Electronic Supplementary Material (ESI) for Journal of Materials Chemistry C.

Electronic supplementary information for the manuscript:

"Design of indigo derivatives as environment-friendly organic semiconductors for sustainable organic electronics"

I. V. Klimovich,[a] L. I. Leshanskaya,[a] S. I. Troyanov,[b] D. V. Anokhin,[a,c] D. V. Novikov,[a,d] A. A. Piryazev,[c] N. N. Dremova,[a] and P. A. Troshin[a]

Contents

Additional Experimental Details

Synthesis of substituted nitrobenzaldehydes

The precursor aldehydes were prepared using procedures previously reported in the literature: 4-bromo-2-nitrobenzaldehyde (CAS: 5551-12-2)[1], 5-bromo-2-nitrobenzaldehyde (CAS: 20357-20-4)[1], 4-chloro-2-nitrobenzaldehyde (CAS: 5551-11-1)[2], 5-chloro-2-nitrobenzaldehyde (CAS: 6628-86-0)[3], 4-Fluoro-2-nitrobenzaldehyde (CAS: 2923-96-8)[4], 5-Fluoro-2-nitrobenzaldehyde (CAS: 395-81-3)[5], 4-formyl-3-nitro- benzonitrile (CAS: 90178-78-2)[6], 4-(trifluoromethyl)-2-nitrobenzaldehyde (CAS: 109466-87-7)[7].

Synthesis of 4,5-difluoro-2-[(N-carboxymethyl)amino] benzoic acid

4,5-difluoro-2-bromobenzoic acid (5.00 g, 21 mmol) was placed in a 100 mL round bottom flask and a solution of 85% KOH (0.66 g, 21 mmol) in 5 mL of H_2O was added under stirring. Then glycine (3.15 g, 42 mmol) was added to the homogeneous slurry followed by copper powder (0.113 g, 2.1 mmol) and cuprous iodide (0.158 g, 0.8 mmol). The reaction flask was immersed into an oil bath at 60 °C and potassium carbonate (2.90 g, 21 mmol) was added. The reaction mixture became blue and a thick precipitate appeared. A portion of 16 mL of deionized H_2O was added and the reaction mixture was stirred for additional 90 min. Afterwards, the mixture was quenched with 63 mL of H_2O and acidified to pH=1 with 10 mL of 32% HCl. This resulted in intense foaming and appearance of a thick precipitate. The mixture was extracted with 300 mL of ethyl ether in 5 portions, and the combined organic extracts were washed with 30 mL of H_2O, 4 × 5 mL of 5% aqueous solution of disodium salt of EDTA, 10 mL of saturated aqueous NaCl and dried with magnesium sulfate. Evaporation of the solvent at 35 ºC gave crude product (2.56 g, 94% yield) as a white solid. ^{1}H NMR (DMSO-D6): δ= 4.00 (s, 2H), 6.68 (dd, J = 6.8, 13.7 Hz, 1H), 7.71 (dd, J = 9.5, 11.5 Hz, 1H), 8.14 (b, 1H), ~12.9 (b, 1H) ppm. ^{13}C NMR (DMSO-D6): δ= 43.53 (s),100.31 (d, J = 21.4 Hz), 106.1 (s), 119.44 (d, J = 17.8 Hz), 139.80 (dd, J = 233.4, 11.5 Hz), 148.43 (d, J = 10.5 Hz), 153.82 (dd, J = 250.24, 13.2 Hz), 168.12 (s), 171.55 (s) ppm.

Synthesis of 5,6-difluoro-N,O-diacetylindoxyl. A portion of 4,5-difluoro-2-[(N-carboxymethyl)amino] benzoic acid (3.00 g, 13 mmol) was dissolved in 20 mL of redistilled acetic anhydride in a 50 mL round bottom flask with a gentle warming. Then anhydrous sodium acetate (1.39 g, 17 mmol) was added and the flask was immersed into an oil bath preheated to 135-137 ºC. The solids readily dissolved, the mixture turned a cloudy yellowish brown and evolution of gas was observed. The cloudiness disappeared and evolution of gas stopped in 10–15 min. The mixture was allowed to cool to a room temperature and a yellowish precipitate appeared. This precipitate was filtered off, washed with a solution of sodium acetate (0.6 g) in 5 mL of acetic acid, and dissolved in 15 mL of ice cold H_2O. The aqueous solution was extracted with diethyl ether (3x50 mL) and combined organic extracts were dried over anhydrous magnesium sulfate. Concentration of this solution at the rotary evaporator to dryness produced 2.59 g of the title product (yield 76%).
^{1}H NMR ($CDCl_3$): δ= 2.38 (s, 3H), 2.60 (s, 3H), 7.30 (dd, J = 7.66, 9.6 Hz, 1H), 7.74 (s, 1H), 8.36 (dd, J = 6.9, 11.1 Hz, 1H) ppm.

References:

1 G. Voss and H. Gerlach, *Chem. Ber.*, 1989, **122**, 1199;
2 M. R. Naffziger et al., *JOC*, 2007, **72**, 9857–9865;
3 L. Gavara et al., *Tetrahedron*, 2010, **66**, 7544–7561;
4 Patent WO2006059164A2, 2006-06-08;
5 G. G. Rajeshwaran and A. K. Mohanakrishnan, *Org. Lett.*, 2011, **13**,1418–1421;
6 D. A. Patrick et al., *J. Med. Chem.*, 2007, **50**, 2468-2485;
7 M. C. Wani et al., *J. Med. Chem.*, 1987, **30**, 1774-1779

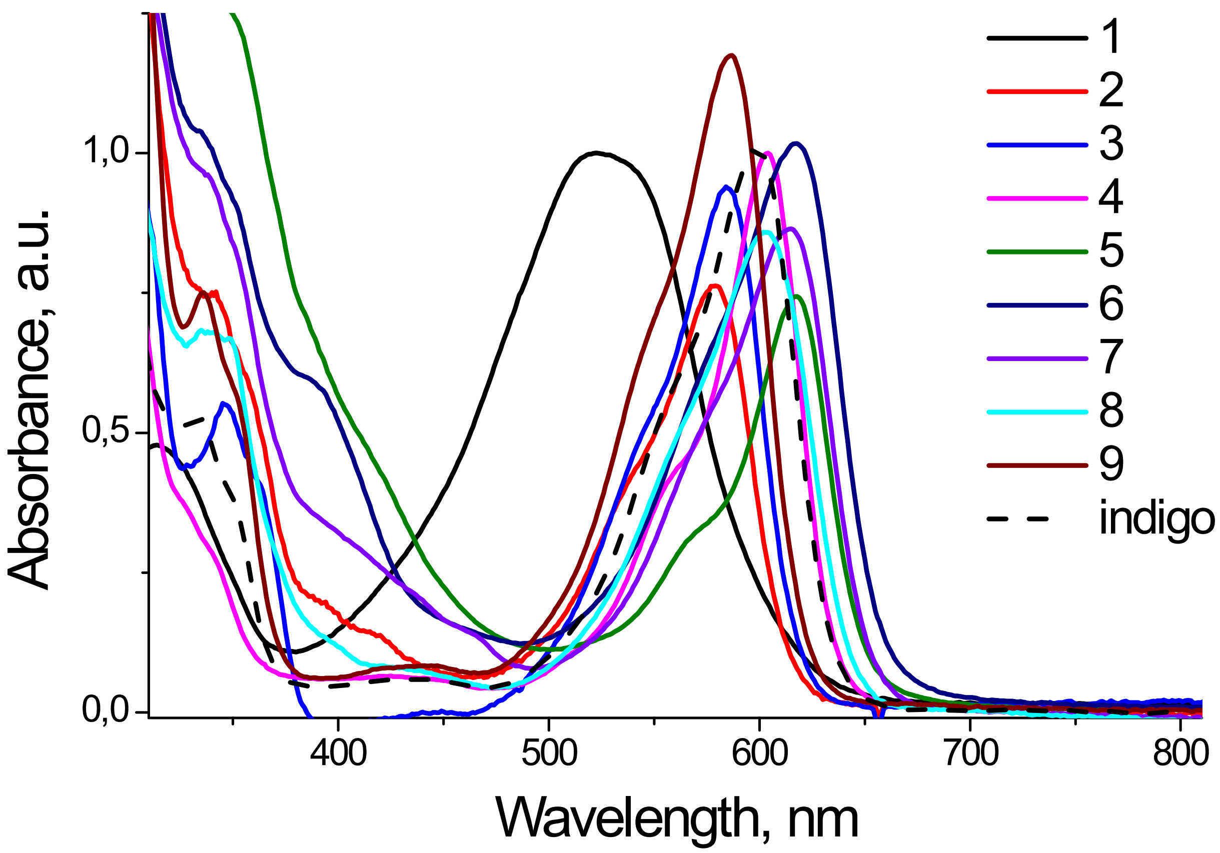


Figure S1 Absorption spectra of indigoids **1-9** in 1,2-dichlorobenzene

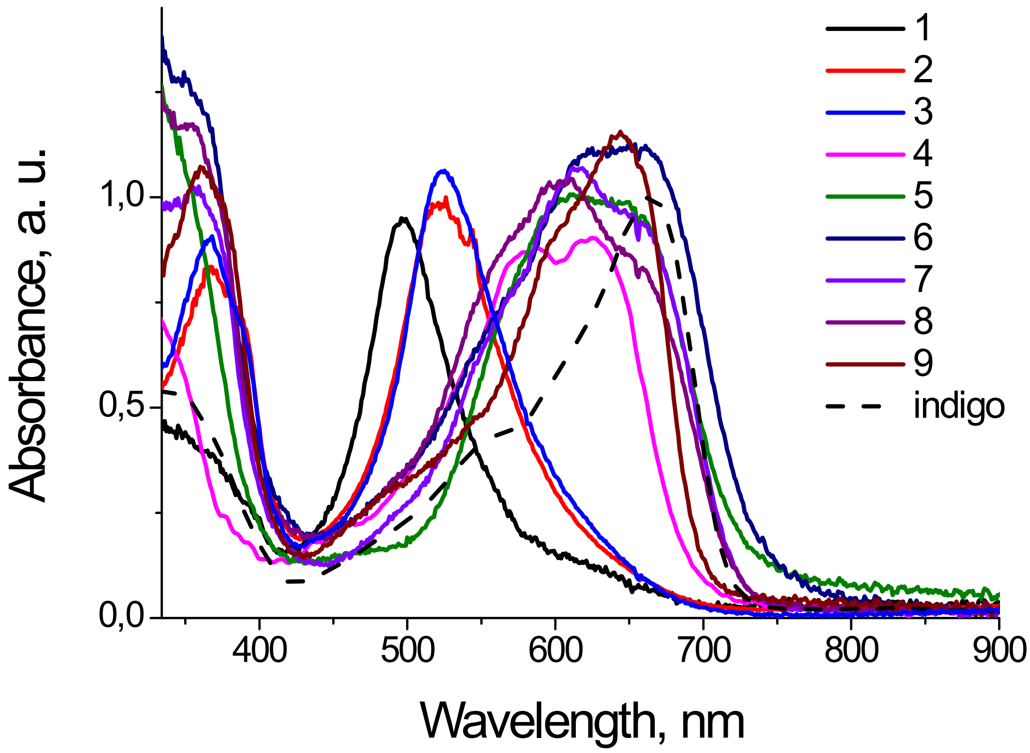


Figure S2 Absorption spectra of thin films of indigoids **1-9**

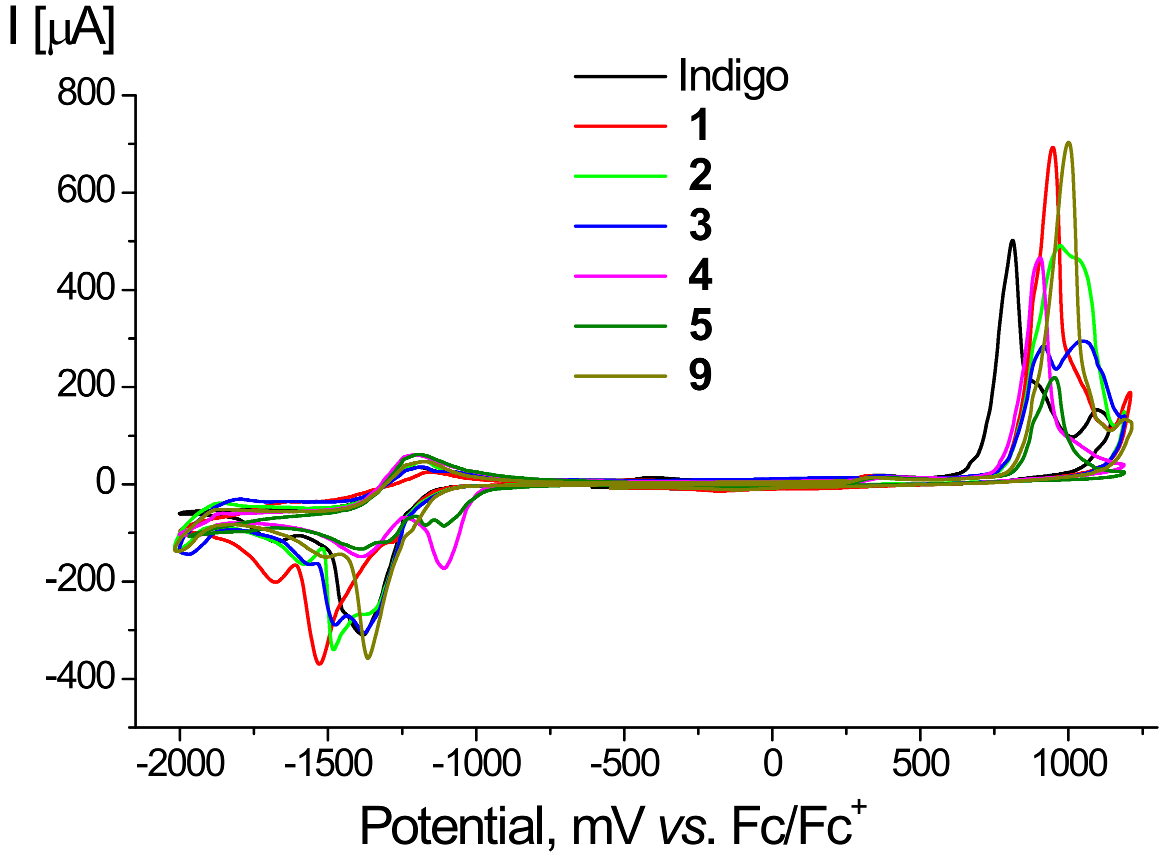


Figure S3 Cyclic voltammograms of indigoids **1-5** and **9**

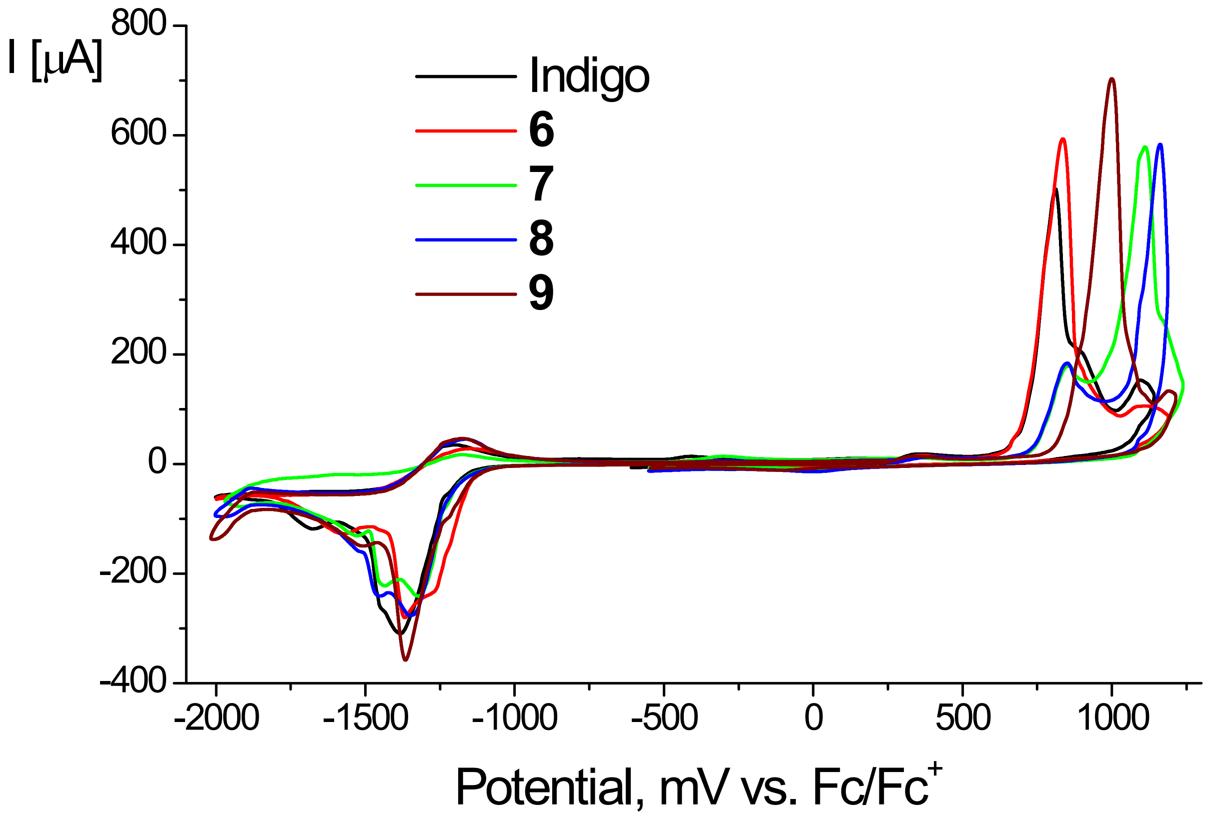


Figure S4 Cyclic voltammograms of indigoids **6-9**

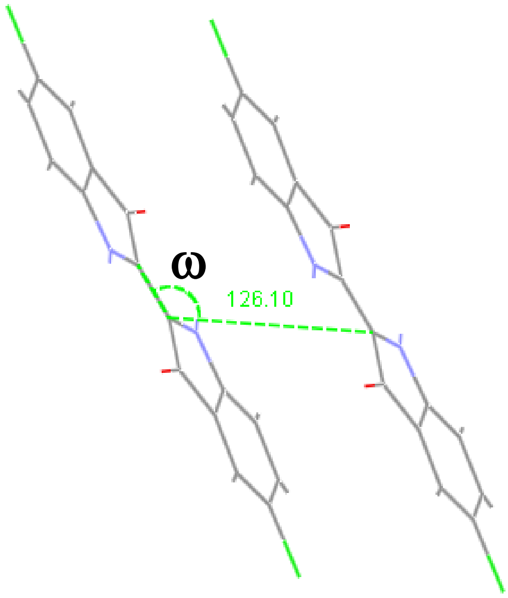


Fig. S5. Definition of the “shift angle” ω

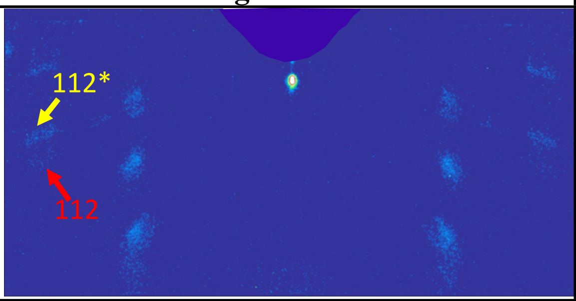
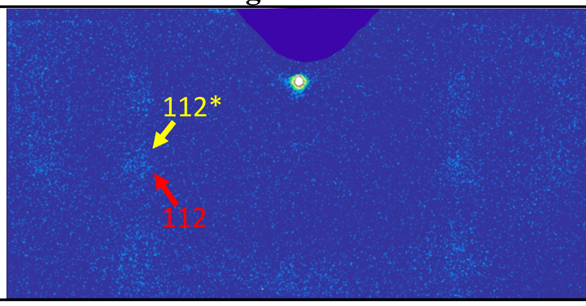
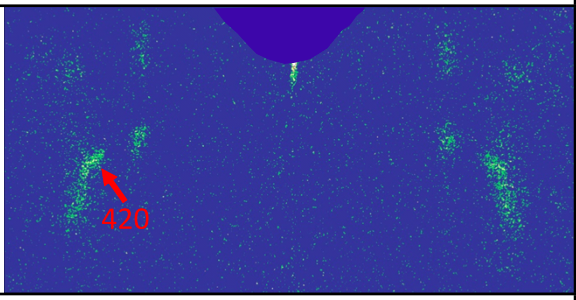
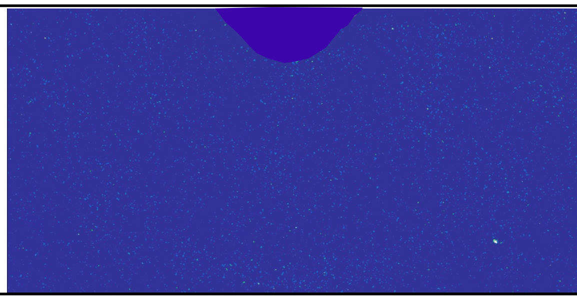
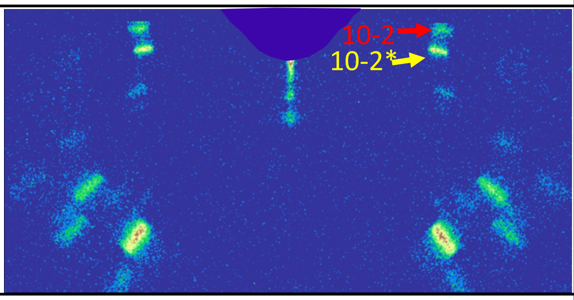
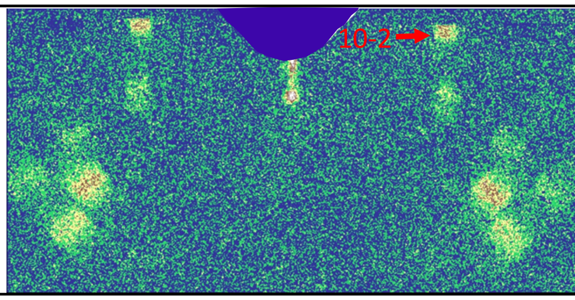
Indigoid	Films grown on TC	Films grown on BCB
3		
4		
9		

Fig. S6. GIWAXS patterns for thin films of indigoids **3**, **4** and **9** grown on TC and BCB. Arrows indicate reflections corresponding to the π-π stacking distance in the bulk (red) and surface (yellow) structure.

