

**Thin films of chlorosubstituted vanadyl phthalocyanine:
charge transport properties and optical spectroscopy
study of structure**

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Supporting Information

Thin Films of Chlorosubstituted Vanadyl Phthalocyanine: Charge Transport Properties and Optical Spectroscopy Study of Structure

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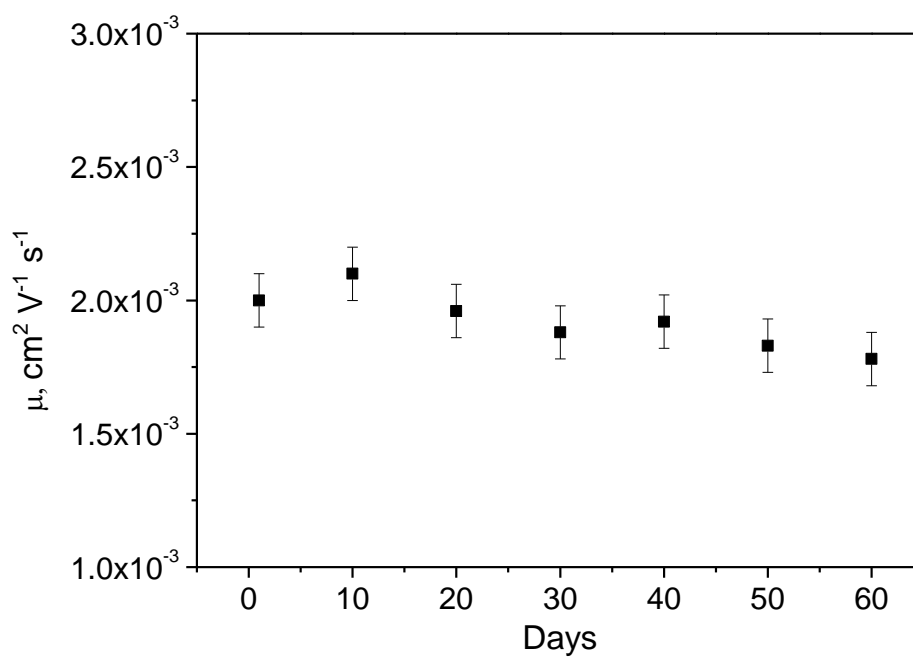


Figure S1. Charge carrier mobility in VOPcCl₁₆ organic field-effect thin film transistor upon exposure to air as a function of time.

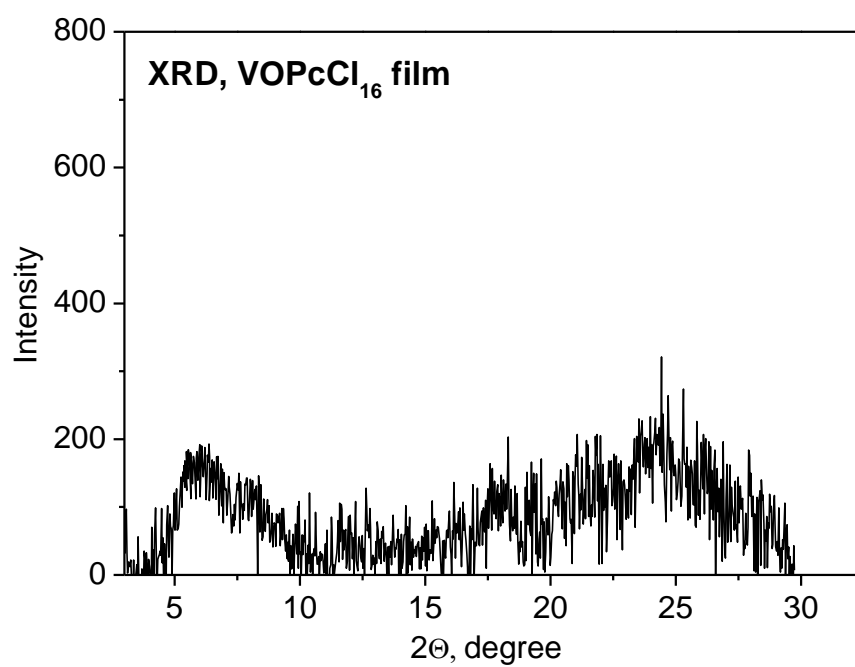


Figure S2. X-ray diffraction pattern of a VOPcCl₁₆ film.

