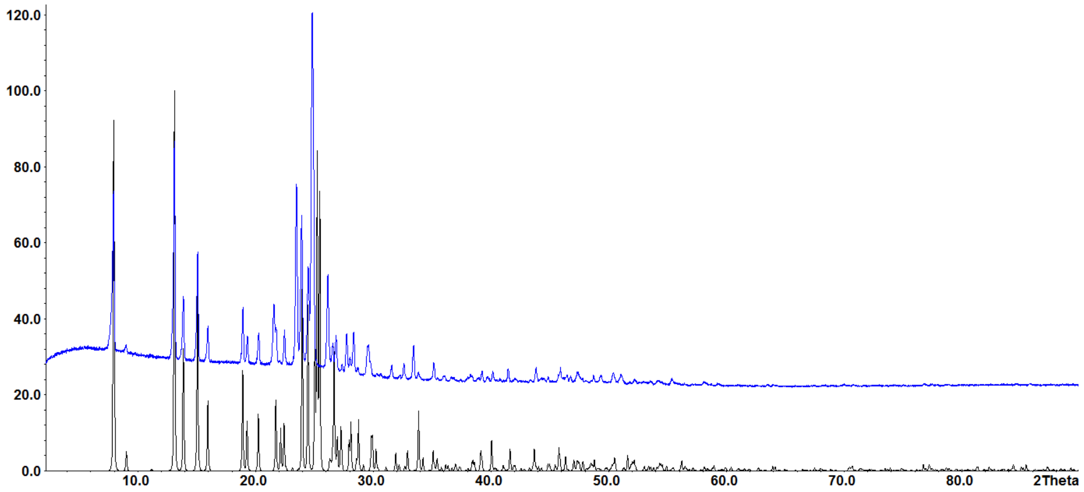


SFig. 1. Packing in the crystal structure of L1 from the XRD powder data, H atoms are omitted.



SFig. 2. The final Rietveld plot, the bottom curve shows the difference between measured (+) and calculated (-) data.