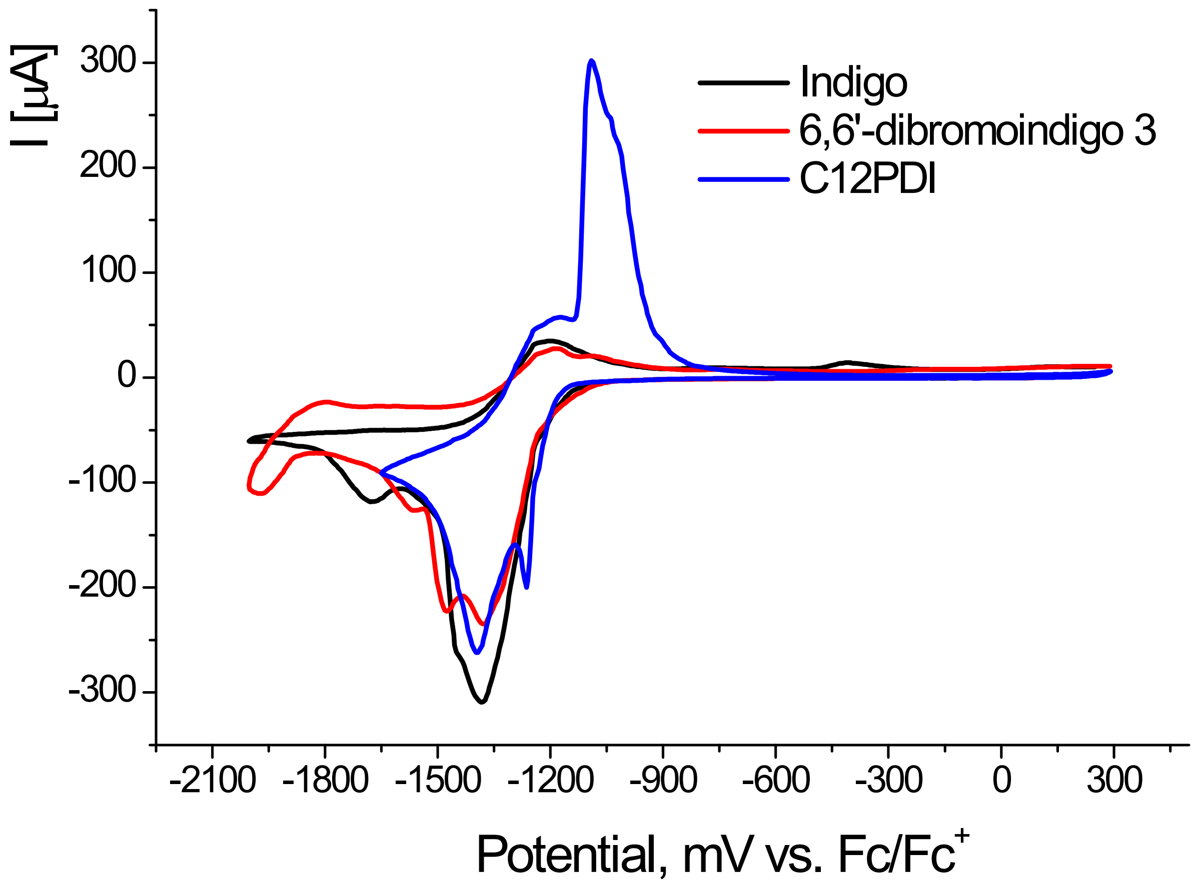


Figure S7 Cyclic voltammograms of indigo, 6,6’-dibromoindigo and C12PDI obtained under the same conditions

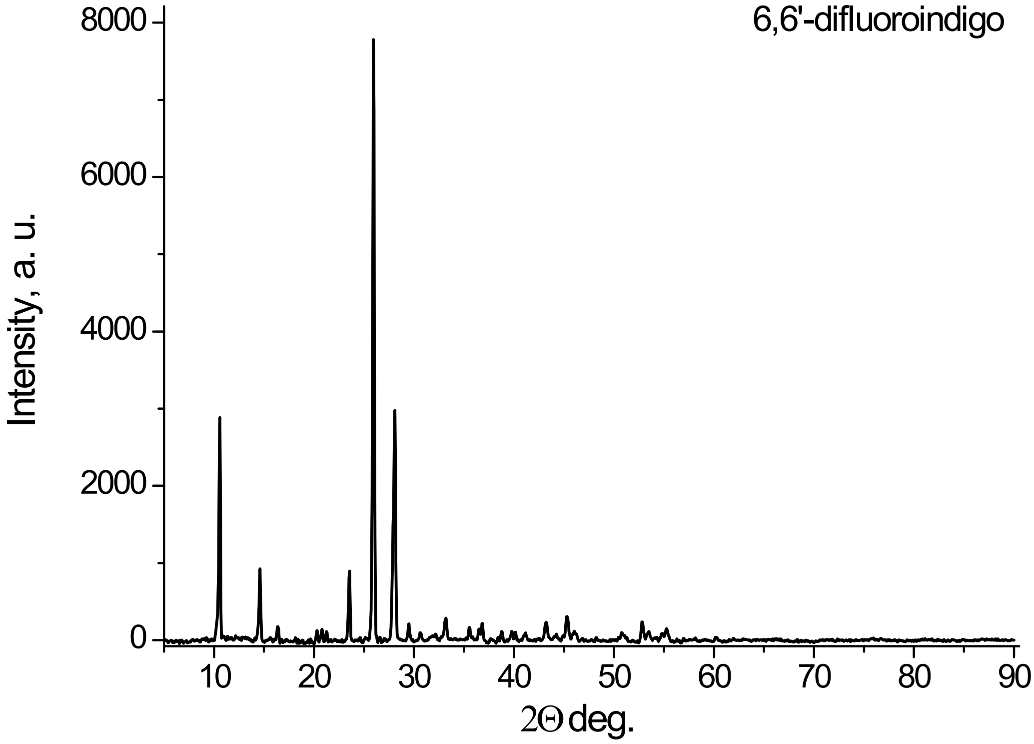


Fig. S8. Powder XRD pattern of indigoid **1**.

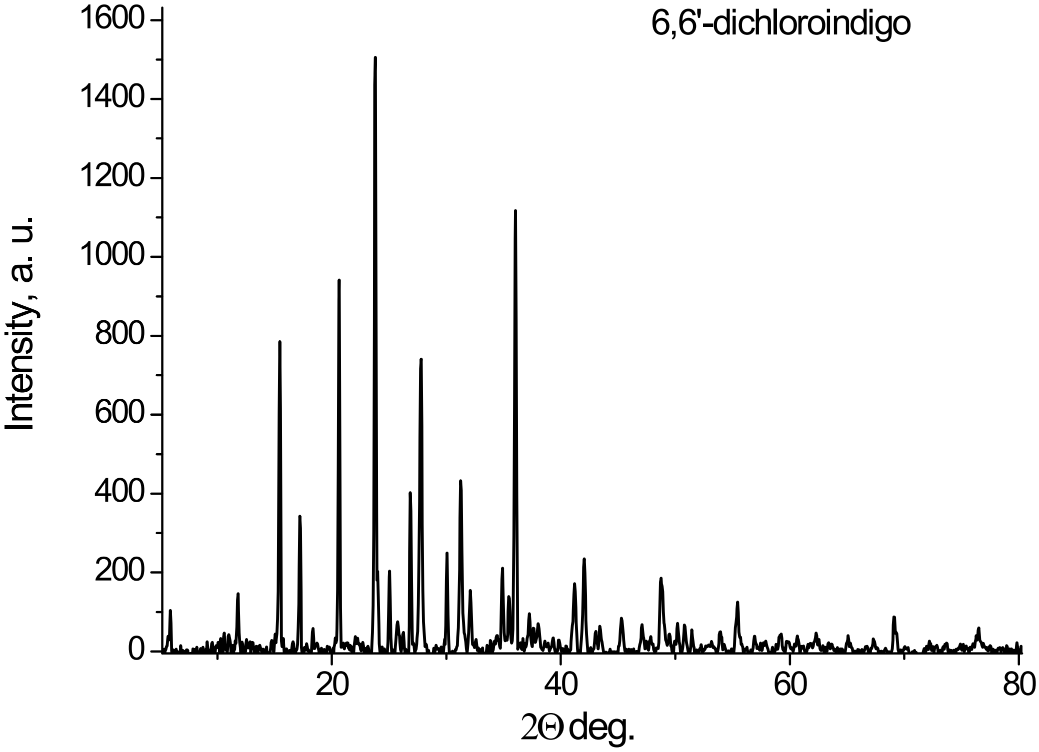


Fig. S9. Powder XRD pattern of indigoid **2**.

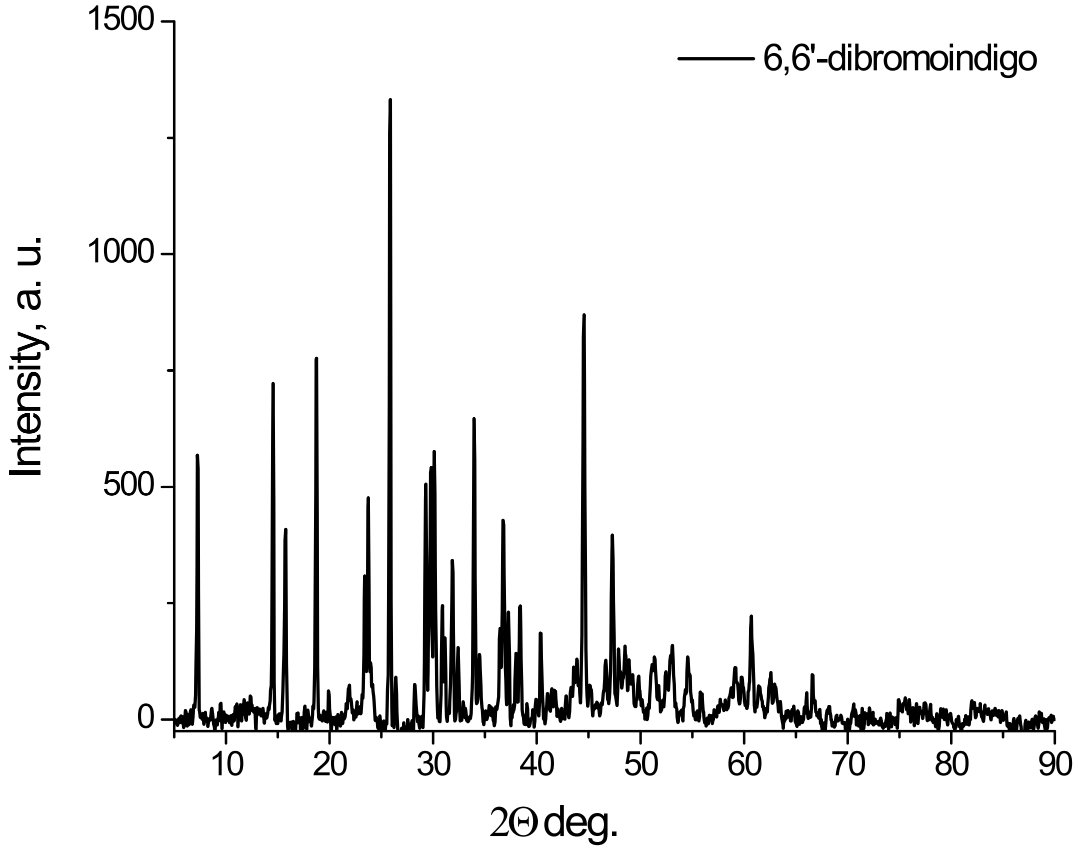


Fig. S10. Powder XRD pattern of indigoid **3**.

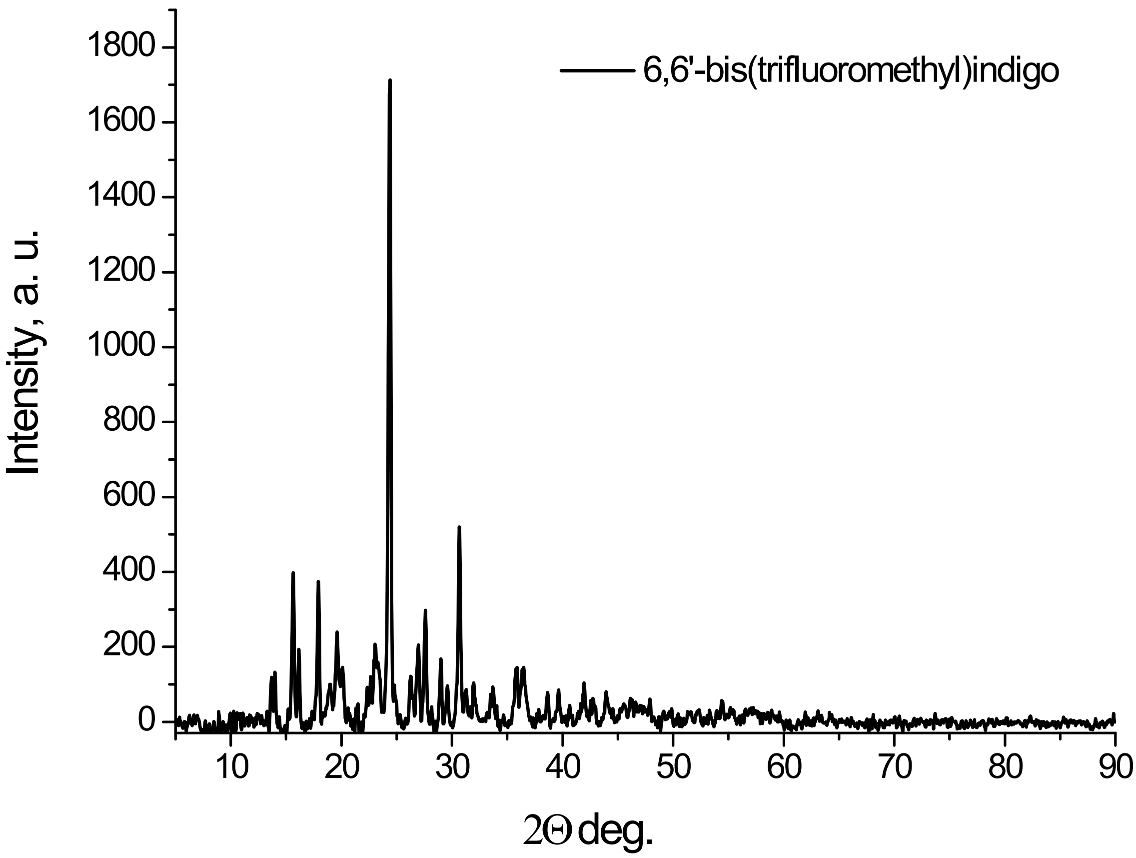


Fig. S11. Powder XRD pattern of indigoid **4**.

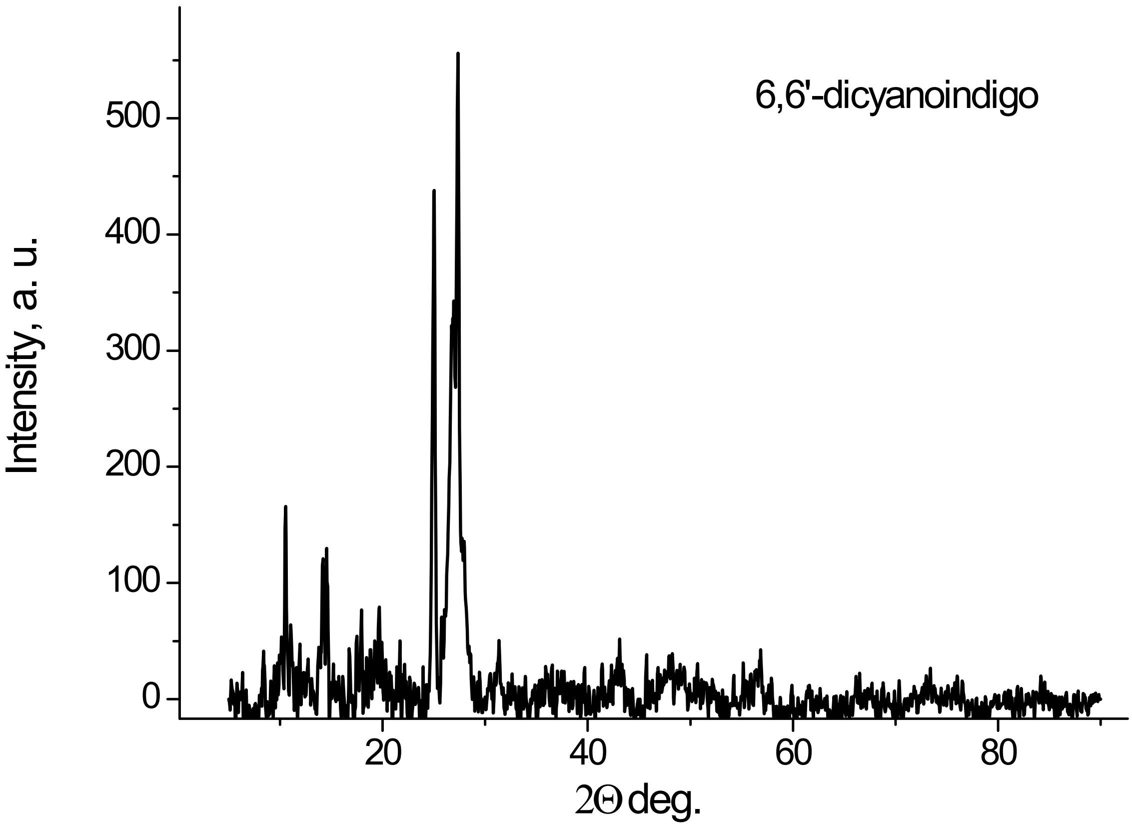


Fig. S12. Powder XRD pattern of indigoid **5**.

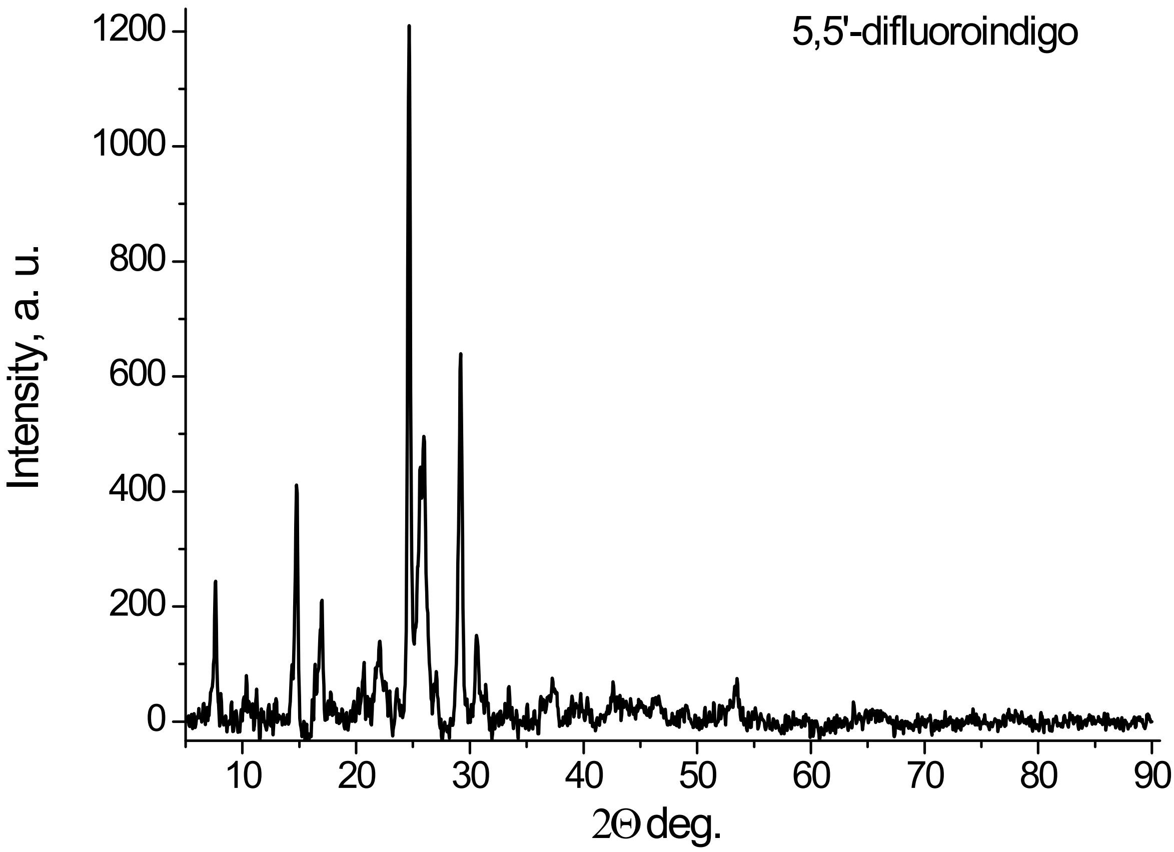


Fig. S13. Powder XRD pattern of indigoid **6**.