Table S1. The B3LYP/6-311++G(2df,p) optimized geometry of the VOPcCl₁₆.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	8	0	0.000000	0.000000	2.331031
2	23	0	0.000000	0.000000	0.757308
3	7	0	0.000000	1.975439	0.208666
4	7	0	-1.961186	0.000000	0.118702
5	7	0	0.000000	-1.975439	0.208666
6	7	0	1.961186	0.000000	0.118702
7	7	0	2.360020	2.372104	0.086477
8	7	0	-2.360020	2.372104	0.086477
9	7	0	-2.360020	-2.372104	0.086477
10	7	0	2.360020	-2.372104	0.086477
11	6	0	1.117413	2.764597	0.273058
12	6	0	0.704189	4.147515	0.491723
13	6	0	1.418919	5.325338	0.703257
14	6	0	0.704449	6.512151	0.892521
15	6	0	-0.704449	6.512151	0.892521
16	6	0	-1.418919	5.325338	0.703257
17	6	0	-0.704189	4.147515	0.491723
18	6	0	-1.117413	2.764597	0.273058
19	6	0	-2.730977	1.117732	-0.074475
20	6	0	-4.075137	0.703841	-0.463384
21	6	0	-5.215732	1.418870	-0.827481
22	6	0	-6.368521	0.704431	-1.166518
23	6	0	-6.368521	-0.704431	-1.166518
24	6	0	-5.215732	-1.418870	-0.827481
25	6	0	-4.075137	-0.703841	-0.463384
26	6	0	-2.730977	-1.117732	-0.074475
27	6	0	-1.117413	-2.764597	0.273058
28	6	0	-0.704189	-4.147515	0.491723
29	6	0	-1.418919	-5.325338	0.703257
30	6	0	-0.704449	-6.512151	0.892521
31	6	0	0.704449	-6.512151	0.892521
32	6	0	1.418919	-5.325338	0.703257
33	6	0	0.704189	-4.147515	0.491723
34	6	0	1.117413	-2.764597	0.273058
35	6	0	2.730977	-1.117732	-0.074475
36	6	0	4.075137	-0.703841	-0.463384
37	6	0	5.215732	-1.418870	-0.827481
38	6	0	6.368521	-0.704431	-1.166518
39	6	0	6.368521	0.704431	-1.166518
40	6	0	5.215732	1.418870	-0.827481
41	6	0	4.075137	0.703841	-0.463384
42	6	0	2.730977	1.117732	-0.074475
43	17	0	-7.805482	-1.552922	-1.604626
44	17	0	-7.805482	1.552922	-1.604626
45	17	0	-5.225200	3.139559	-0.890619

46	17	0	-5.225200	-3.139559	-0.890619
47	17	0	-3.139367	-5.337983	0.773342
48	17	0	-1.553374	-7.991941	1.148968
49	17	0	1.553374	-7.991941	1.148968
50	17	0	3.139367	-5.337983	0.773342
51	17	0	5.225200	-3.139559	-0.890619
52	17	0	7.805482	-1.552922	-1.604626
53	17	0	7.805482	1.552922	-1.604626
54	17	0	5.225200	3.139559	-0.890619
55	17	0	-3.139367	5.337983	0.773342
56	17	0	-1.553374	7.991941	1.148968
57	17	0	1.553374	7.991941	1.148968
58	17	0	3.139367	5.337983	0.773342

Table S2. The experimental and calculated (B3LYP/6-311++G(2df,p)) Raman and IR wavenumbers (cm^{-1}) of the VOPcCl₁₆.

