Electronic Supplementary Information

Tetracene-based field-effect transistors using solution-processes

Ching-Ting Chien,[a] Chih-Chun Lin,[b] Motonori Watanabe,[a] Yan-Duo Lin,[a] Ting-Han Chao,[c] Ta-chung Chiang,[b] Xin-Hua Huang, Yuh-Sheng Wen,[a] Chih-Hsin Tu,[b] Chia-Hsing Sun,[b] and Tahsin J. Chow[*a]

[a]*Institute of Chemistry, Academia Sinica, No.128, Sec. 2, Academia Rd., Nankang, Taipei 11529, Taiwan. Fax: +886-2-27884179; Tel: +886-2-27898552; E-mail: tjchow@chem.sinica.edu.tw* (T. J. Chow)
[b]*Department of Chemistry, Soochow University, No.70, Linxi Rd. Shilin Dist., Taipei 11102, Taiwan. Tel: +886-2-28819471*
[c]*Department of Chemistry, National of Taiwan Normal University, Ting-Chow Rd. Taipei 11677, Taiwan. Tel: +886-2-77346108*

Contents:

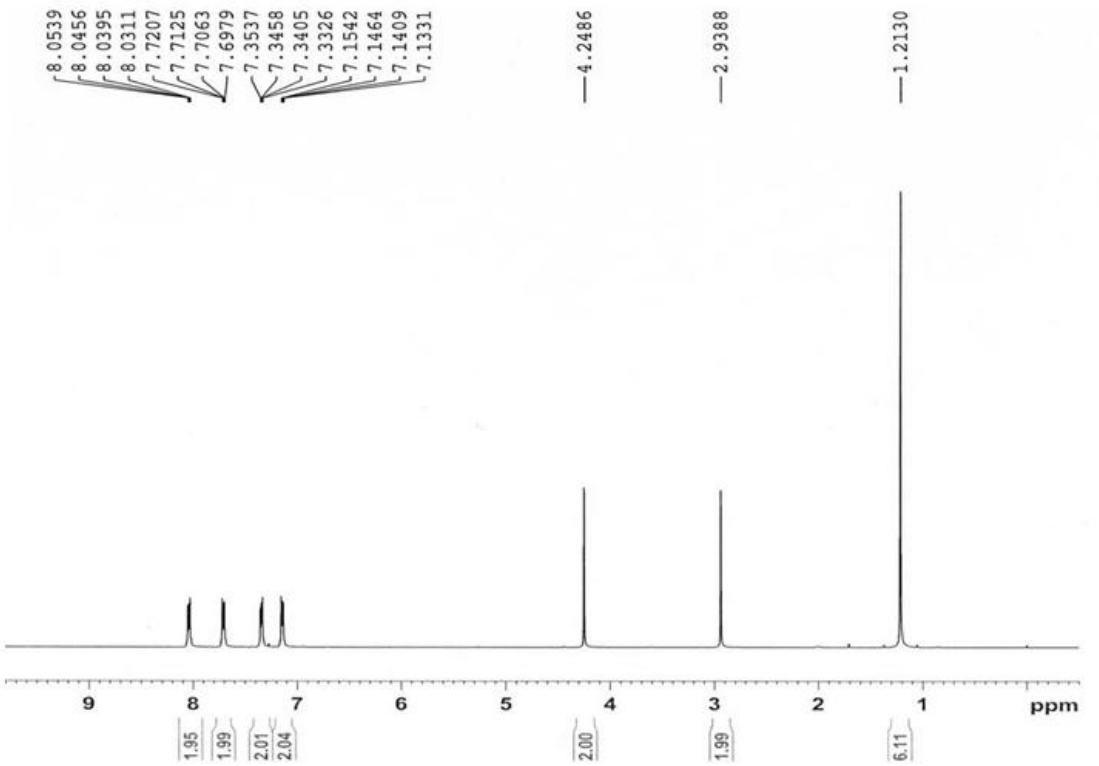

Fig. S1 ^{1}H NMR (400 MHz) spectrum of **4** (*exo* form) in $CDCl_3$

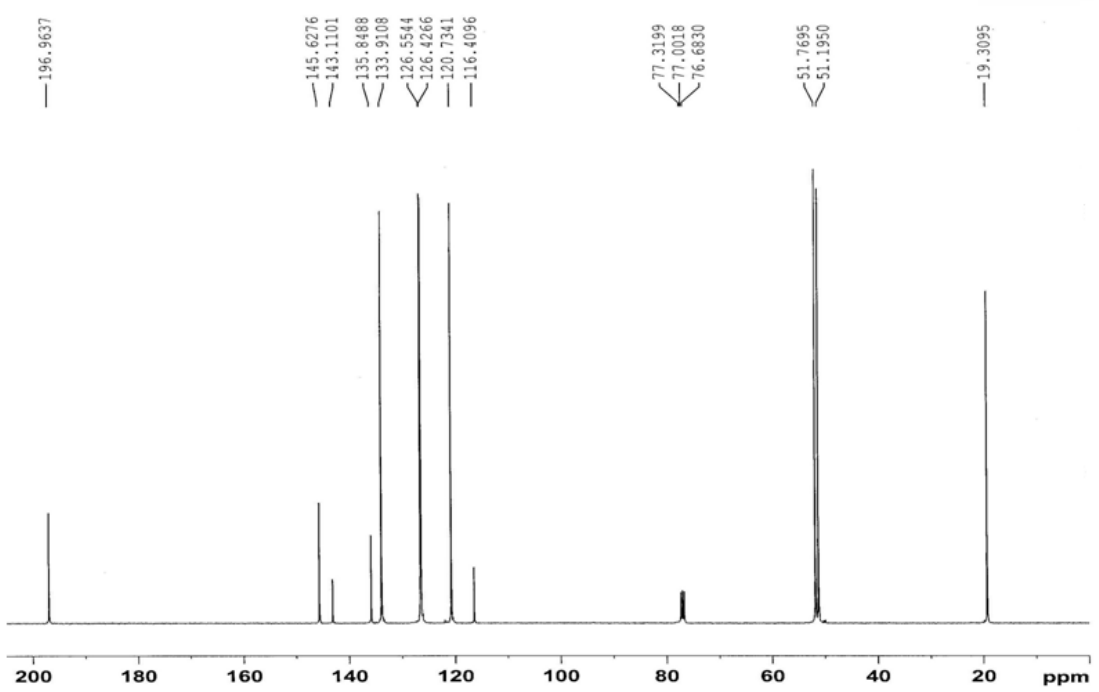

Fig. S2 ^{13}C NMR (100 MHz) spectrum of **4** (*exo* form) in $CDCl_3$

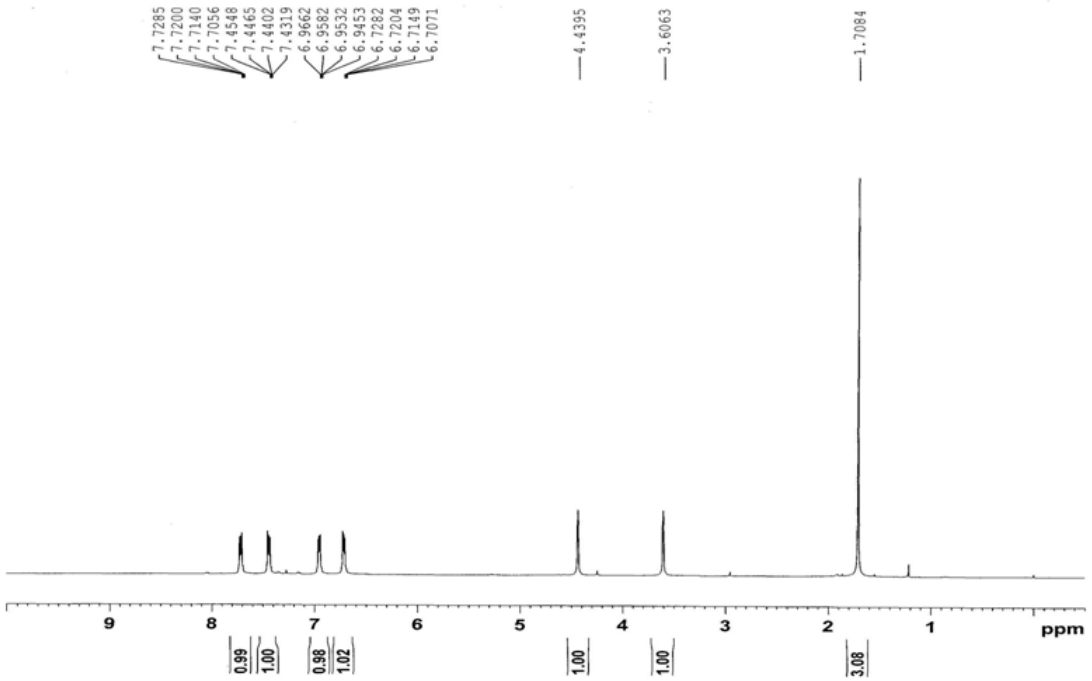

Fig. S3 ^{1}H NMR (400 MHz) spectrum of **4** (*endo* form) in $CDCl_3$