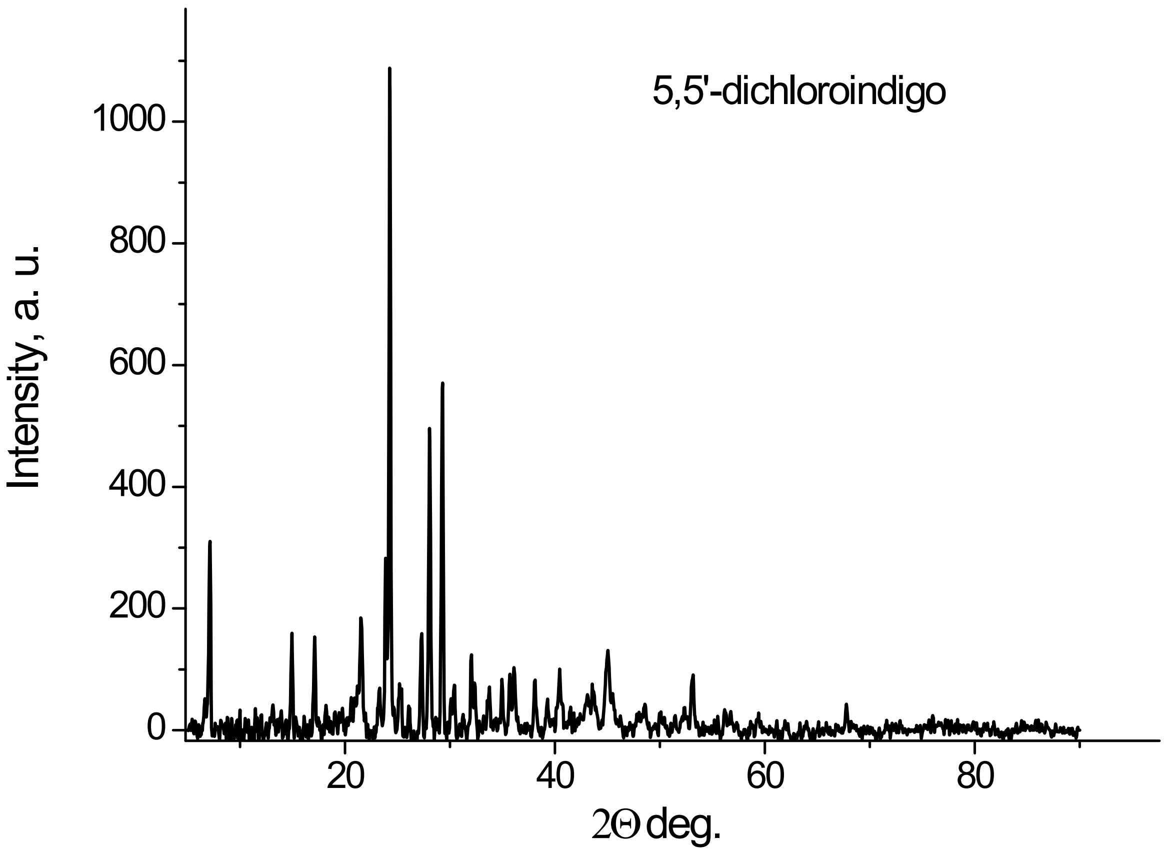


Fig. S14. Powder XRD pattern of indigoid **7**.

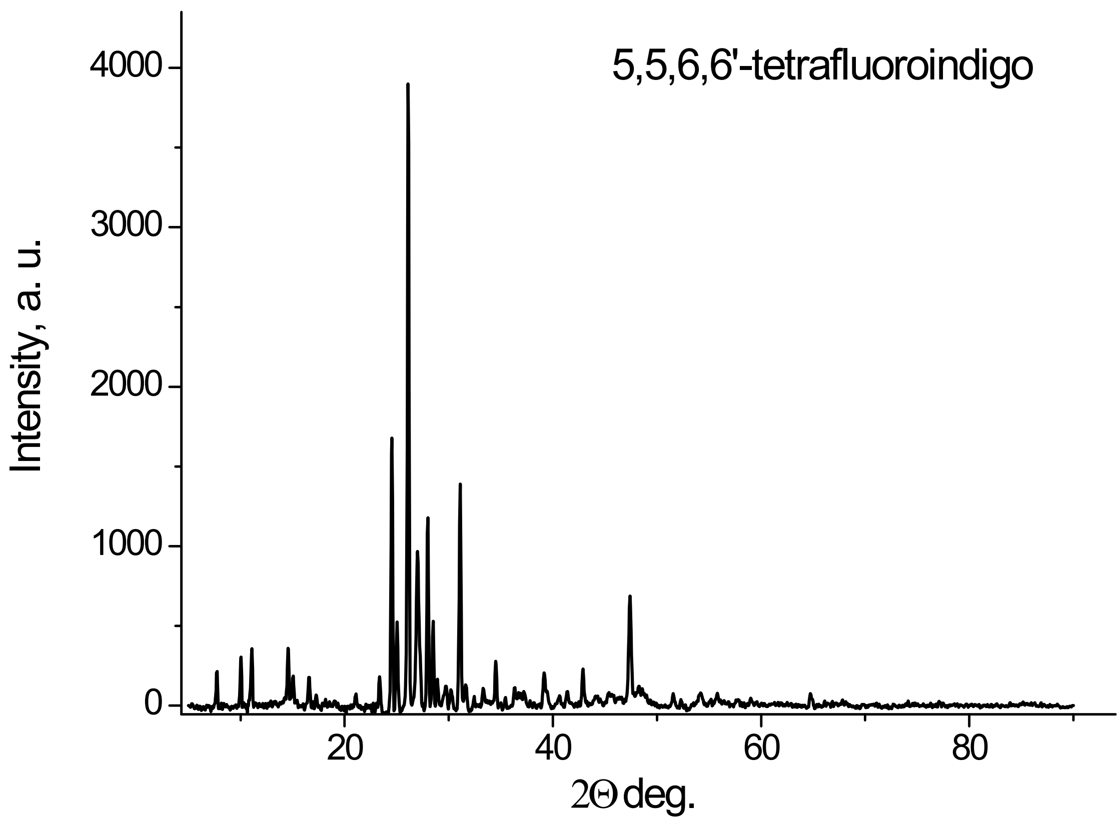


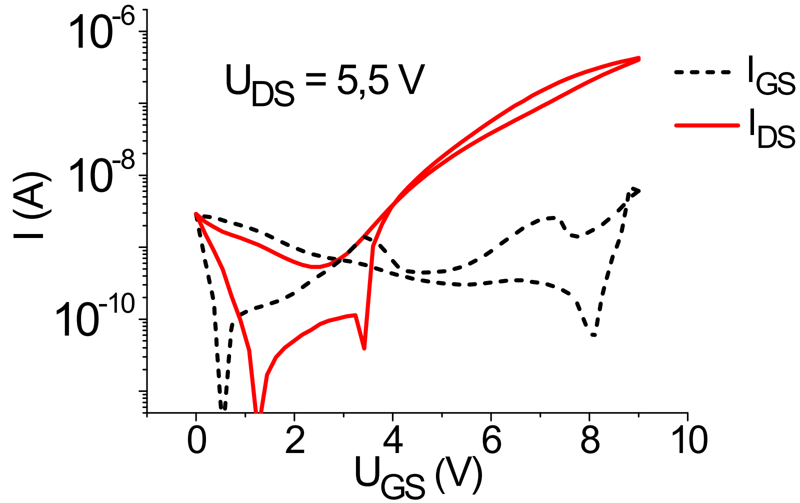
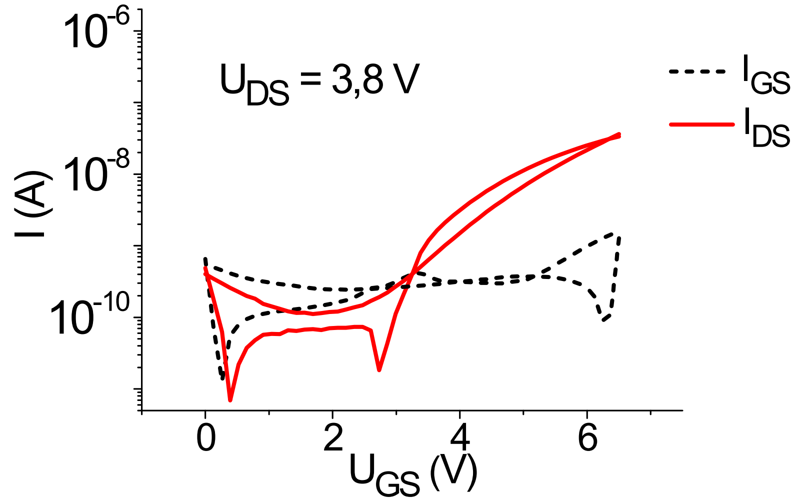
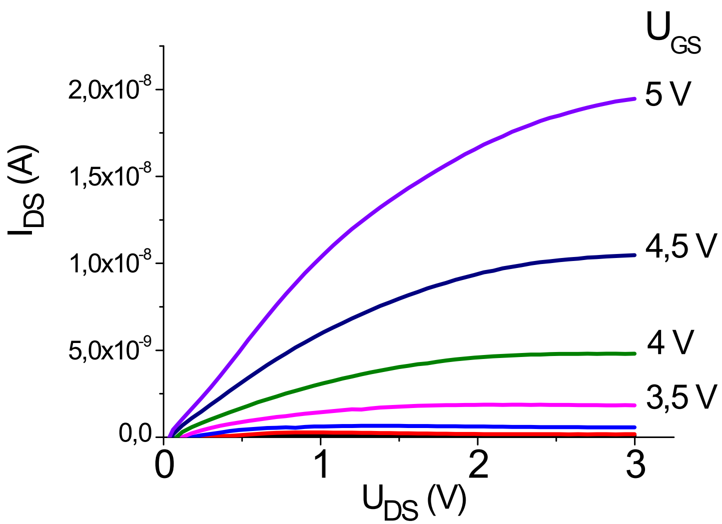
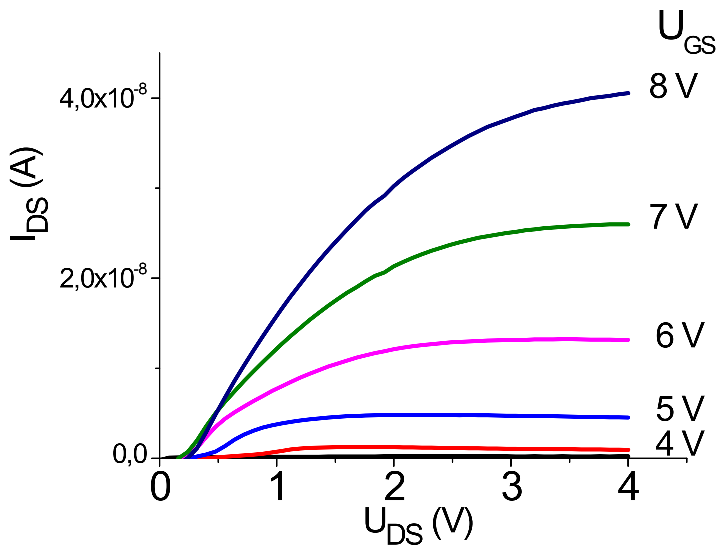
Fig. S15. Powder XRD pattern of indigoid **9**.

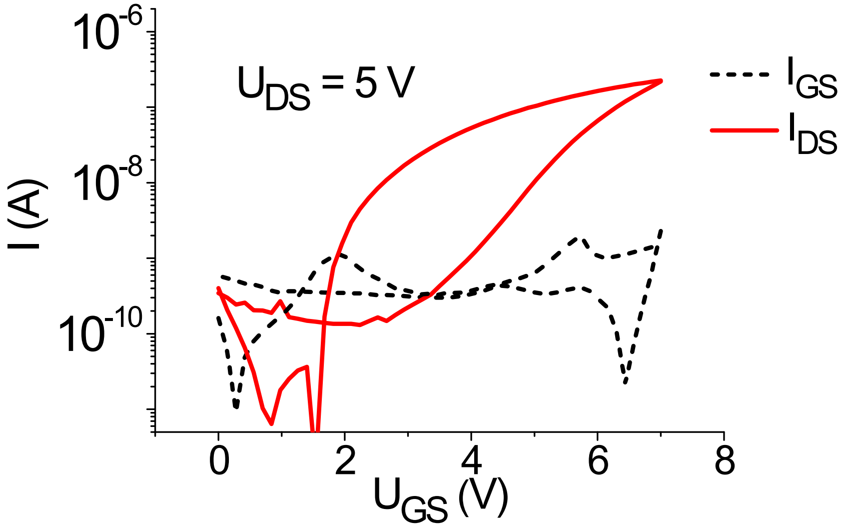
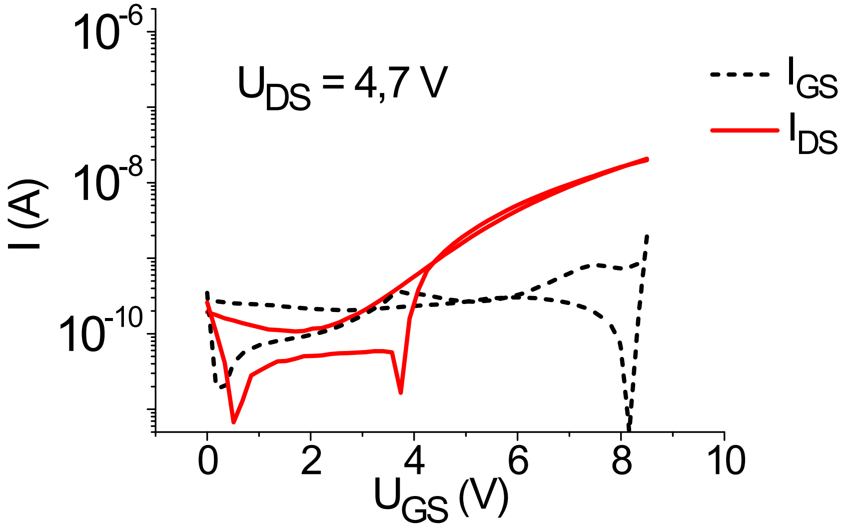
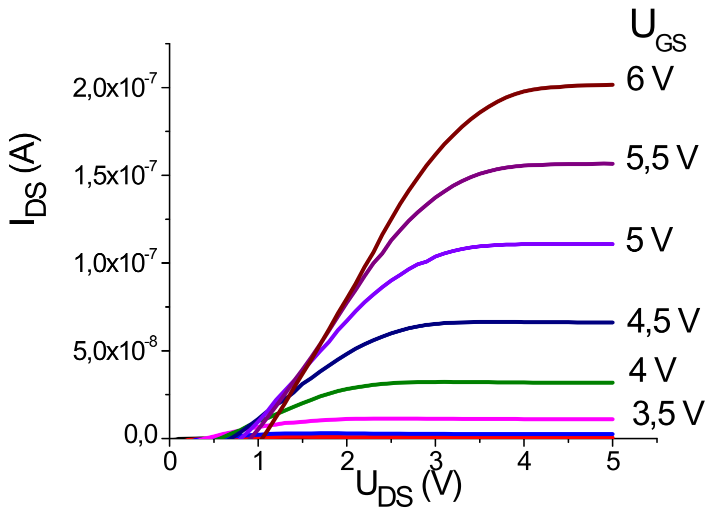
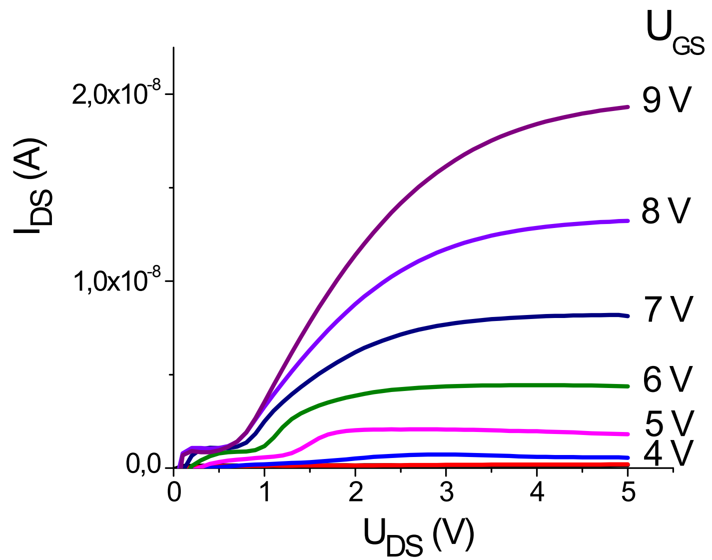
Table S1 Characteristics of OFETs fabricated with silver source and drain electrodes

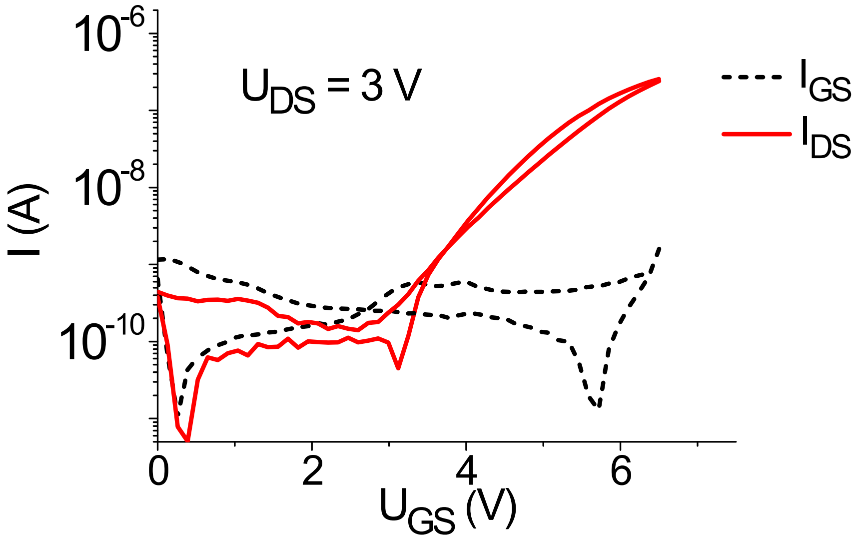
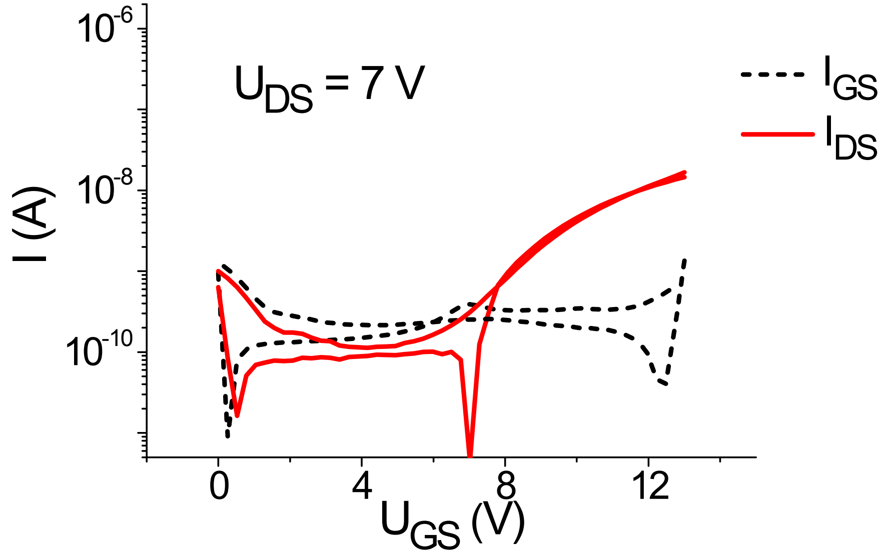
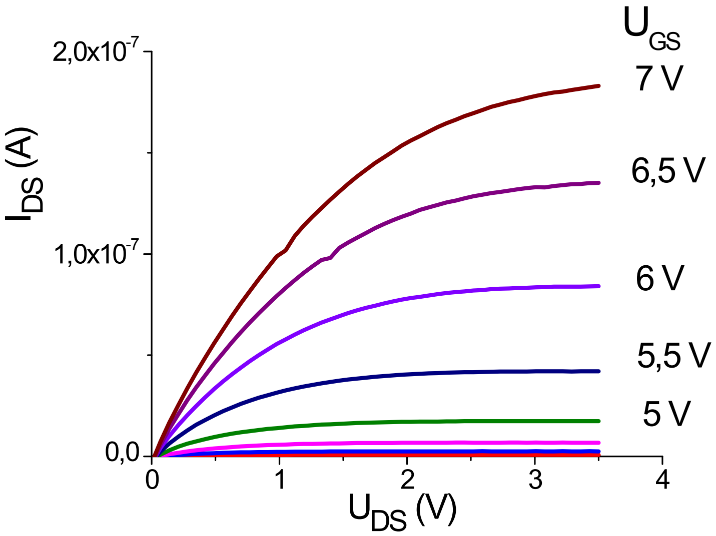
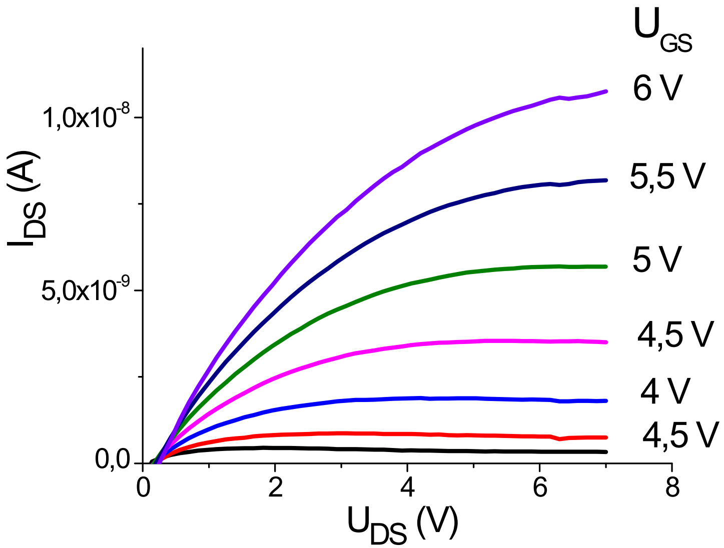
Indigoid	Diel.	I_{on}/I_{off}	$I_{on}/I_{off}(TC)$ / $I_{on}/I_{off}(BCB)$	μ, $cm^{2}\cdot V^{-1}\cdot s^{-1}$	$\mu_e(TC)/\mu_e(BCB)$
1	TC	~$4\cdot 10^{3}$	8.0	$3.8\cdot 10^{-3}$	2.1
	BCB	~$5\cdot 10^{2}$		$1.8\cdot 10^{-3}$	
2	TC	~$3\cdot 10^{4}$	150	$5.5\cdot 10^{-3}$	21
	BCB	~$2\cdot 10^{2}$		$6.9\cdot 10^{-4}$	
3	TC	~$6\cdot 10^{4}$	300	$7.4\cdot 10^{-3}$	28.5
	BCB	~$2\cdot 10^{2}$		$2.6\cdot 10^{-4}$	
4	TC	~$1\cdot 10^{4}$	-	$1.9\cdot 10^{-3}$	-
	BCB	-		-	
5*	TC	13	2	$1.0\cdot 10^{-6}$	0.13
	BCB	6		$7.6\cdot 10^{-6}$	
6	TC	125	-	$1.6\cdot 10^{-4}$	-
	BCB	-		-	
7	TC	~$3\cdot 10^{3}$	16	$1.2\cdot 10^{-3}$	24
	BCB	186		$5\cdot 10^{-5}$	
8	TC	550	11	$3.4\cdot 10^{-4}$	15.6
	BCB	50		$2.2\cdot 10^{-5}$	
9	TC	~$5\cdot 10^{4}$	25	$3.6\cdot 10^{-3}$	1.9
	BCB	~$2\cdot 10^{3}$		$1.9\cdot 10^{-3}$	
Indigo	TC	10^{4}	100	$3.0\cdot 10^{-3}$	16.7
	BCB	$1\cdot 10^{2}$		$1.8\cdot 10^{-4}$	