Experimental wavenumbers		Calculated wavenumbers	Calculated IR intensities	Symmetry	Assignment
Raman	IR				
	205	209	1.82	B ₂	O-V-N _α , N _β , C _γ and C _δ out-of-plane motions
	222	218	0.0879	A ₁	C _β -C _γ -Cl, C _γ -C _δ -Cl, C _β '-C _γ '-Cl, C _γ '-C _δ '-Cl, N _α -N _β
223		229	0	A ₂	N _α -V-N _α , C _β -C _γ -Cl, C _γ -C _δ -Cl, C _β '-C _γ '-Cl, C _γ '-C _δ '-Cl, N _α -V=O
	236	235	0.12	A ₁	C _γ -C _δ -Cl, C _γ '-C _δ '-Cl, N _α -V-N _α
238		235	0.06	B ₁	C _β '-C _γ '-Cl, C _γ '-C _δ '-Cl, N _α -V-N _α
	259	254	0.61	A ₁	V-N _α , N _α , C _γ and C _δ out-of-plane motions
	276	271	2.21	B ₁	N _α , N _β out-of-plane motions, V-N _α
290		284	1.87	B ₂	N _α -V=O, N _α out-of-plane motions
298	294	297	0.39	B ₂	V-N _α , N _α -V=O, C _β -C _γ -C _δ , C _β '-C _γ '-Cl
	310	304	0.09	B ₁	V-N _α , N _α -V=O, C _β '-C _γ '-C _δ , C _β -C _γ -Cl
320		332	0.01	A ₁	C _β '-C _γ '-C _δ , C _β -C _γ -C _δ , V-N _α , V-N _α
334	330	340	9.78	B ₂	benzene ring deformations (OP), N _α -V=O
		342	8.25	B ₁	benzene ring deformations (OP), N _α -V=O
349	343		0.60	B ₁	N _α -V=O, benzene ring deformations (IP)
		350	0.37	B ₂	N _α -V=O, benzene ring deformations (IP)
369	365	375	3.92	B ₁	C _γ ' and C _β out-of-plane motions, N _α '-V=O, N _α '-V
374	374	377	4.29	B ₂	C _γ and C _β ' out-of-plane motions, N _α -V=O, N _α -V
	384	378	2.23	A ₁	N _β , C _β ', C _β out-of-plane motions
420	417	391	1.37	B ₁	V-N _α , N _α '-V=O, C _β -C _γ -C _δ
		393	2.45	B ₂	V-N _α , N _α -V=O, C _β '-C _γ '-C _δ
456	462	455	5.68	A ₁	macroring breathing, V-N _α , V-N _α
	506	506	59.42	B ₁	V-N _α , benzene def., N _β -C _α -C _β , N _β -C _α '-C _β ', C _δ '-Cl
		508	64.96	B ₂	V-N _α , benzene def., N _β -C _α -C _β , N _β -C _α '-C _β ', C _δ -Cl
519		516	0.14	A ₁	macroring breathing, V-N _α , V-N _α
541	543	560	5.39	B ₂	isoindole out-of-plane def.
		563	0.04	B ₁	isoindole out-of-plane def.
590		593	0	A ₂	isoindole def.
	606	610	29.45	B ₁	C _γ -Cl, C _β -C _β -C _γ , C _α '-N _α '-C _α ', C _γ '-Cl, V-N _α
		612	23.04	B ₂	C _γ '-Cl, C _β '-C _β '-C _γ ', C _α -N _α -C _α , C _γ -Cl, V-N _α