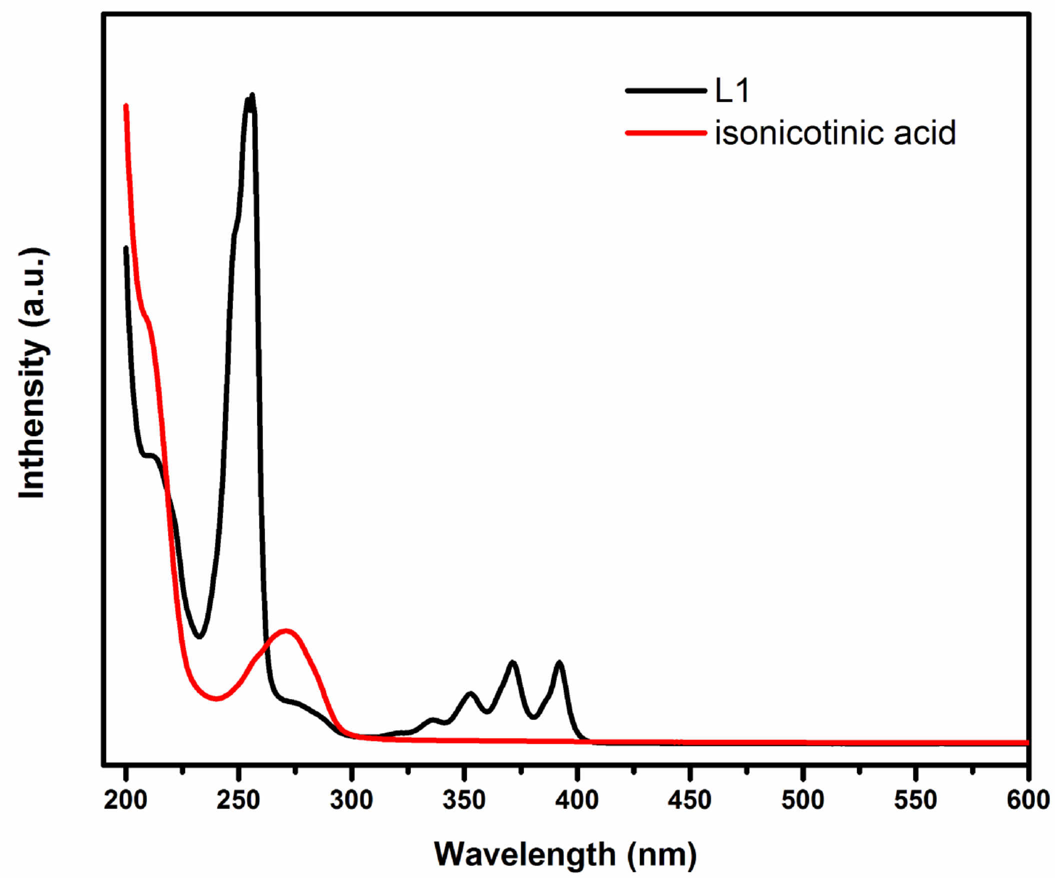


SFig. 3. XRD powder pattern of **L1** (blue) with the generated powder diffraction pattern of the single crystal structure of **L1** (black).

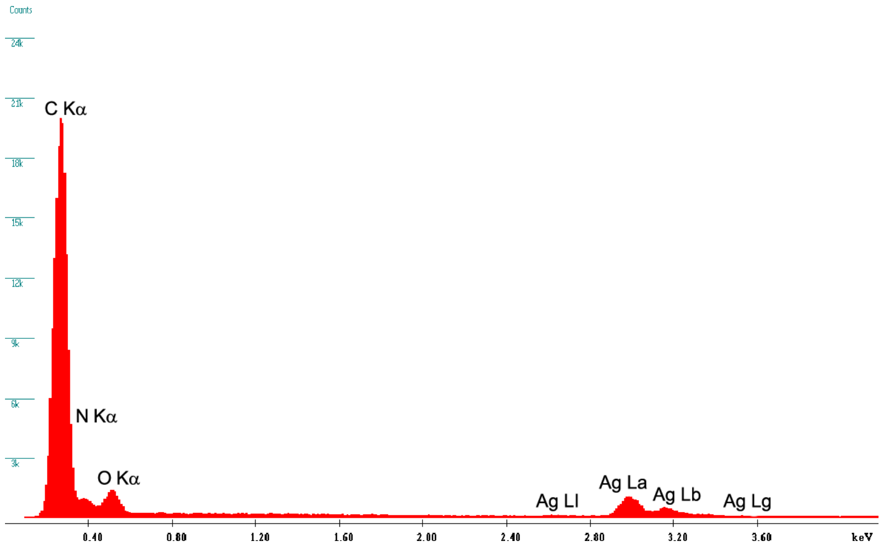
Table S4. Comparing the structures of **L1** between XRD data from single crystal and from powder.

Compond	**Single crystal**	**Powder**
Empirical formula	$C_{28} H_{20} N_2 O_4$	$C_{28} H_{20} N_2 O_4$
Formula weight	448.46	448.46
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/c$	$P2_1/c$
a (Å)	4.0224(8)	4.12360(14)
b (Å)	19.576(4)	19.5132(10)
c (Å)	13.525(3)	13.4955(8)
α/°	90.00	90.0
β/°	93.77(3)	94.2311(25)
γ /°	90.00	90.0
V (Å^3)	1062.7(4)	1082.95(12)
Z	2	2
Angle between Anthracene plane (°)	0	0
centroid-centroid distance Distance	4.0224	4.1236
between Anthracene plane (Å)	3.4003	3.5334
Offset (Å)	2.1489	2.1259