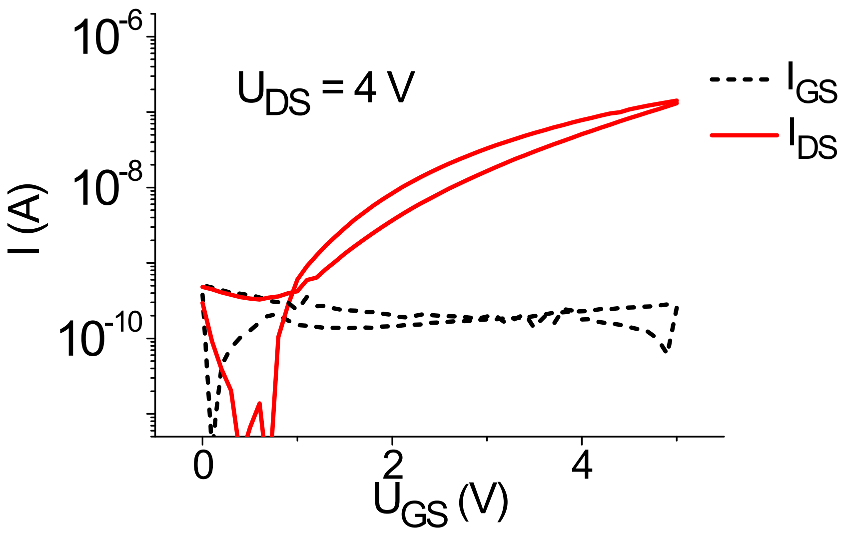
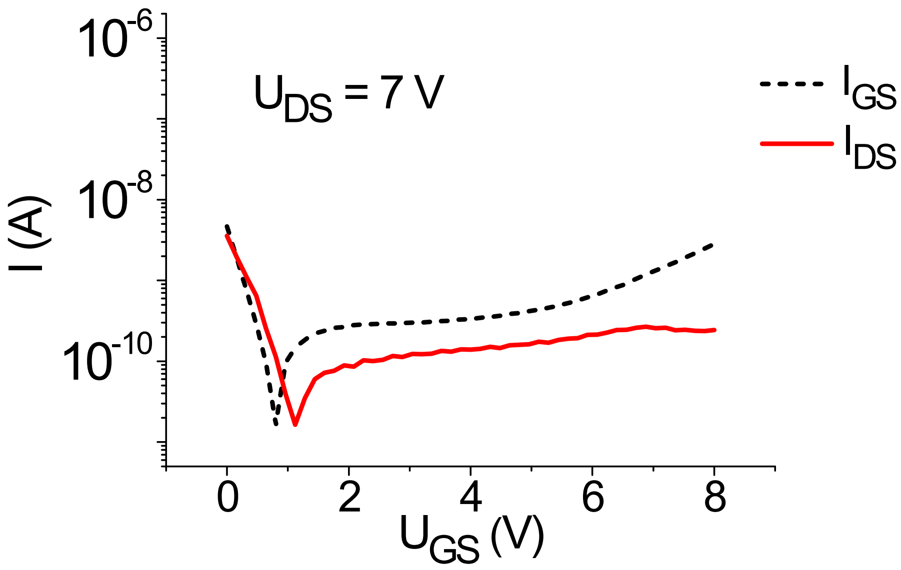
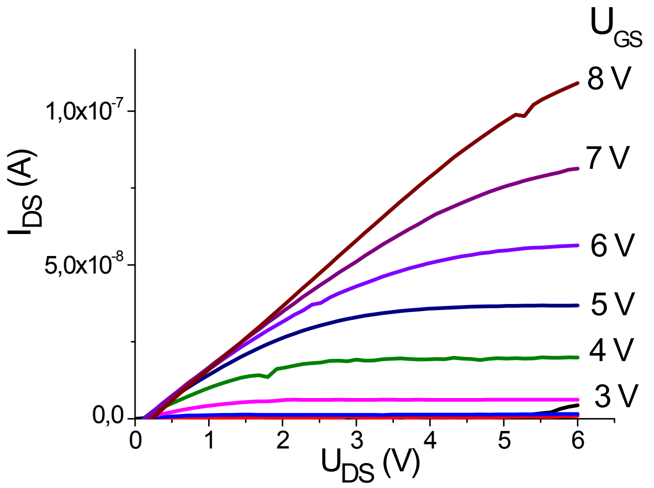
* Parameters calculated for OFETs might be not very precise due to very low semiconductor performance of 6,6'-dicyanoindigo

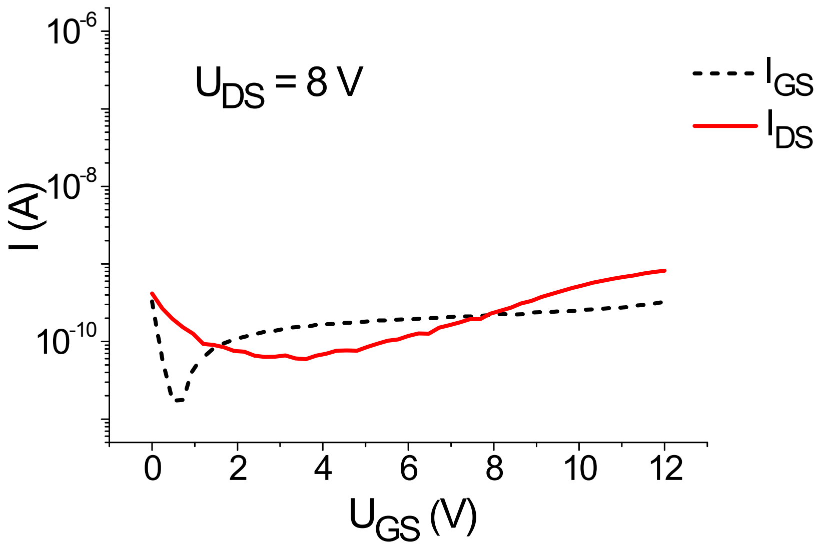
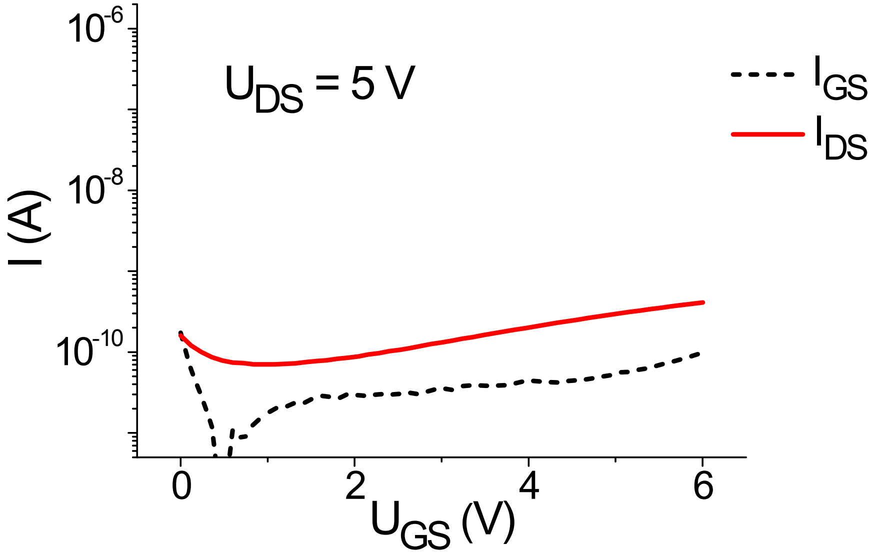
Table S2 Transfer and output characteristics of OFETs fabricated with silver source and drain electrodes

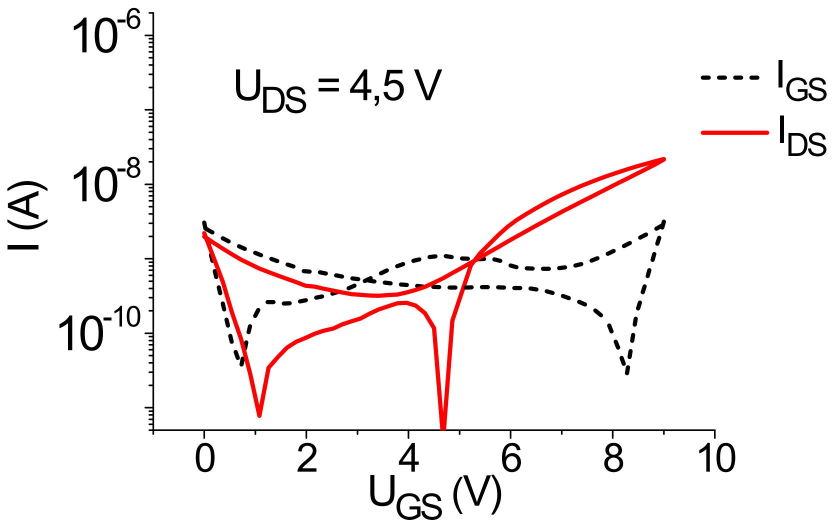
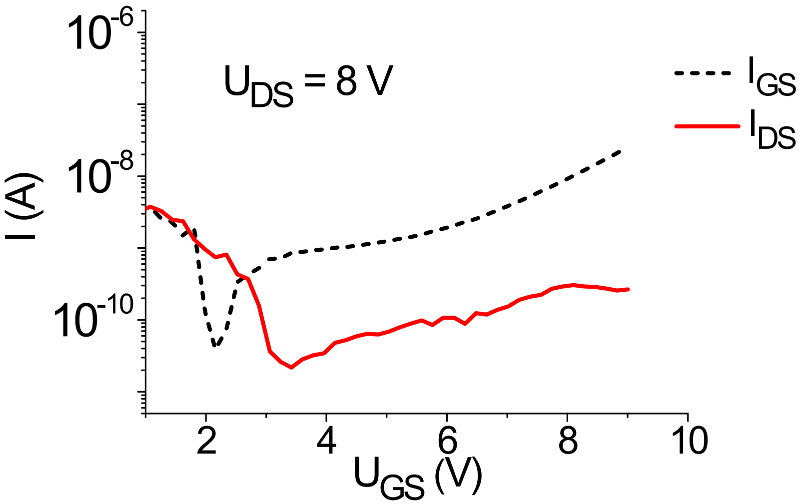
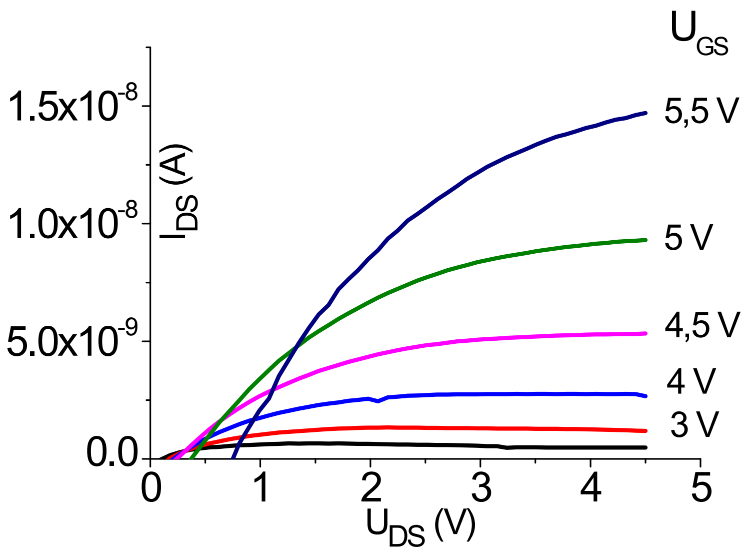
Indigoid	Films grown on TC	Films grown on BCB
1		
		

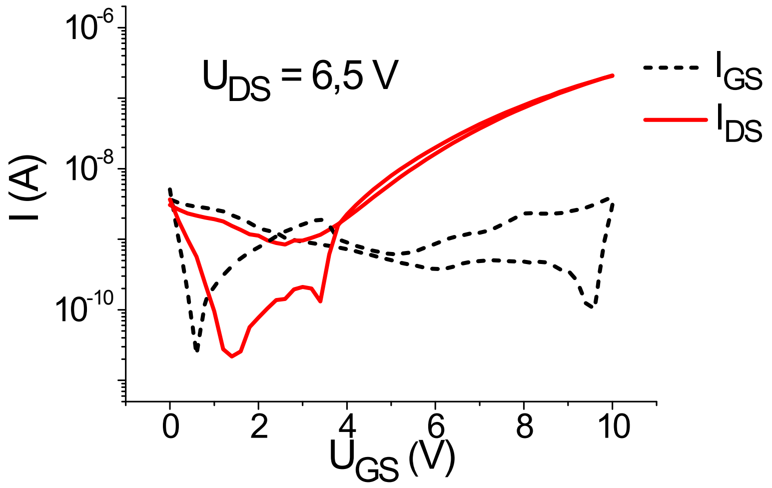
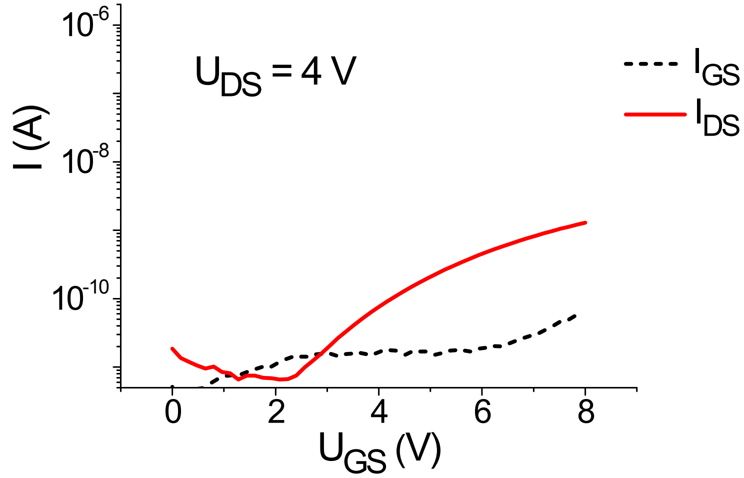
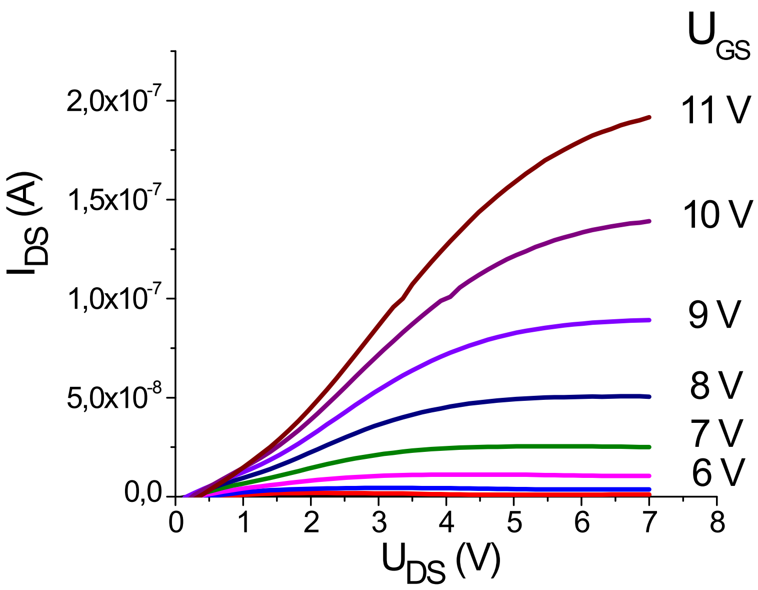
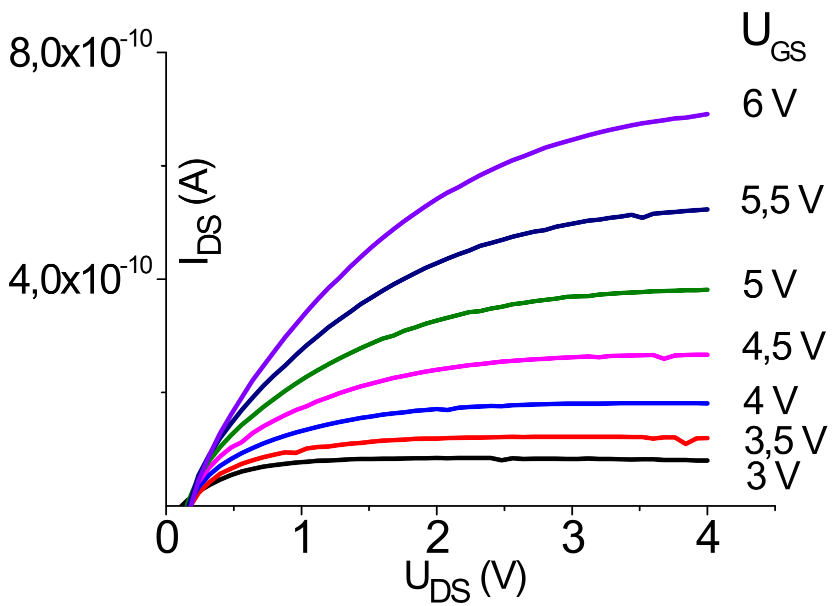
<table>
<tr><th>Indigoid</th><th>Films grown on TC</th><th>Films grown on BCB</th></tr>
<tr><td rowspan="2">2</td><td>
</td><td>
</td></tr>
<tr><td>
</td><td>
</td></tr>
</table>

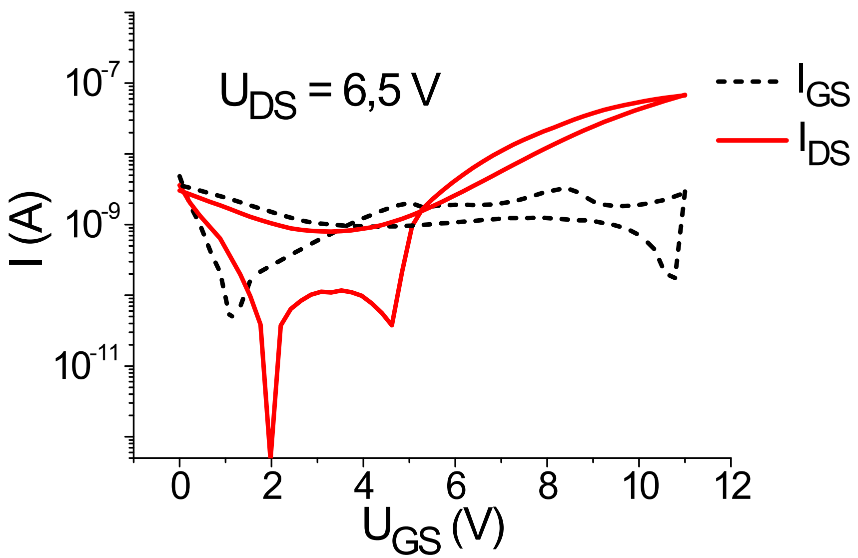
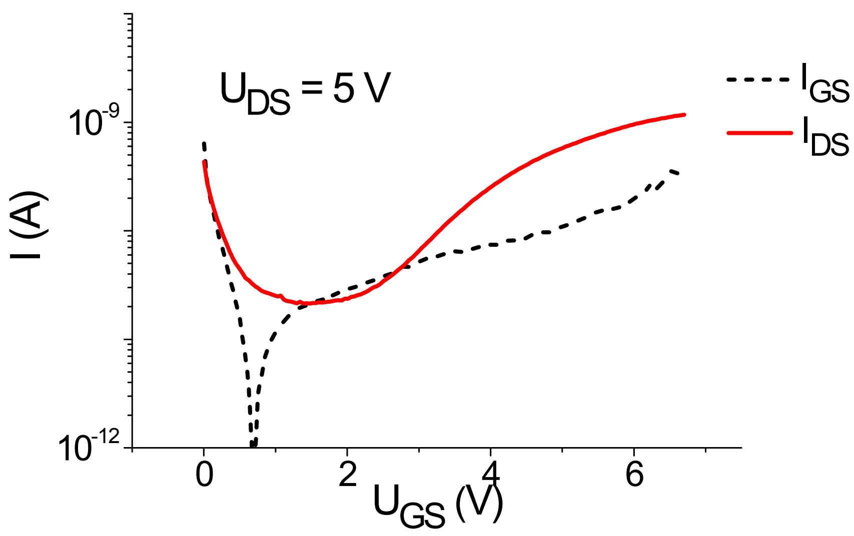
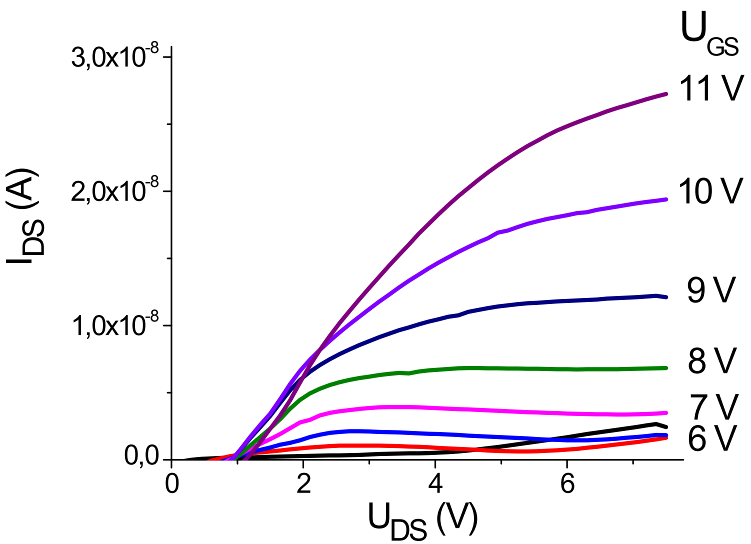
Indigoid	Films grown on TC	Films grown on BCB
3		
		