610		629	0.21	B ₁	C _γ -Cl, C _γ out-of-plane motions
		628	0.77	B ₂	C _γ '-Cl, C _γ ' out-of-plane motions
	646	630	0.59	A ₁	C _β -C _γ -C _δ
648		640	0	A ₂	C _γ '-Cl, C _γ -Cl, C _δ '-Cl, C _δ -Cl, C _α -C _β -C _γ , C _α '-C _β '-C _γ '
658	670	648	1.22	B ₁	C _γ -C _δ -Cl, C _β -C _γ -Cl, C _α -C _β -C _γ , C _α -N _β -C _α '
		650	1.49	B ₂	C _γ -C _δ '-Cl, C _β '-C _γ '-Cl, C _α '-C _β '-C _γ ', C _α -N _β -C _α '
684		683	0.05	A ₁	C _α -N _β -C _α , macroring def.
704		707	0	A ₂	N _α '-C _α '-N _β , N _α -C _α -N _β , isoindole def., C _γ -Cl, C _γ '-Cl
719		722	0	A ₂	C _γ , C _γ , C _δ , C _δ ', C _β , C _β ' out-of-plane motions
742		741	0.15	A ₁	C _α -N _α -C _α , C _α '-N _α '-C _α ', V-N _α ', V-N _α
	747	756	57.79	B ₂	macroring def.
757	755	758	73.44	B ₁	macroring def.
		767	19.70	B ₂	C _α out-of-plane motions, C _α '-C _β '-C _γ '
	764	769	50.73	B ₁	C _α ' out-of-plane motions, C _α -C _β -C _γ
776	772	776	154.29	B ₁	C _α '-N _α '-C _α ', V-N _α ', C _γ '-Cl, C _α -C _β -C _β
782	778	776	217.02	B ₂	C _α -N _α -C _α , V-N _α , C _γ -Cl, C _α '-C _β '-C _β '
805		783	1.97	A ₁	V-N _α , N _α -C _α -N _α , inner ring breathing, N _α -V=O
820	819	812	7.30	A ₁	macroring breathing, C _δ '-Cl, C _δ -Cl, C _γ -Cl, C _γ '-Cl
	947	946	183.29	B ₂	C _β -C _γ -C _δ , C _γ -Cl, isoindole def.
		949	177.53	B ₁	C _β '-C _γ '-C _δ ', C _γ '-Cl, isoindole def.
962		954	2.42	A ₁	C _α -N _α -C _α , C _α '-N _α '-C _α ', V-N _α , V-N _α ', C _β -C _γ -C _δ , C _γ -Cl, C _β '-C _γ '-C _δ ', C _γ '-Cl
	970	958	11.75	B ₁	C _γ -C _δ -C _δ , C _δ -Cl, C _α -C _β , N _α -C _α -N _β , C _β '-C _γ '-C _δ ', C _γ '-Cl
		958	11.41	B ₂	C _γ '-C _δ '-C _δ ', C _δ '-Cl, C _α -C _β , N _α '-C _α '-N _β , C _β -C _γ -C _δ , C _γ -Cl
976		978	0	A ₂	C _α -N _β -C _α , C _γ '-C _δ '-C _δ ', C _γ -C _δ -C _δ , C _δ '-Cl, C _δ -Cl
1012	1007	1073	131.58	A ₁	V=O
1080		1084	0	A ₂	C _α -N _α , benzene deformations, C _δ '-Cl, C _δ -Cl, C _γ '-Cl, C _γ -Cl
1100	1082	1101	115.34	B ₂	C _α '-N _α ', benzene deformations, C _δ '-Cl, C _γ '-Cl, C _α -N _α -C _α
	1088	1109	111.62	B ₁	C _α -N _α , benzene deformations, C _δ -Cl, C _γ -Cl, C _α '-N _α '-C _α '
	1139	1146	401.77	B ₂	C _α '-N _α ', C _β '-C _γ '-C _δ ', C _δ '-Cl, C _γ '-Cl, C _α '-N _β , benzene breathing
1150	1146	1148	504.92	B ₁	C _α -N _α , C _β -C _γ -C _δ , C _δ -Cl, C _γ -Cl, C _α -N _β , benzene breathing
1172		1187	0.02	A ₁	Benzene def., C _α -N _α -C _α , C _δ -Cl, C _γ -Cl, C _α '-N _α '-C _α ', C _δ '-Cl, C _γ '-Cl, macroring breathing
1190	1184	1191	25.49	A ₁	Benzene def., C _α -N _α -C _α , C _δ -Cl, C _γ -Cl, C _α '-N _α '-C _α ', C _δ '-Cl, C _γ '-Cl, macroring breathing
	1192	1201	491.74	B ₂	C _α -N _α -C _α , isoindole def., C _δ -Cl, C _γ -Cl, benzene breathing
1206	1208	1202	470.09	B ₁	C _α '-N _α '-C _α ', isoindole def., C _δ '-Cl, C _γ '-Cl, benzene breathing
	1267	1281	152.67	B ₂	C _δ -C _δ , C _β -C _β , C _β -C _γ -C _δ , N _β -C _α -C _β
	1273	1283	174.81	B ₁	C _δ '-C _δ ', C _β '-C _β ', C _β '-C _γ '-C _δ ', N _β -C _α '-C _β '
1290	1292	1304	125.81	B ₂	C _β -C _β , C _δ -C _δ , isoindole def.
		1305	172.65	B ₁	C _β '-C _β ', C _δ '-C _δ ', isoindole def.
1302		1314	1.91	A ₁	C _α -N _α -C _α , C _γ -C _δ , C _α '-N _α '-C _α ', C _γ '-C _δ '
	1302	1314	495.44	B ₂	C _α -N _α , C _α -C _β , Pyrrole def., C _α -N _α -C _α
		1315	400.45	B ₁	C _α '-N _α ', C _α '-C _β ', Pyrrole def., C _α '-N _α '-C _α '
1320	1313	1333	8.87	A ₁	isoindole def.
	1366	1383	7.13	A ₁	macroring def.
1386	1390	1386	205.56	B ₂	C _α '-C _β ', C _γ '-C _δ ', isoindole def.