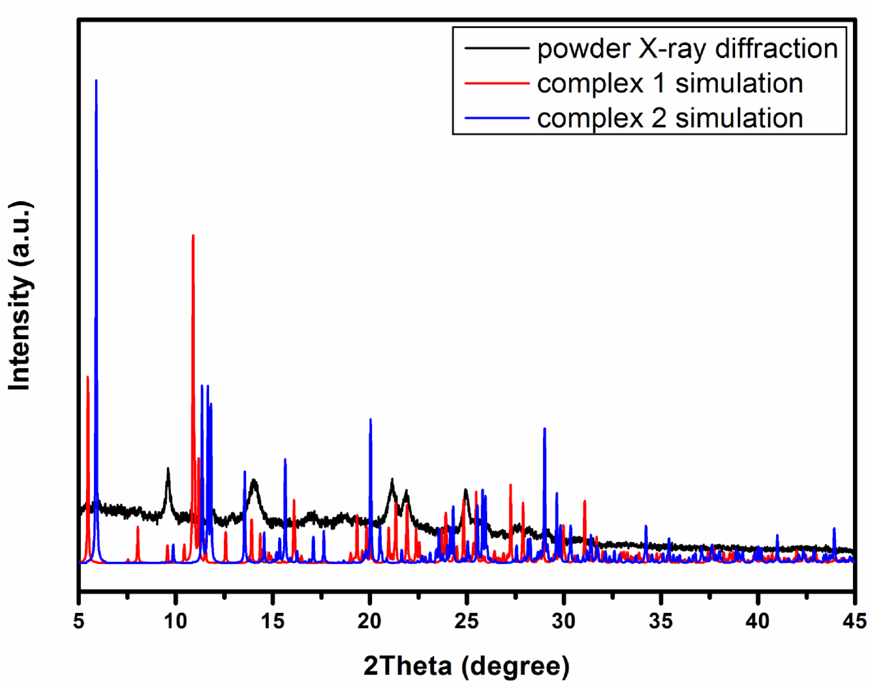
2.) Absorption spectrum of ligand L1



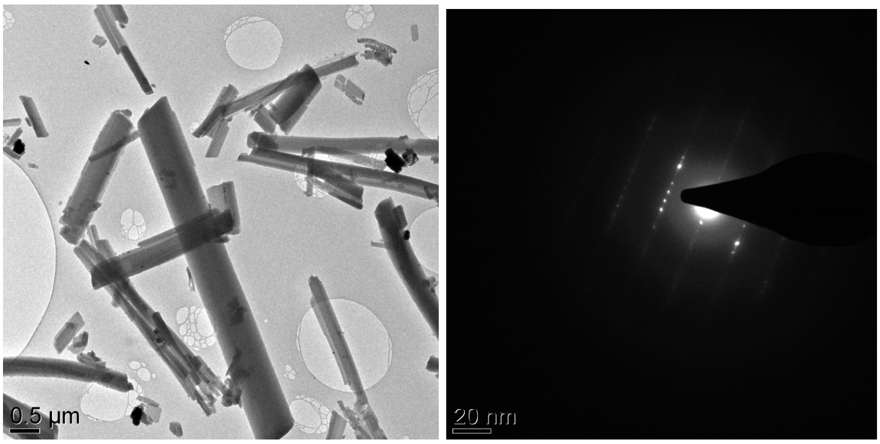
3.) Additional Information on Nanowires



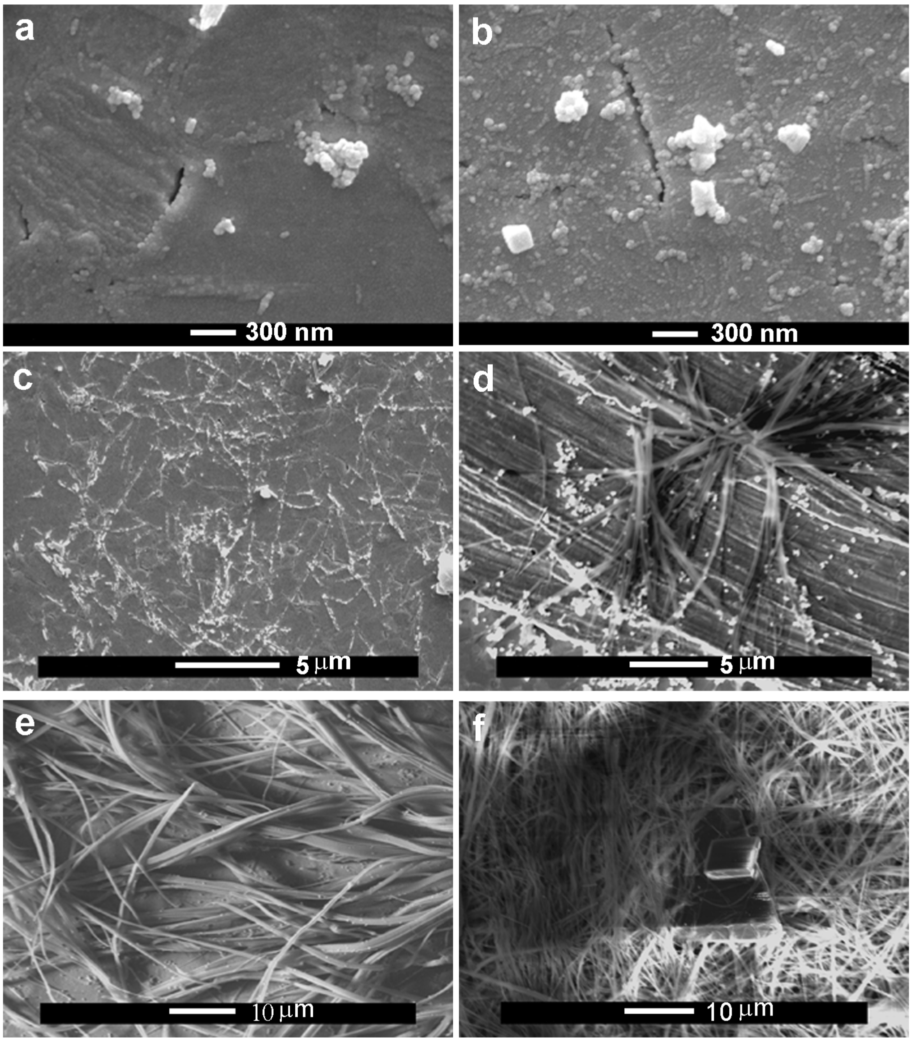
SFig. 4. Typical EDX analysis of the nanowires, which indicate the nanowires contains elements of C, N, O and Ag.



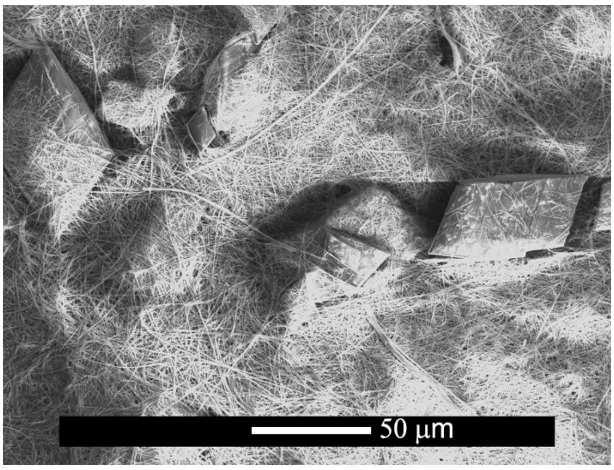
SFig. 5. XRD pattern of the nanowires formed in CH_2Cl_2/EtOH solution.



SFig. 6. TEM images for the nanowires (left), SAED patterns of a single nanowire (right).



SFig. 7. SEM images of the polymers obtained at different time in ethanol/ dichloromethane: a) 3days; b) 7days; c) 10 days; d) 13 days; e) 30 days; f) 40 days.



SFig 8. SEM images of the nanowires with complex **2** formed after 50 days in CH_2Cl_2/EtOH solution.