Indigoid	Films grown on TC	Films grown on BCB
4		
		

Indigoid	Films grown on TC	Films grown on BCB
5		

<table>
<tr><th>Indigoid</th><th>Films grown on TC</th><th>Films grown on BCB</th></tr>
<tr><td rowspan="2">6</td><td>
</td><td>
</td></tr>
<tr><td>
</td><td></td></tr>
</table>

Indigoid	Films grown on TC	Films grown on BCB
7		
		

Indigoid	Films grown on TC	Films grown on BCB
8		
		

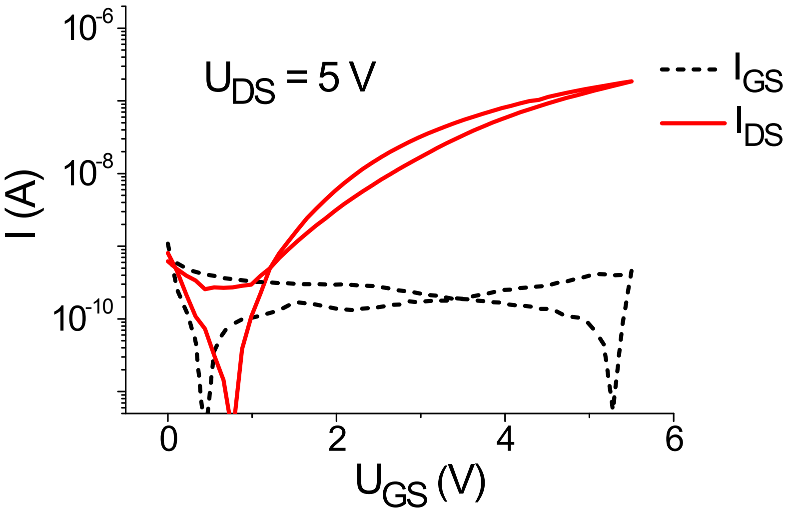
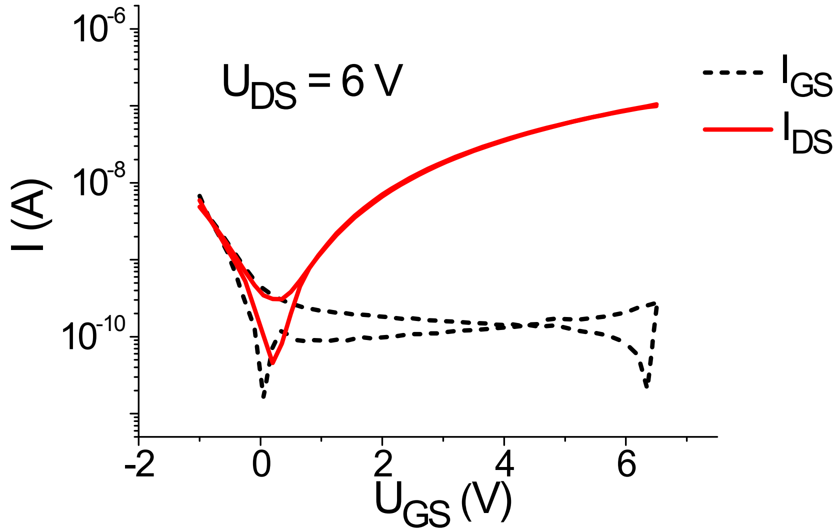
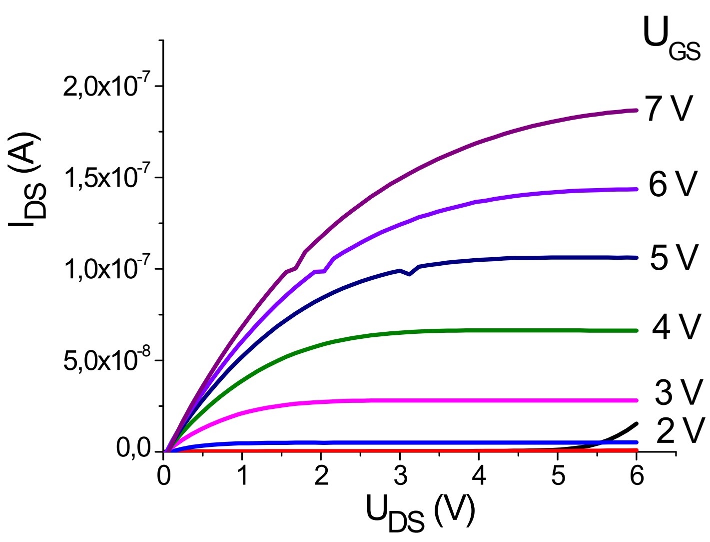
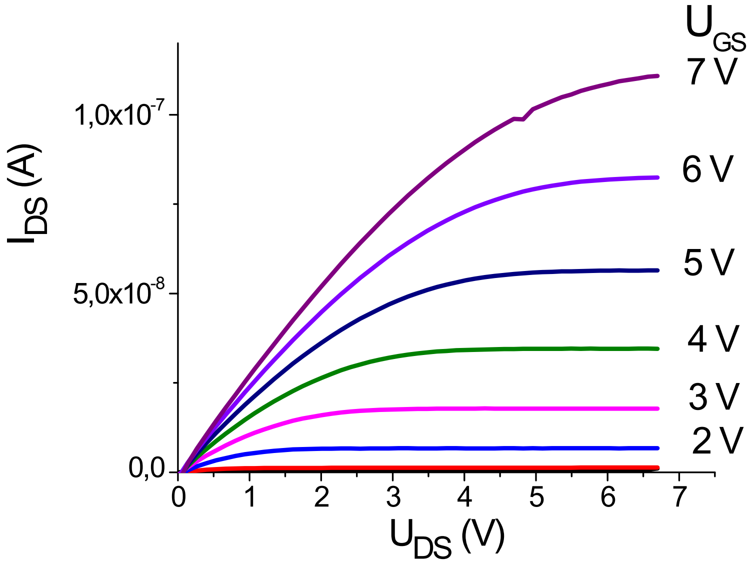
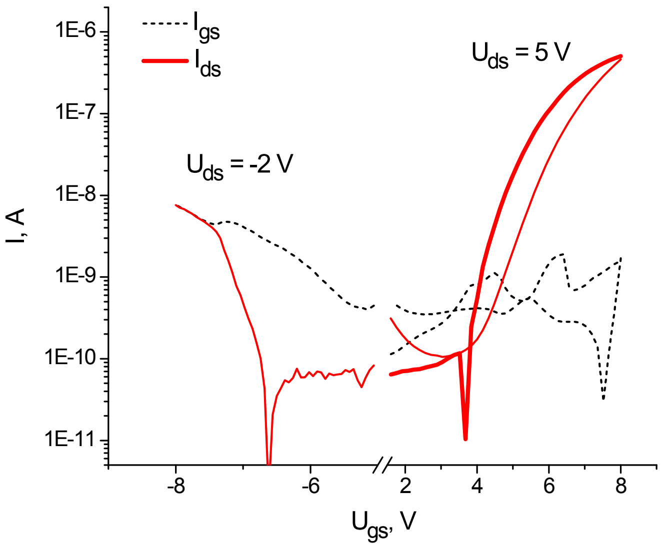
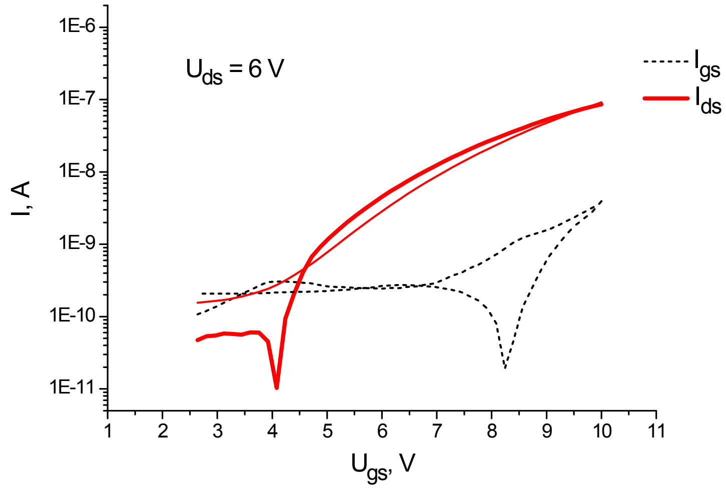
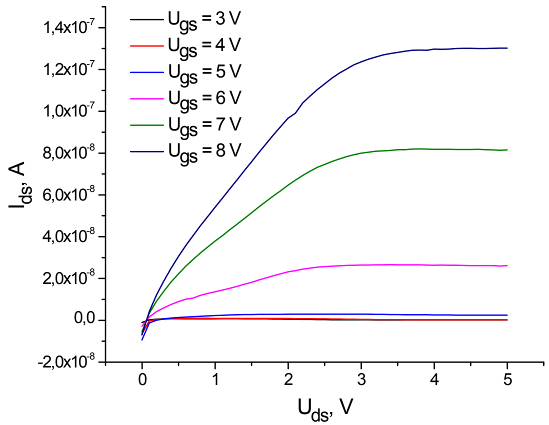
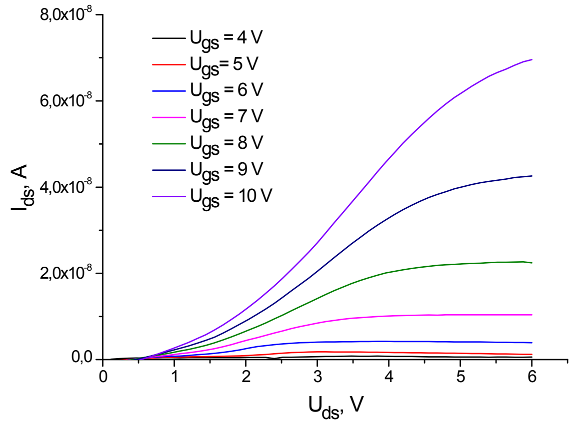
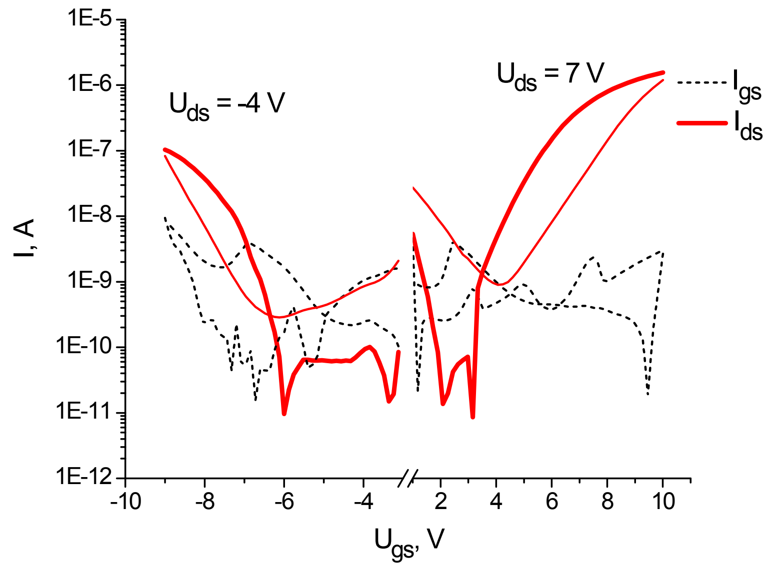
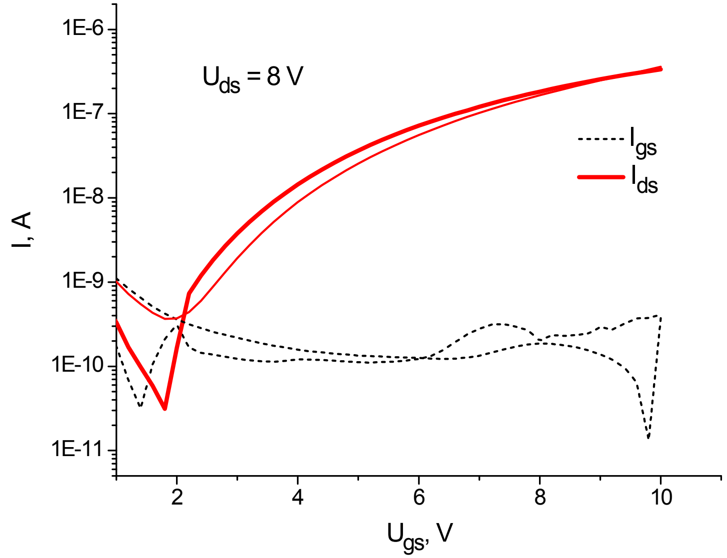
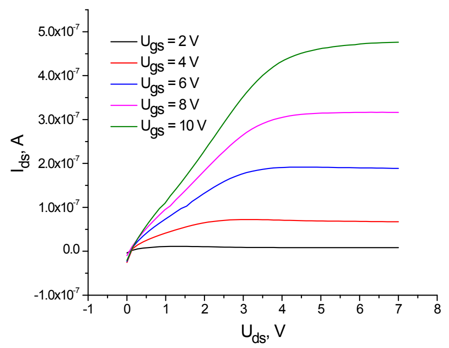
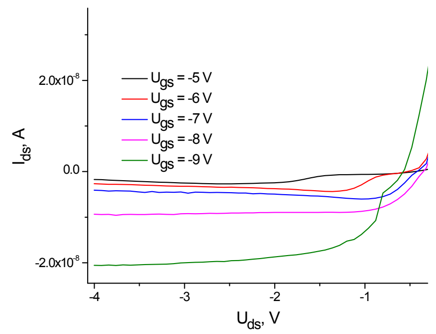
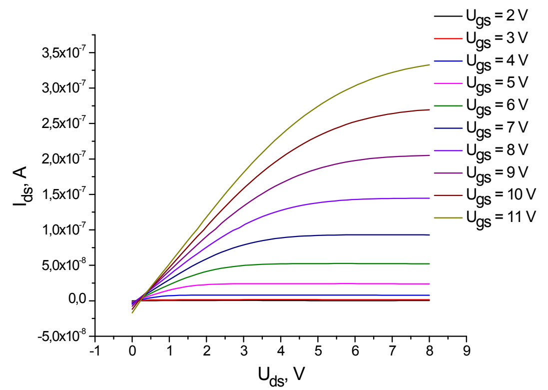
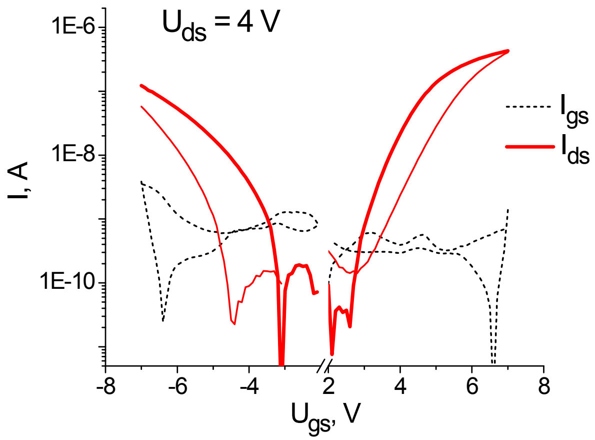
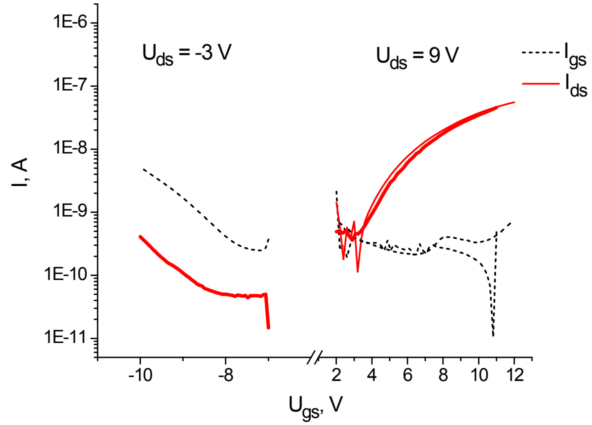
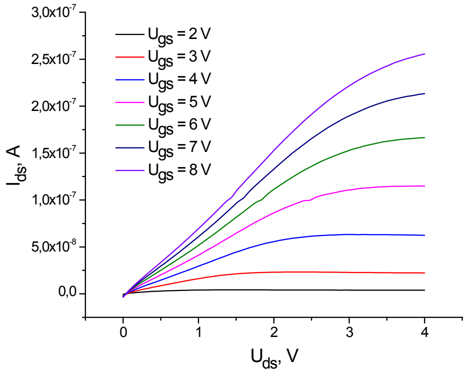
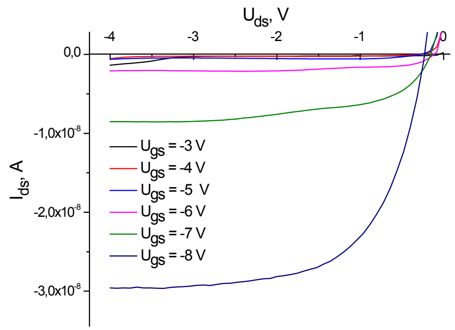
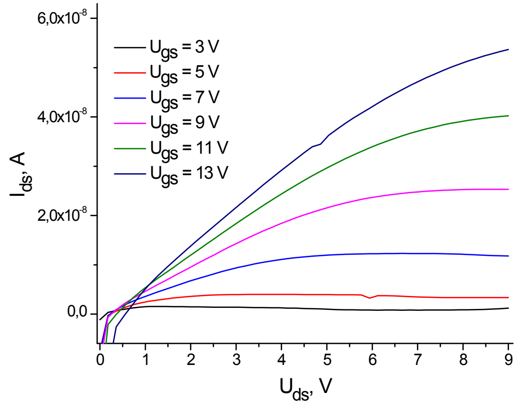
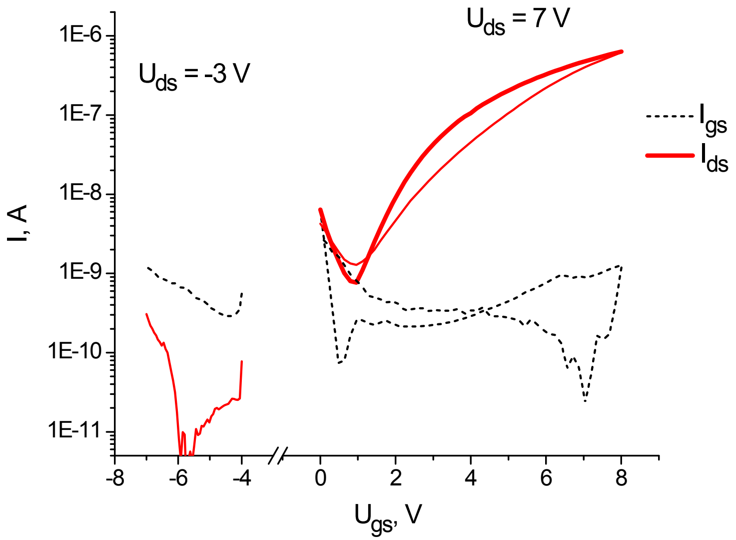
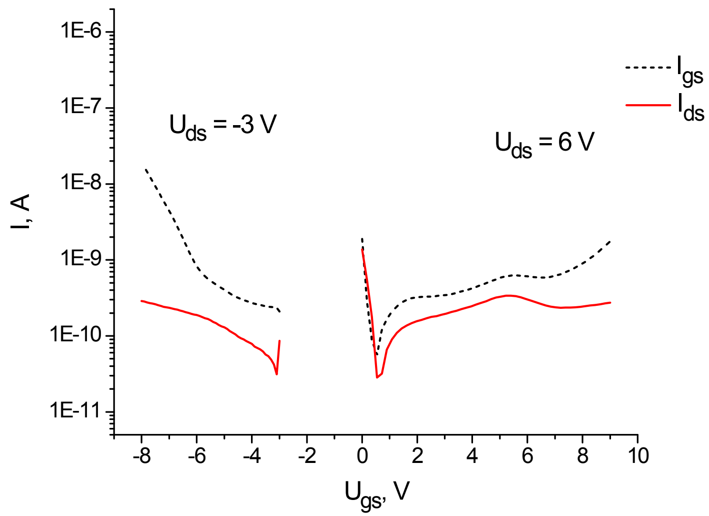
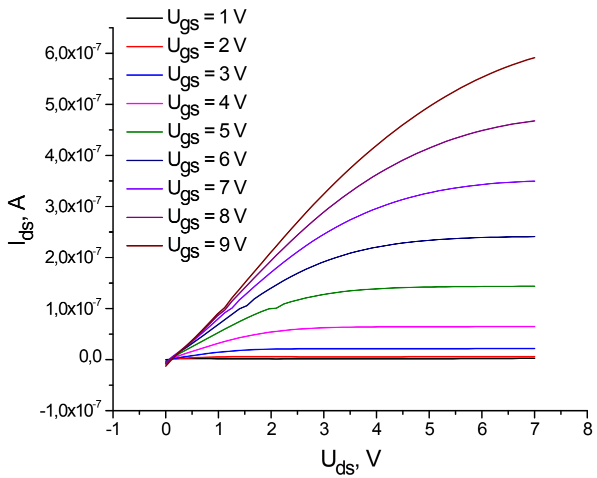
Indigoid	Films grown on TC	Films grown on BCB
9		
		