1393		1386	199.49	B ₁	C _α -C _β , C _γ -C _δ , isoindole def.
1422		1463	0.56	B ₂	C _{α'} -N _β , C _α -C _β , C _β -C _β
1439	1437	1467	1.90	B ₁	C _α -N _β , C _{α'} -C _{β'} , C _{β'} -C _{β'}
1473		1494	0	A ₂	C _{α'} -N _β , C _α -N _β , C _{α'} -C _{β'} , C _α -C _β
	1482	1506	57.66	B ₁	C _{α'} -N _β , C _{α'} -C _{β'} , C _α -N _β , C _α -N _α -C _α
	1497	1510	40.34	B ₂	C _α -N _β , C _α -C _β , C _γ -C _δ
1500		1513	0.14	A ₁	C _α -N _β , C _{α'} -N _β , C _{α'} -C _{β'} , C _α -C _β
1517		1536	0.40	A ₁	C _β -C _β , C _{β'} -C _{β'} , C _δ -C _δ , C _{δ'} -C _{δ'} , C _α -N _α , C _{α'} -N _{α'}
	1519	1539	11.54	B ₂	C _β -C _β , C _δ -C _δ , C _β -C _γ
		1539	12.34	B ₁	C _{β'} -C _{β'} , C _δ -C _δ , C _{β'} -C _{γ'}
1535		1561	0	A ₂	C _β -C _γ , C _{β'} -C _{γ'} , C _α -C _β , C _{α'} -C _{β'} , C _α -N _β , C _{α'} -N _β
	1537	1562	23.09	B ₂	C _β -C _γ , C _γ -C _δ , C _α -C _β , C _α -N _α
1542		1562	23.80	B ₁	C _{β'} -C _{γ'} , C _{γ'} -C _{δ'} , C _{α'} -C _{β'} , C _{α'} -N _{α'}
1565		1562	0	A ₂	C _β -C _γ , C _{β'} -C _{γ'} , C _γ -C _δ , C _{γ'} -C _{δ'} , C _α -N _α , C _{α'} -N _{α'}
	1563	1563	14.99	A ₁	C _α -N _β , C _{α'} -N _β

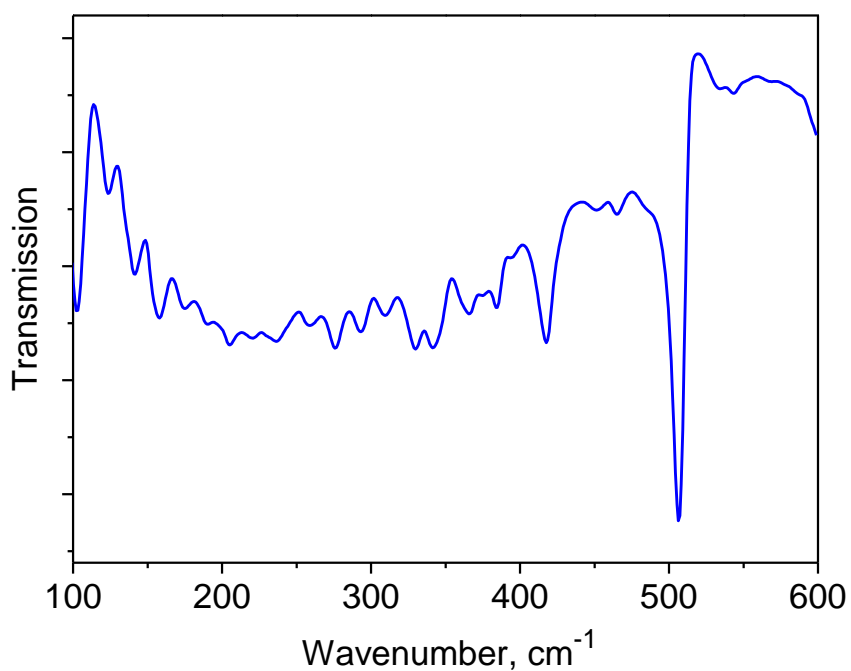


Figure S3. The experimental far IR spectra of VOPcCl₁₆.