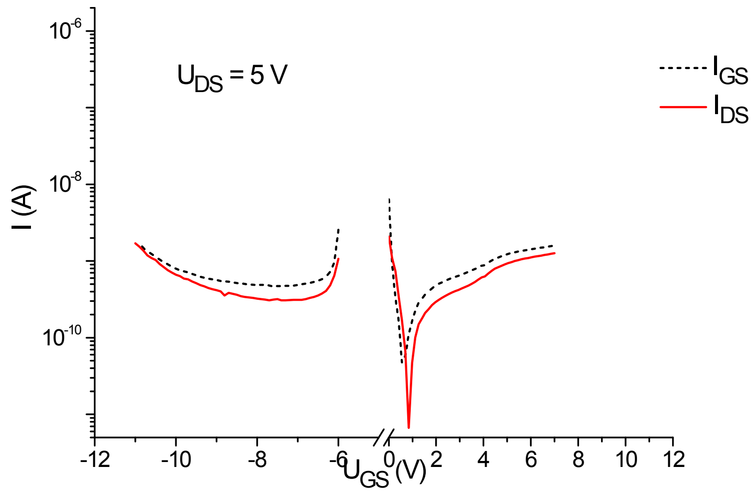
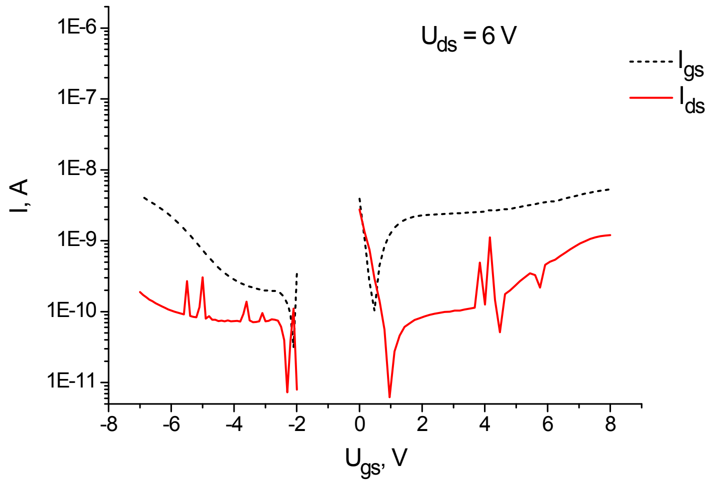
Table S3 Transfer and output characteristics of OFETs fabricated with gold source and drain electrodes

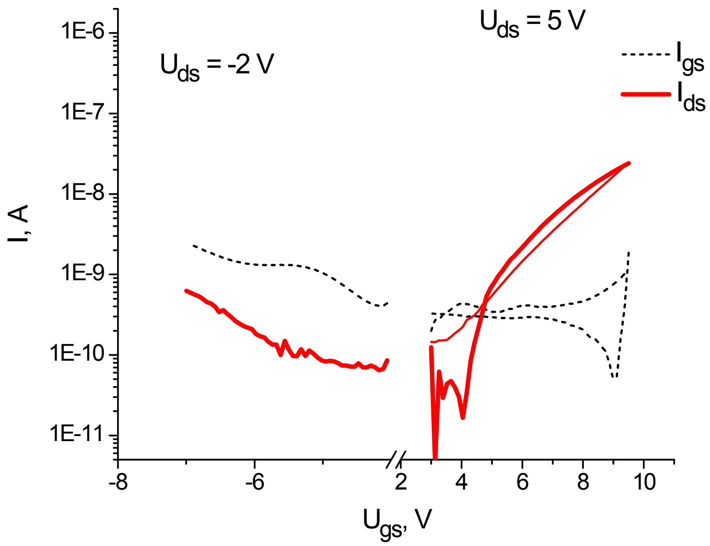
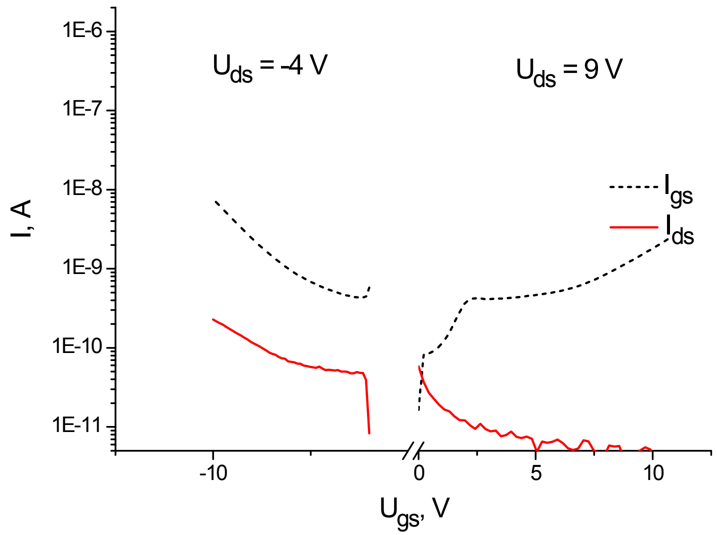
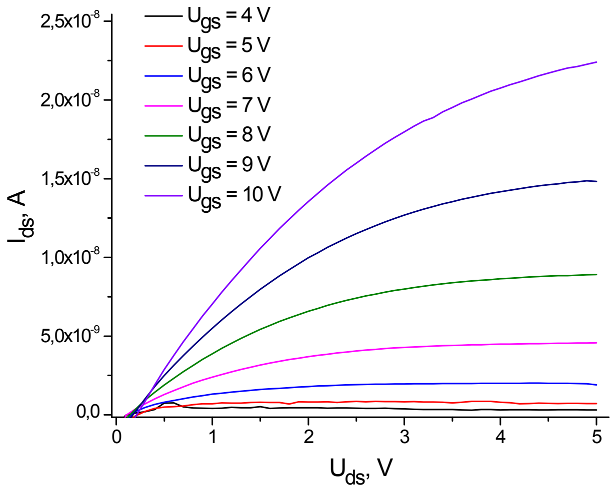
<table>
<tr><th>Indigoid</th><th>Films grown on TC</th><th>Films grown on BCB</th></tr>
<tr><td rowspan="2">1</td><td>
</td><td>
</td></tr>
<tr><td>
</td><td>
</td></tr>
</table>

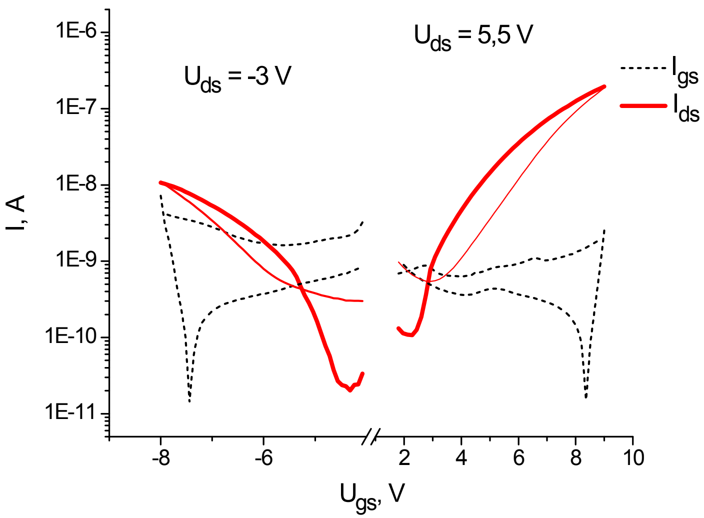
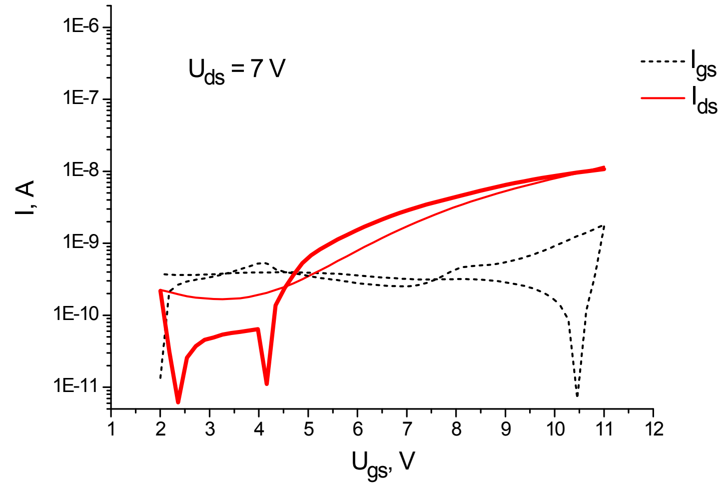
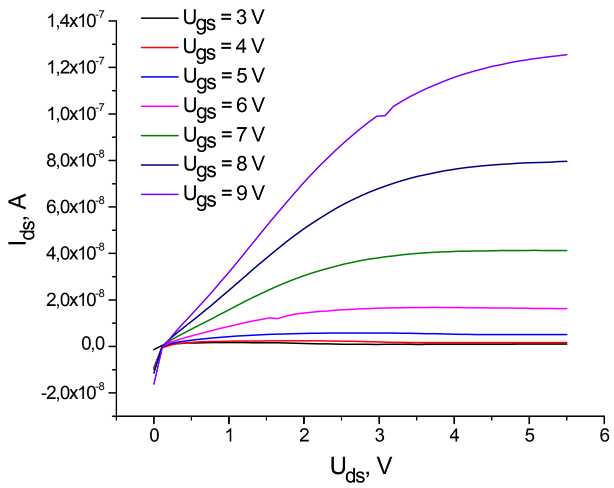
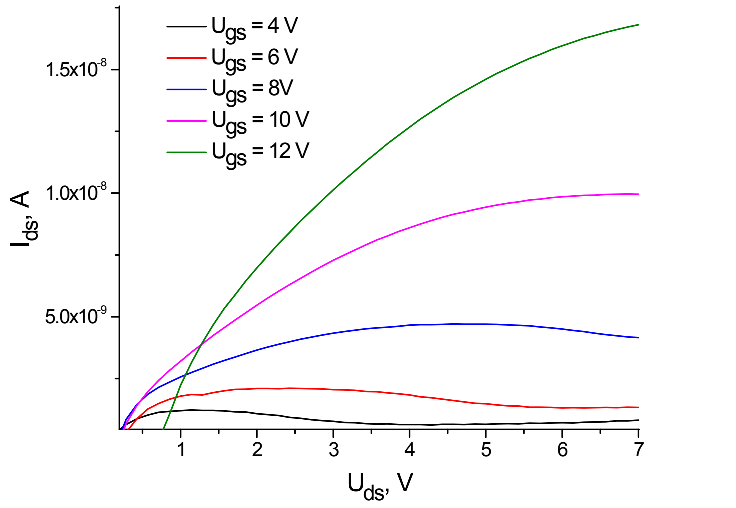
<table>
<tr><th>Indigoid</th><th colspan="2">Films grown on TC</th><th>Films grown on BCB</th></tr>
<tr><td rowspan="2">2</td><td colspan="2">
</td><td>
</td></tr>
<tr><td>
</td><td>
</td><td>
</td></tr>
</table>

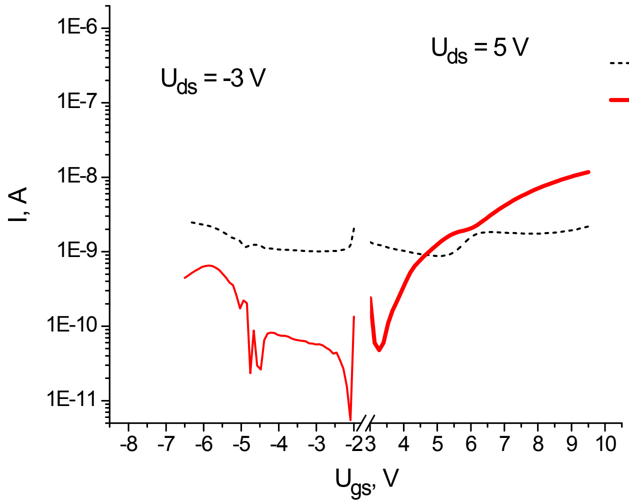
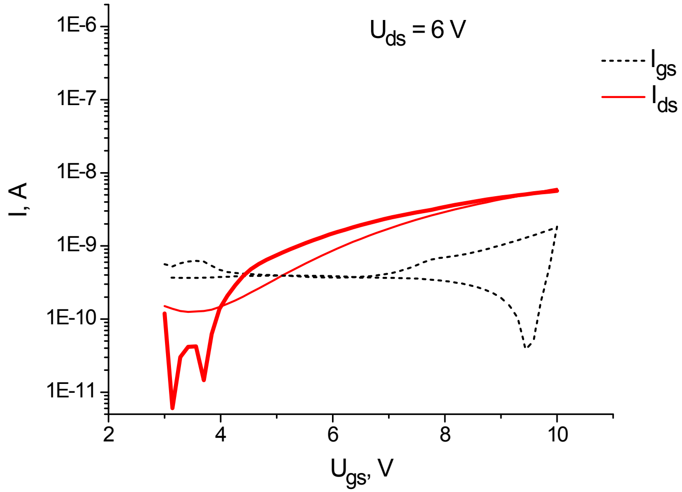
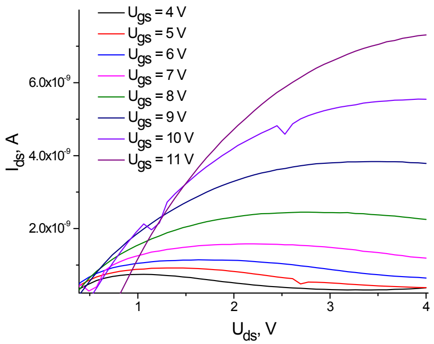
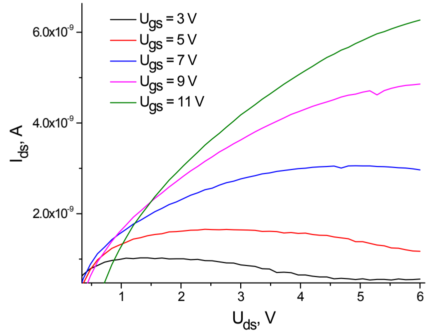
<table>
<tr><th>Indigoid</th><th colspan="2">Films grown on TC</th><th>Films grown on BCB</th></tr>
<tr><td rowspan="2">3</td><td colspan="2">
</td><td>
</td></tr>
<tr><td>
</td><td>
</td><td>
</td></tr>
</table>

Indigoid	Films grown on TC	Films grown on BCB
4		
		

Indigoid	Films grown on TC	Films grown on BCB
5		

<table>
<tr><th>Indigoid</th><th>Films grown on TC</th><th>Films grown on BCB</th></tr>
<tr><td rowspan="2">6</td><td>
</td><td>
</td></tr>
<tr><td>
</td><td></td></tr>
</table>

Indigoid	Films grown on TC	Films grown on BCB
7		
		

Indigoid	Films grown on TC	Films grown on BCB
8		
		

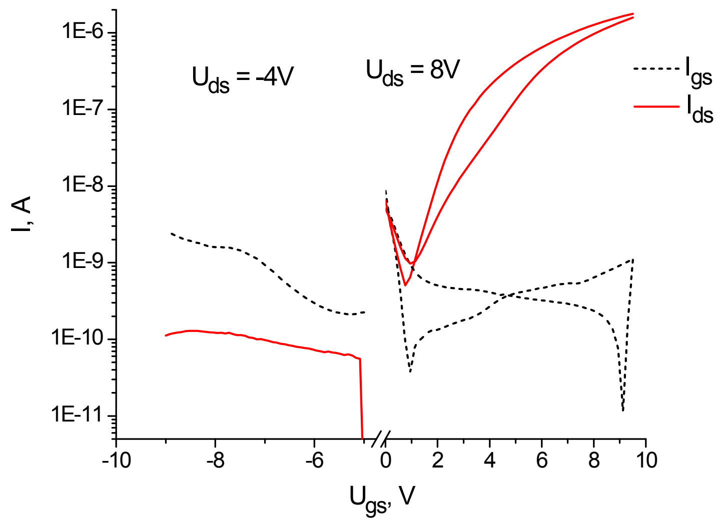
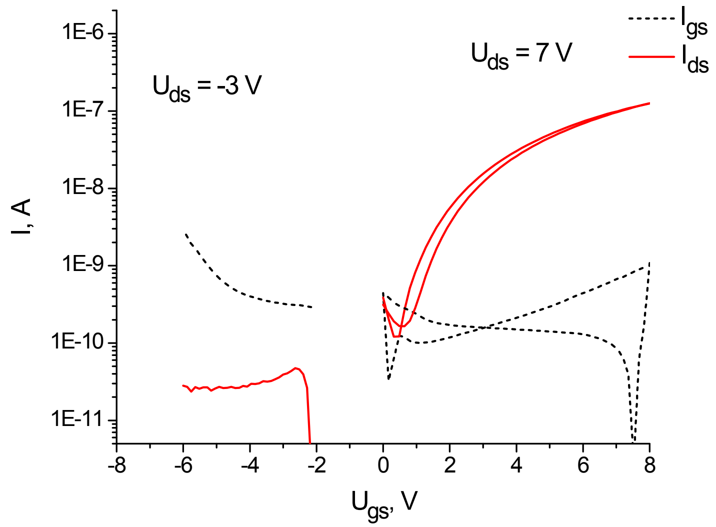
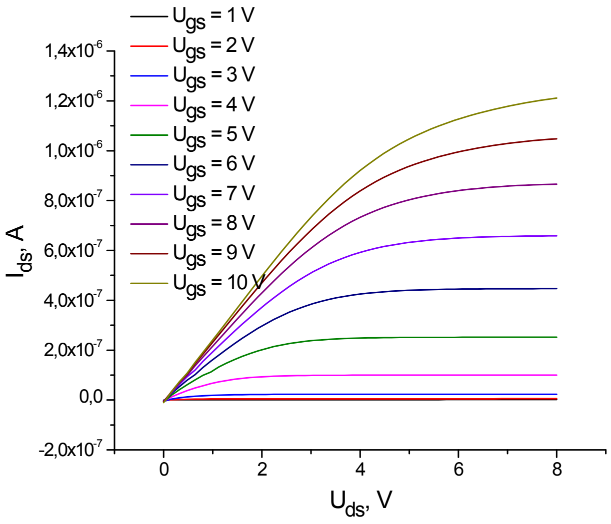
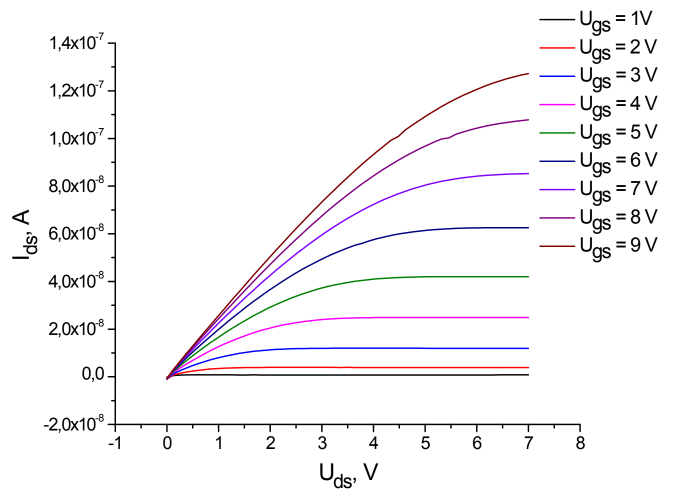
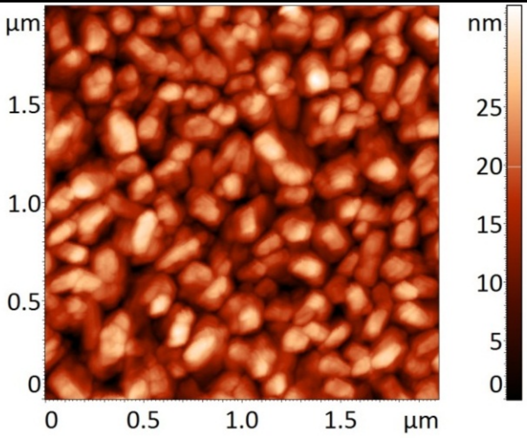
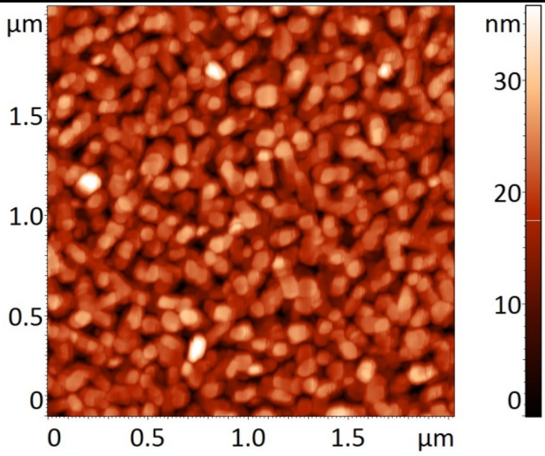
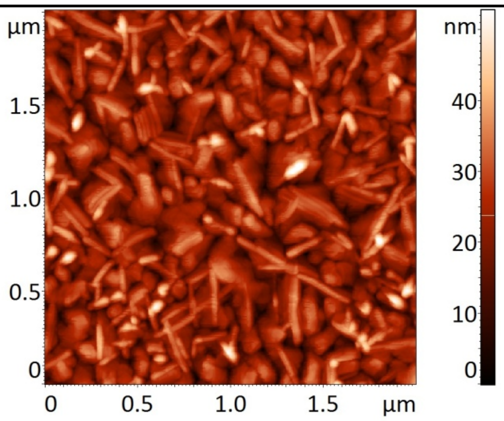
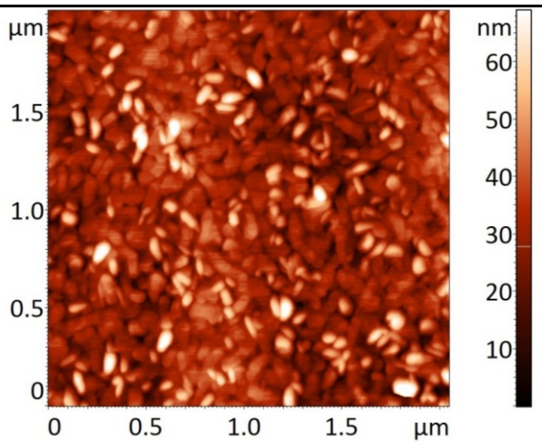
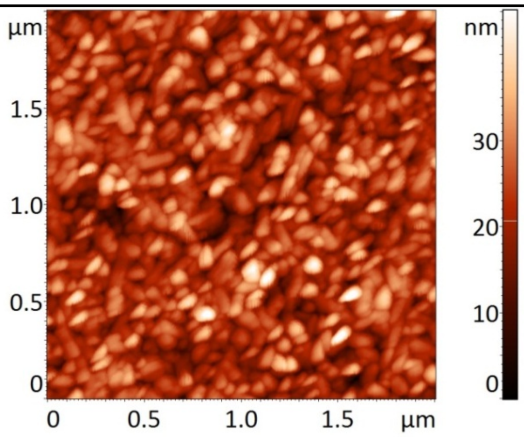
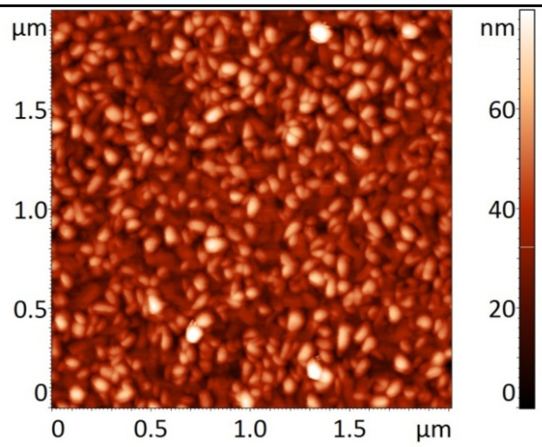
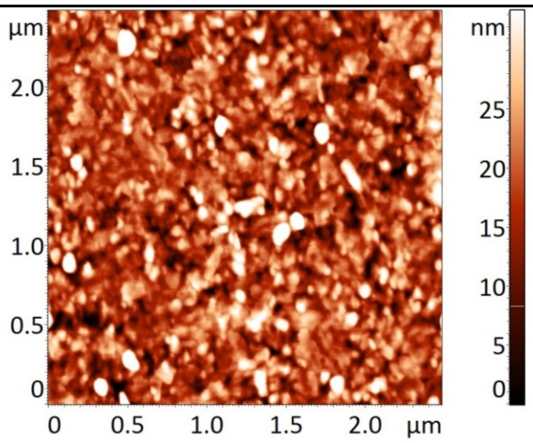
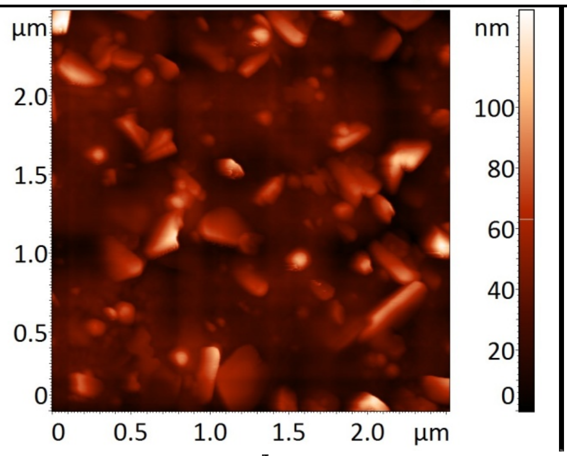
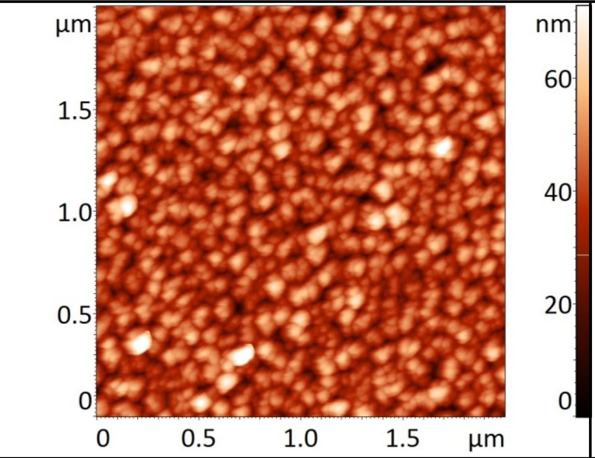
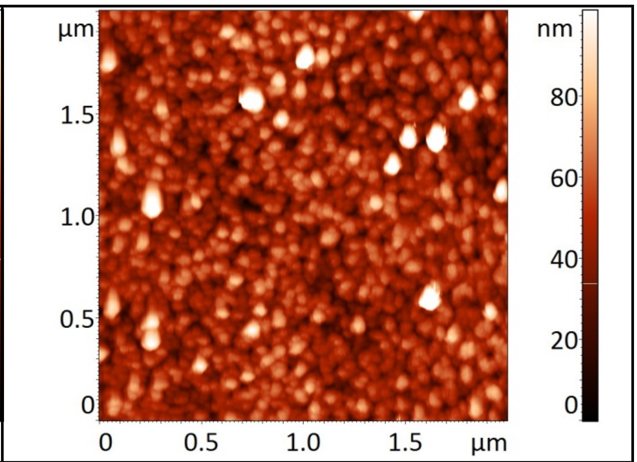
<table>
<tr><th>Indigoid</th><th>Films grown on TC</th><th>Films grown on BCB</th></tr>
<tr><td rowspan="2">9</td><td>
</td><td>
</td></tr>
<tr><td>
</td><td>
</td></tr>
</table>

Table S4 AFM topography images of indigoid films grown on TC and BCB dielectrics

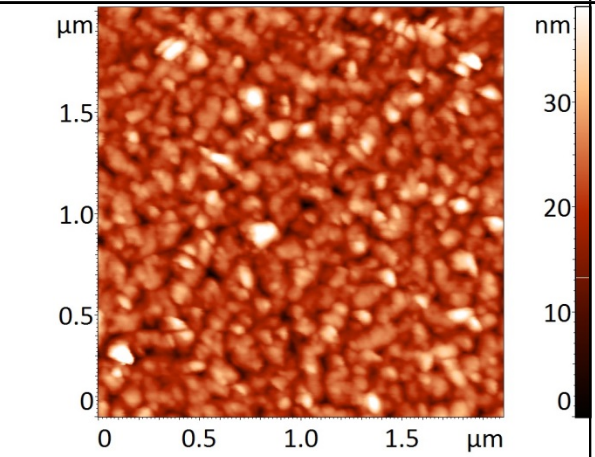
<table>
<tr><th>No.</th><th>Film grown on TC</th><th>film grown on BCB</th></tr>
<tr><td>1</td><td>
</td><td>
</td></tr>
<tr><td>2</td><td>
</td><td>
</td></tr>
<tr><td>3</td><td>
</td><td>
</td></tr>
<tr><td>4</td><td>
</td><td>
</td></tr>
</table>

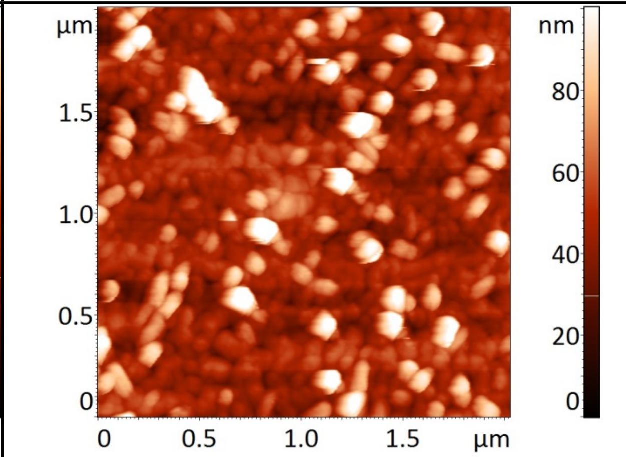
5


µm
1.5
1.0
0.5
0
0 0.5 1.0 1.5 µm
nm
60
40
20
0

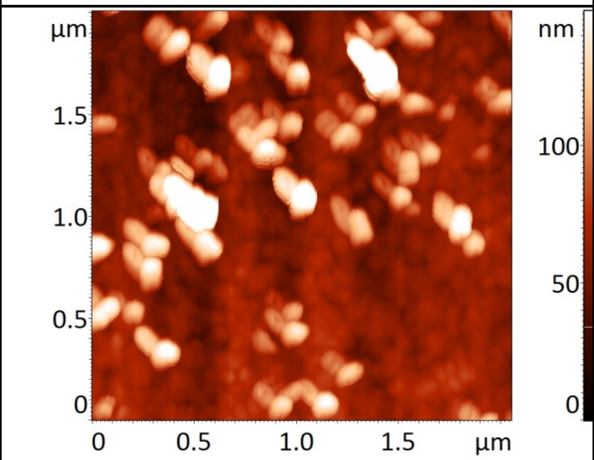

µm
1.5
1.0
0.5
0
0 0.5 1.0 1.5 µm
nm
80
60
40
20
0

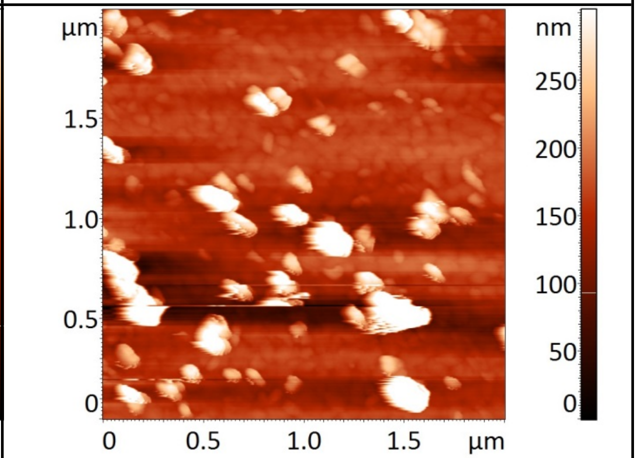
6


µm
1.5
1.0
0.5
0
0 0.5 1.0 1.5 µm
nm
30
20
10
0

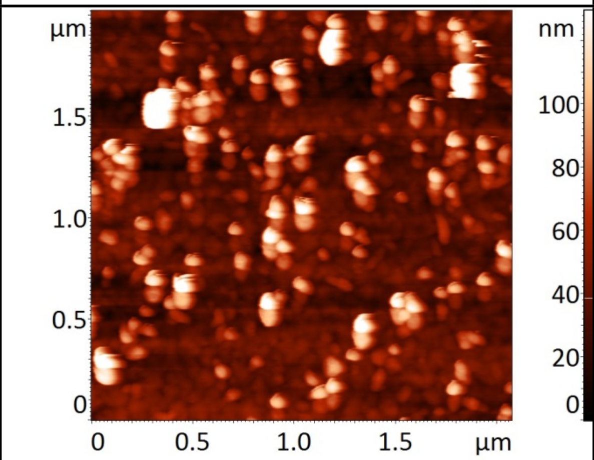

µm
1.5
1.0
0.5
0
0 0.5 1.0 1.5 µm
nm
80
60
40
20
0

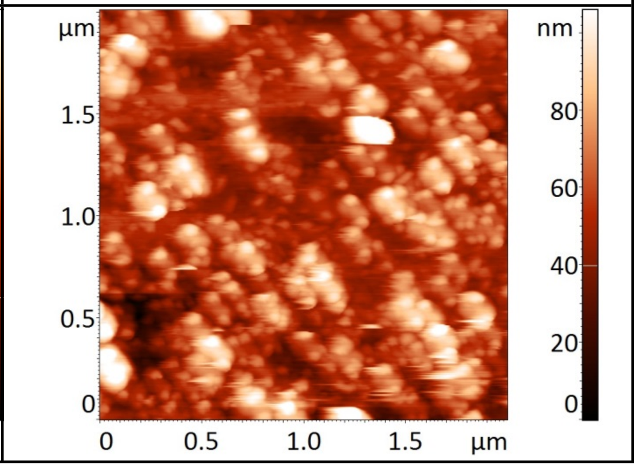
7


µm
1.5
1.0
0.5
0
0 0.5 1.0 1.5 µm
nm
100
50
0

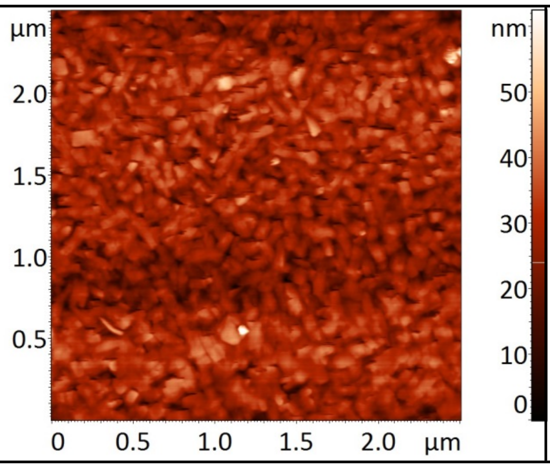

µm
1.5
1.0
0.5
0
0 0.5 1.0 1.5 µm
nm
250
200
150
100
50
0

8


µm
1.5
1.0
0.5
0
0 0.5 1.0 1.5 µm
nm
100
80
60
40
20
0


µm
1.5
1.0
0.5
0
0 0.5 1.0 1.5 µm
nm
80
60
40
20
0

9


µm
2.0
1.5
1.0
0.5
0
0.5
1.0
1.5
2.0
µm
nm
50
40
30
20
10
0

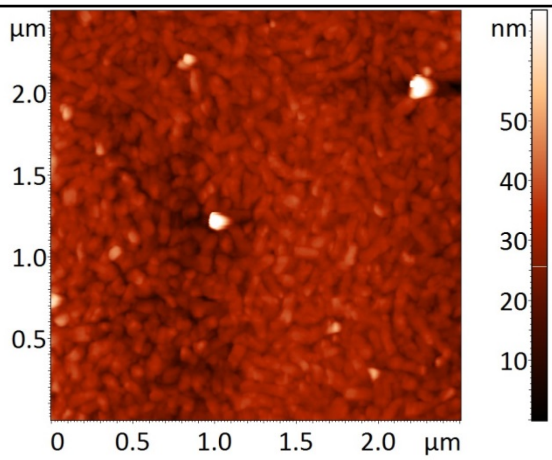
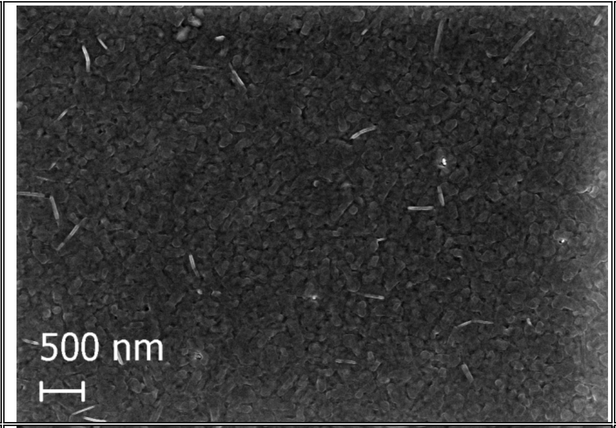
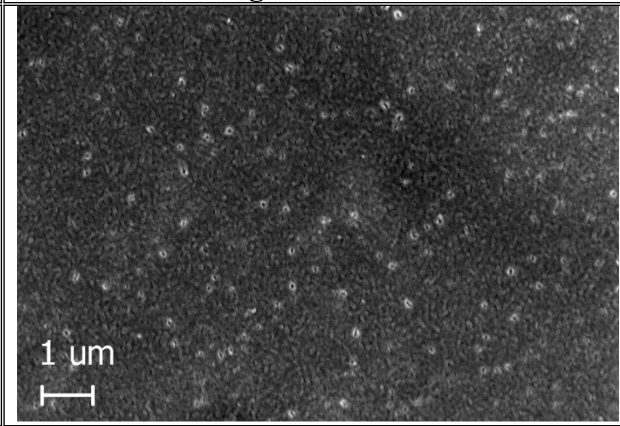
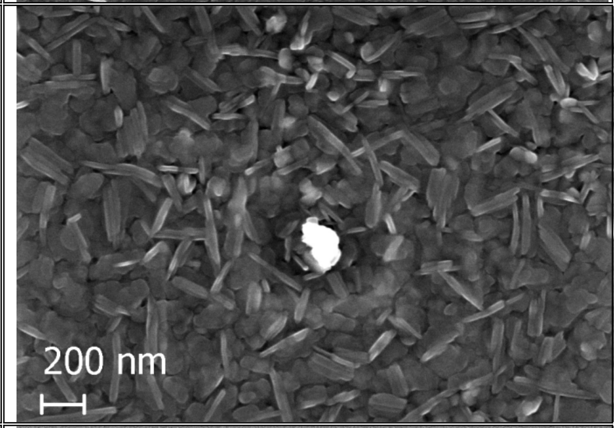
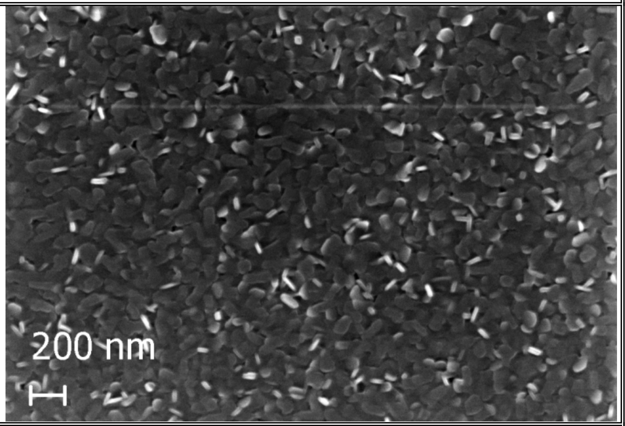
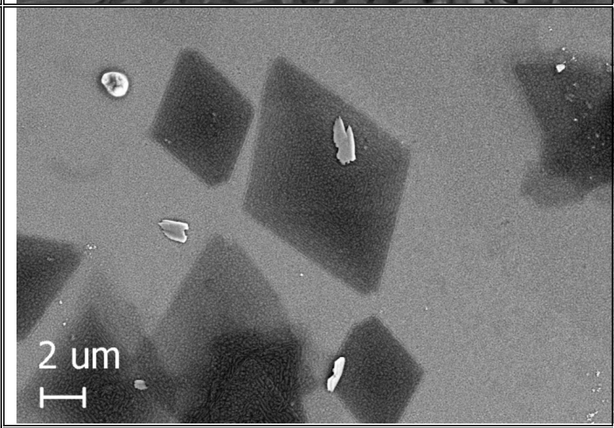
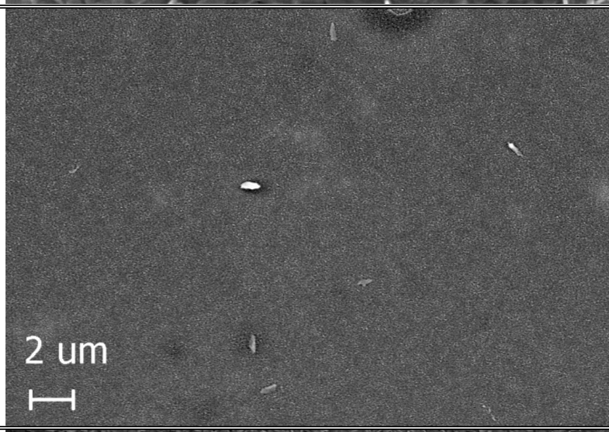
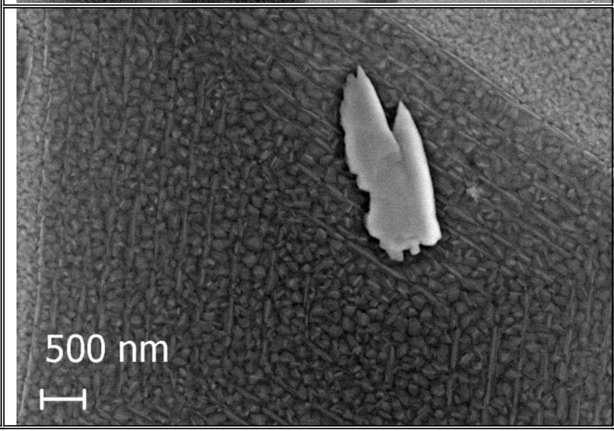
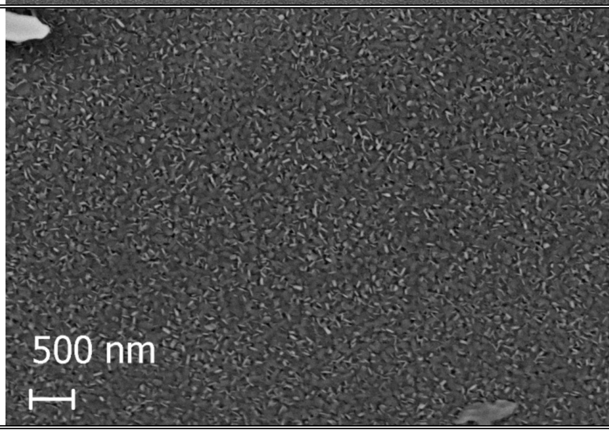
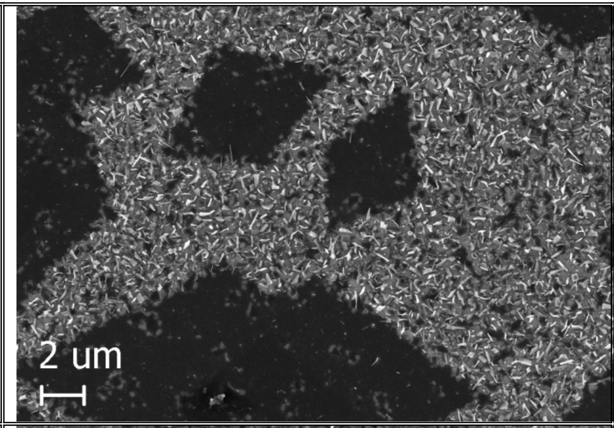
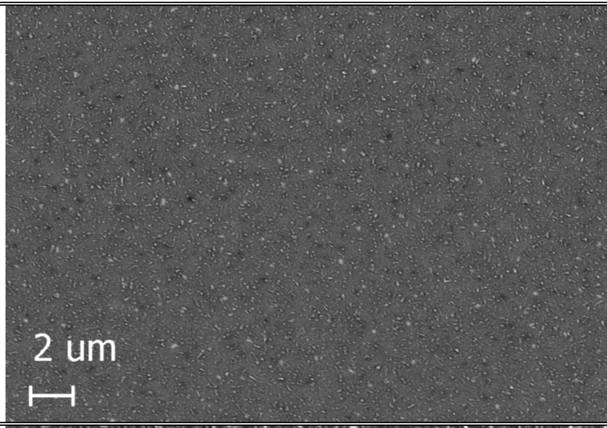
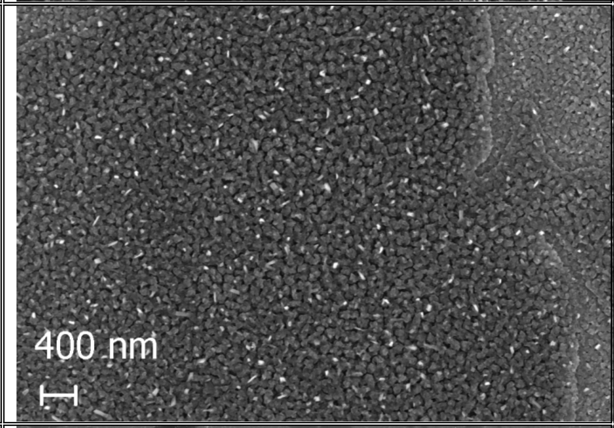
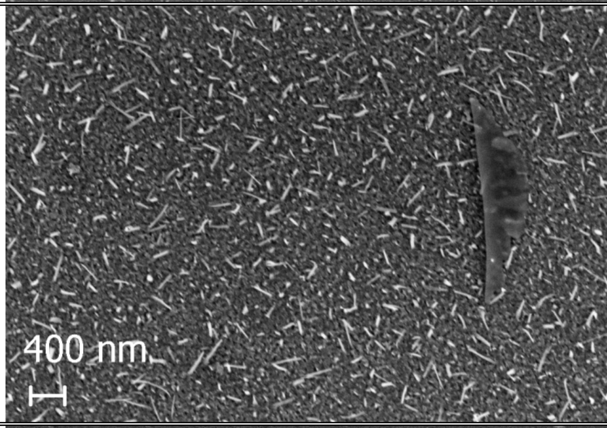
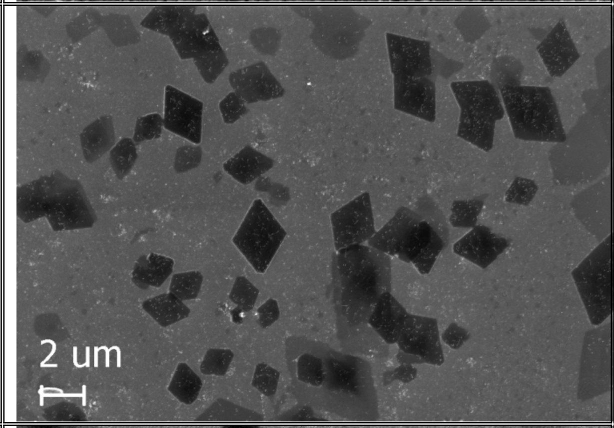
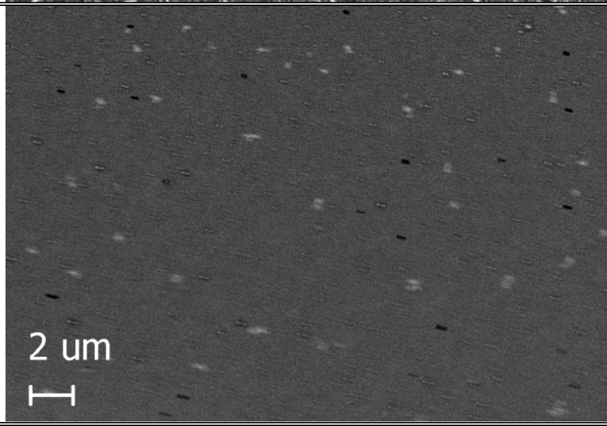
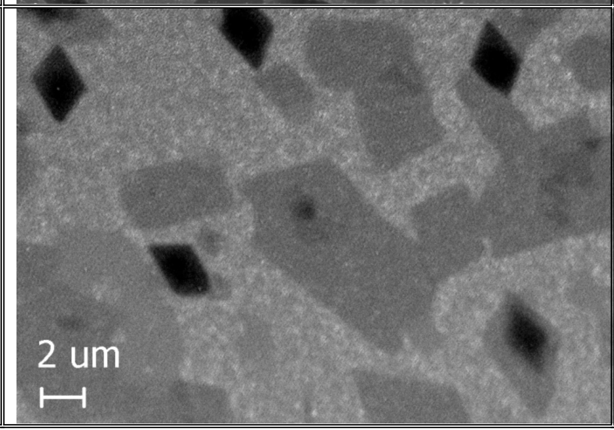
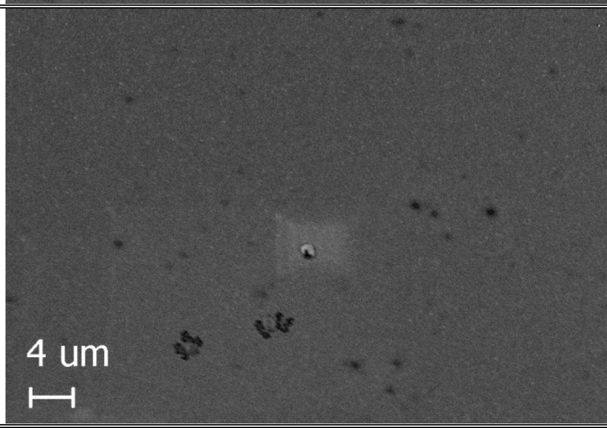
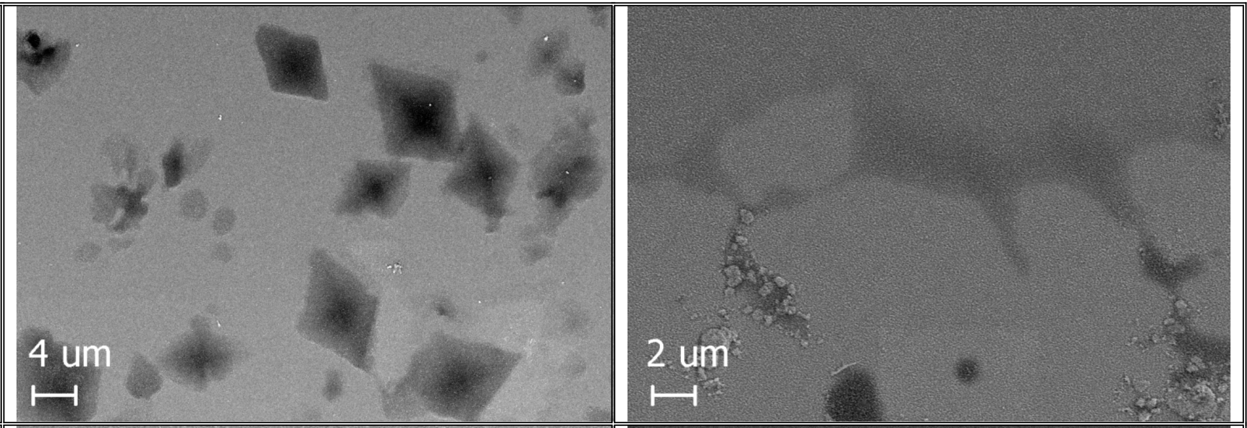

µm
2.0
1.5
1.0
0.5
0
0.5
1.0
1.5
2.0
µm
nm
50
40
30
20
10

Table S5 SEM images of indigoid films grown on TC and BCB dielectrics

No.	Film grown on TC	film grown on BCB
1		
2		
3		
		

4		
5		
6		
7		

8



9

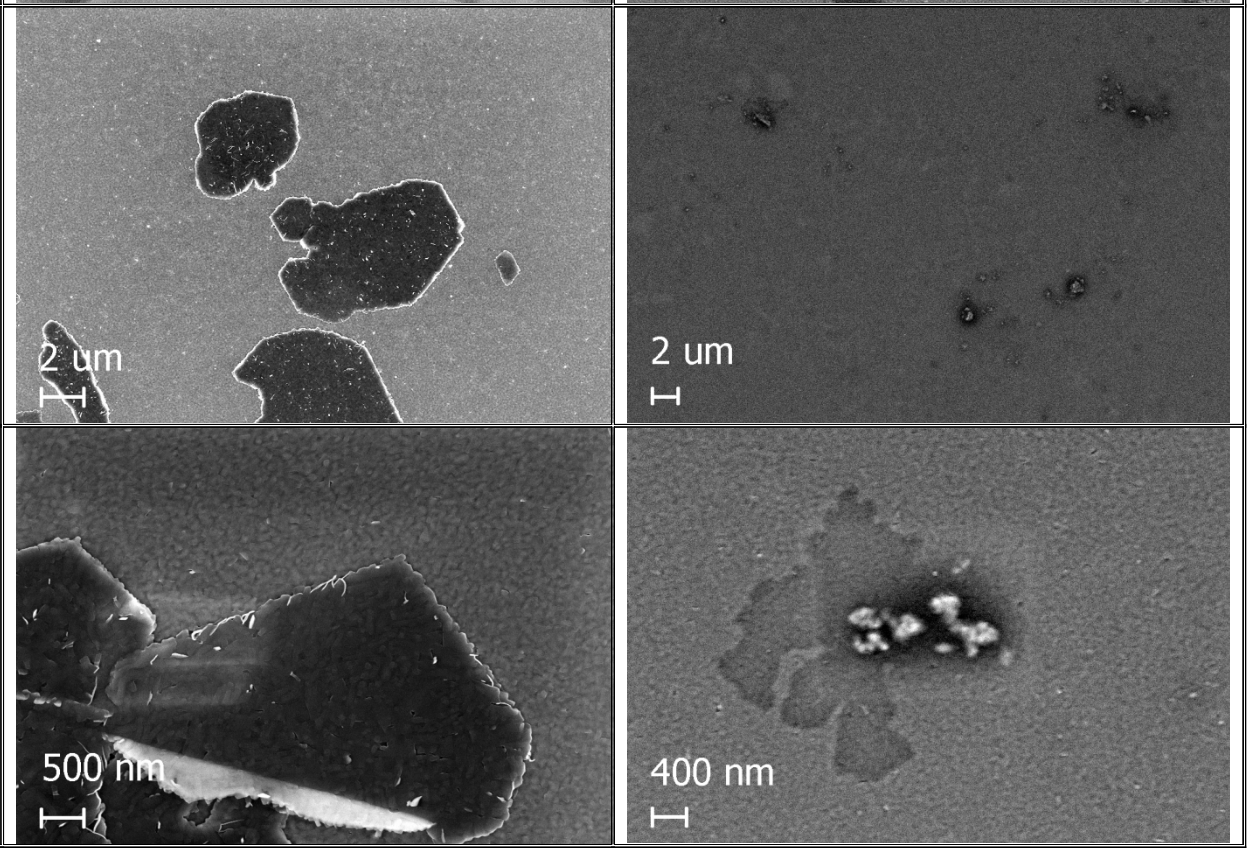


Table S6. Crystallographic data and some details of data collection and refinement for indigo derivatives **1**, **4**, **6**, **7**, and **9**.[a]

Compound	**1**	**4**	**6**	**7**	**9**
formula	$C_{16}H_8F_2N_8O_2$	$C_{18}H_8F_6N_8O_2$	$C_{16}H_8F_2N_8O_2$	$C_{16}H_8Cl_2N_8O_2$	$C_{16}H_6F_4N_8O_2$
M_r	298.24	398.26	298.24	331.14	334.23
crystal system	Monoclinic	Orthorhombic	Monoclinic	Monoclinic	Monoclinic
space group	$\boldsymbol{P2_1/c}$	$\boldsymbol{Iba2}$	$\boldsymbol{P2_1/c}$	$\boldsymbol{P2_1/c}$	$\boldsymbol{P2_1/c}$
a [Å]	8.273(1)	28.211(1)	8.249(1)	13.1129(8)	12.708(1)
b [Å]	6.0598(4)	8.6741(7)	6.0281(7)	4.5375(2)	4.6341(4)
c [Å]	12.2500(7)	12.6299(6)	12.284(1)	11.7091(7)	11.596(7)
α [°]	90	90	90	90	90
β [°]	101.07(1)	90	94.35(1)	110.090(5)	115.352(7)
γ [°]	90	90	90	90	90
V [Å^3]	602.70(9)	3090.6(3)	609.07(11)	654.30(6)	617.12(9)
Z	2	8	2	2	2
D_c [g cm^{-3}]	1.643	1.712	1.626	1.681	1.681
refls collected / R_{int}	8834/0.049	24964 /0.025	9551 /0.033	9060 /0.111	7911/0.064
data / parameters	1409 /100	3750 /254	1511 / 117	1748 / 116	1315 / 1130
R_1 [$I \geq 2\sigma(I)$]/wR_2(all)	0.053 / 0.150	0.039 / 0.108	0.054 / 0.140	0.058 / 0.119	0.064 / 0.154
$\Delta\rho_{max / min}$ [e Å^{-3}]	0.34 / -0.26	0.45 / -0.26	0.42 / -0.38	0.53 / -0.31	0.39 / -0.26

[a] **1** - 6,6'-difluoroindigo; **4** - 6,6'-bis(trifluoromethyl)indigo; **6** - 5,5'-difluoroindigo; **7** - 5,5'-dichloroindigo; **9** - 5,5',6,6'-tetrafluoroindigo;

Table S7. Main peaks detected at the powder XRD pattern of indigoid **1** compared to the single crystal X-ray data.

No.	Powder XRD (T=293 K)		Single crystal X-ray (T=100 K)	
	Position	Intensity	Position	Intensity
1	10.60	2885	10.90	2145
2	14.60	925	14.70	4516
3	16.35	176	16.55	692
4	20.30	125	20.50	530
5	20.80	141	20.80	1255
7	23.55	894	23.95	1343
8	25.95	7783	26.40	10000
9	28.10	2975	28.20	1706
10	29.50	213	29.45	190
11	33.20	288	33.25	442
12	36.50	144	36.35	99
13	36.85	217	36.70	481
14	38.75	111	38.65	105
15	39.80	114	39.85	137
16	41.15	95	41.15	284
17	43.20	232	43.10	10
18	45.30	307	45.35	206
20	51.00	56	50.95	59
22	53.50	111	53.60	396
23	54.85	87	54.65	148
24	55.25	150	55.00	92

Table S8. Main peaks detected at the powder XRD pattern of indigoid **2** compared to the single crystal X-ray data.

No.	Powder XRD (T=293 K)		Single crystal X-ray (T=100 K)	
	Position	Intensity	Position	Intensity
1	5.90	1869	5.90	104
2	11.85	1536	11.80	147
3	15.50	2468	15.45	785
4	17.25	2088	17.20	343
5	20.70	2368	20.65	941
6	23.85	1928	23.80	1506
7	25.10	1706	25.05	204
8	25.90	2068	25.75	75
9	26.90	1713	26.85	402
10	27.90	4000	27.80	741
11	30.15	1634	30.05	250
12	31.25	1712	31.25	433
13	32.10	1661	32.10	154
14	34.90	1607	34.90	211
15	35.60	1547	35.45	139
16	36.10	1648	36.05	1117
17	37.20	1551	37.25	96
18	37.65	1529	37.60	59
19	38.10	1606	38.00	71
20	41.40	1596	41.20	172
21	42.15	1699	42.05	235
22	43.05	1594	43.05	50
23	43.45	1535	43.40	64
24	45.30	1564	45.30	84
25	47.20	1551	47.10	68
26	47.75	1521	47.85	37
27	48.85	1553	48.75	186
28	50.20	1523	50.20	72
29	50.80	1575	50.80	67
30	51.55	1530	51.45	55
31	55.40	1521	55.45	125

Table S9. Main peaks detected at the powder XRD pattern of indigoid **3** compared to the single crystal X-ray data.

No.	Powder XRD (T=293 K)		Single crystal X-ray (T=100 K)	
	Position	Intensity	Position	Intensity
1	7.25	568	7.20	2058
2	14.55	722	14.50	585
3	15.75	409	15.75	3138
4	18.75	777	18.75	6129
5	19.90	61	19.95	747
6	21.90	74	21.90	955
7	23.40	308	23.40	2681
8	23.75	476	23.70	1950
9	23.95	122	24.05	456
10	24.15	75	24.30	660
11	25.85	1332	25.85	10000
12	26.40	90	26.50	675
13	28.20	76	28.20	507
14	29.30	506	29.20	284
15	29.80	542	29.70	2484
16	30.10	576	30.25	2543
17	30.90	245	31.00	1927
18	31.85	342	31.85	270
19	32.40	155	32.50	671
20	33.95	647	33.90	1957
21	34.45	140	34.65	500
22	36.45	195	36.35	203
23	36.75	428	36.75	656
24	37.25	231	37.25	468
25	38.00	142	38.00	532
26	38.40	244	38.55	446
27	39.90	43	39.95	321
28	40.35	186	40.30	440
29	43.85	130	43.80	406
30	44.55	870	44.45	516
31	46.65	128	46.65	223
32	47.30	396	47.20	563
33	47.90	151	48.05	647
34	48.05	103	48.20	436
35	48.50	157	48.50	401
36	48.90	128	49.05	301
38	49.85	93	49.85	314
39	52.90	137	52.95	290
40	53.10	159	53.15	501
41	54.55	135	54.50	253
42	54.75	98	54.80	326
43	62.60	101	62.55	231
44	62.95	76	62.85	184

Table S10. Main peaks detected at the powder XRD pattern of indigoid **4** compared to the single crystal X-ray data.

No.	Powder XRD (T=293 K)		Single crystal X-ray (T=100 K)	
	Position	Intensity	Position	Intensity
1	13.70	119	13.90	2542
2	14.00	132	14.00	2624
3	15.65	398	15.35	3093
4	17.90	375	17.65	1155
5	19.00	100	18.85	4798
6	19.60	239	19.75	2154
7	22.65	120	22.60	542
8			23.65	3253
9	24.40	1713	24.05	10000
10	24.80	98	24.90	1034
11			25.70	634
12	26.95	205	26.85	4220
13	27.60	298	27.95	834
14			28.20	1674
15	29.00	168	28.95	411
16	29.60	95	29.70	490
17	30.65	520	31.00	939
18	31.30	86	31.40	415
19	33.70	93	34.85	1526
20	35.90	146	35.75	554
21	36.50	145	36.50	238

Table S11. Main peaks detected at the powder XRD pattern of indigoid **5**

No.	Experimental		Calculated
	Position	Intensity	Position
1	10.55	166	10.54
2	14.20	121	14.20
3	14.55	130	14.55
4	17.95	77	17.96
5	19.70	79	19.75
6	25.05	438	25.08
7	26.75	322	26.73
8	26.85	328	26.82
9	26.95	343	26.97
10	27.35	556	27.35
11	27.95	136	27.92
12	31.35	51	31.32

Unit cell parameters: a=13.06±0.03 Å, b=11.58±0.02 Å; c=6.69±0.01 Å, $\alpha=\gamma=90^{o}$, $\beta=111.3\pm0.1^{o}$

Table S12. Main peaks detected at the powder XRD pattern of indigoid **6**

No.	Experimental		Calculated
	Position	Intensity	Position
1	7.65	244	7.57
2	14.75	411	14.72
3	17.00	211	16.96
4	24.65	1210	24.65
5	25.35	223	25.36
6	25.65	443	25.63
7	25.95	496	26.00
8	29.20	640	29.21
9	30.60	150	30.64
10	53.50	75	53.49

New room-temperature phase with the unit cell parameters: a=12.30±0.01 Å, b=7.02±0.01 Å; c=7.22±0.01 Å, α=γ=90°, β=108.5±0.1°

Table S13. Main peaks detected at the powder XRD pattern of indigoid **7** compared to the single crystal X-ray data.

No.	Powder XRD (T=293 K)		Single crystal X-ray (T=100 K)	
	Position	Intensity	Position	Intensity
1	7.15	310	7.20	1782
2	14.95	159	15.20	4177
3	17.10	153	17.50	3342
4	21.50	185	22.10	1906
5	23.30	69	23.25	1049
6	23.85	282	24.05	3533
7	24.25	1088	24.35	10000
8	24.65	38	24.85	986
9	25.20	76	25.15	676
10	25.40	68	25.40	1597
11	27.30	159	27.90	1525
12	28.05	496	28.35	4986
13	29.30	571	29.65	6085
14	30.40	74	30.70	1856
15	32.05	124	32.05	1009
16	32.35	78	32.45	475
17	35.70	92	35.80	780
18	38.10	82	38.15	989
19	40.45	101	40.35	617
20	53.15	91	53.50	901

Table S14. Main peaks detected at the powder XRD pattern of indigoid **9**

No.	Experimental		Calculated
	Position	Intensity	Position
1	7.75	215	7.74
2	14.55	359	14.54
3	24.55	1678	24.53
4	25.05	526	25.03
5	26.10	3900	26.07
6	27.00	966	27.01
7	28.00	1179	28.00
8	28.50	529	28.52
9	31.10	1391	31.11
10	34.50	278	34.50
11	39.15	205	39.14
12	42.90	229	42.90
13	47.40	688	47.43

New room-temperature phase with the unit cell parameters: a=12.93±0.01 Å, b=4.54±0.01 Å; c=12.26±0.01 Å, $\alpha=\gamma=90^{o}$, $\beta=111.4\pm0.1^{o}$