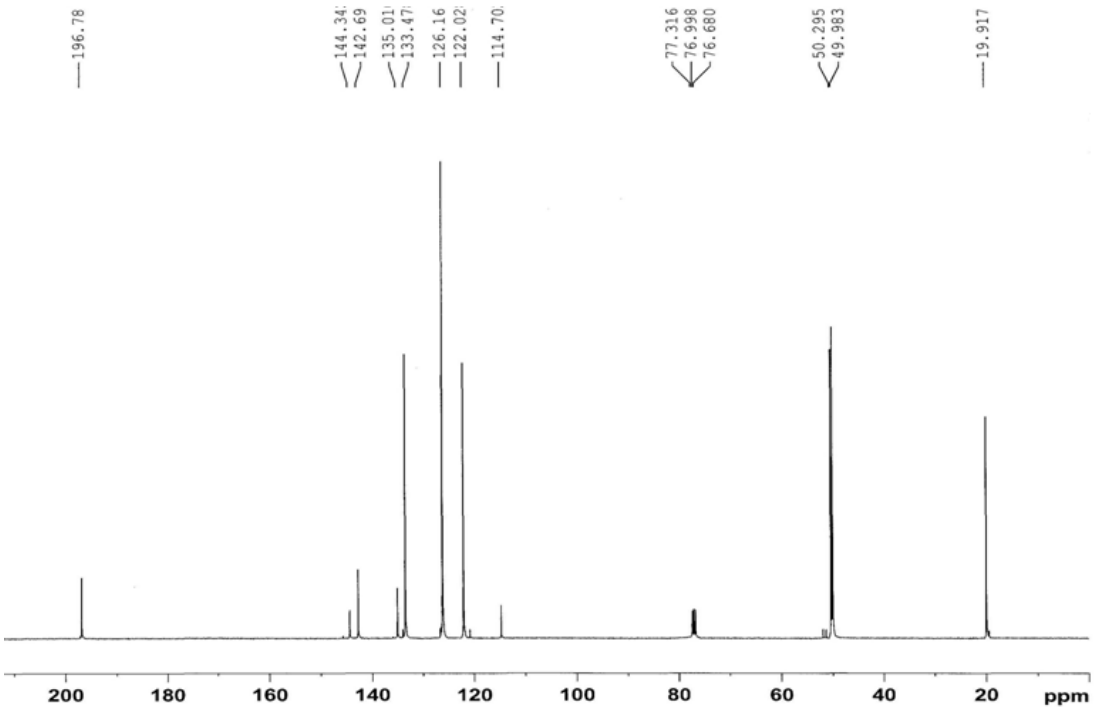

Fig. S4 ^{13}C NMR (100 MHz) spectrum of **4** (*endo* form) in $CDCl_3$

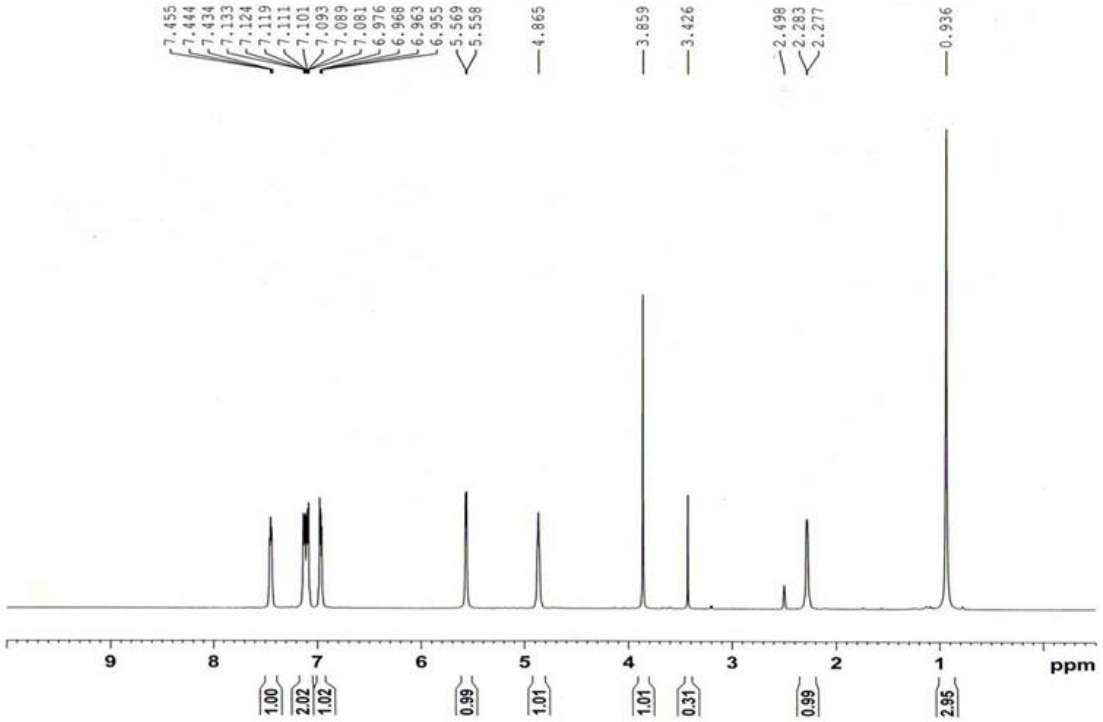

Fig. S5 ^{1}H NMR (400 MHz) spectrum of **5** (*exo* form) in d_6-DMSO

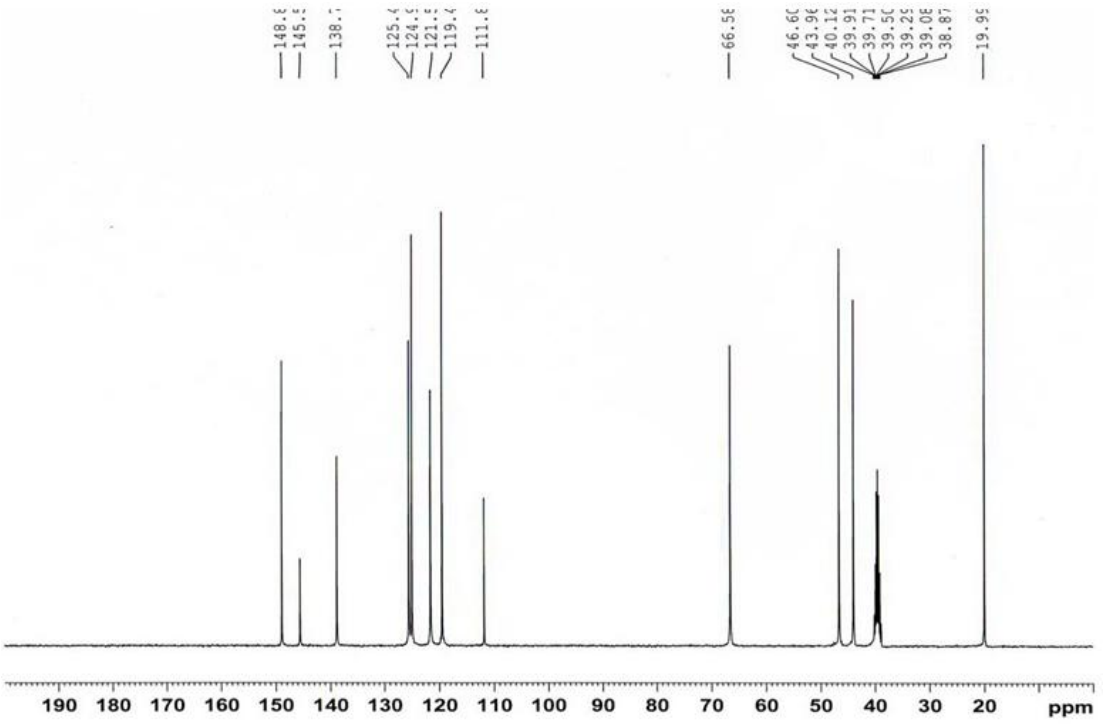

Fig. S6 ^{13}C NMR (100 MHz) spectrum of **5** (*exo* form) in d_6-DMSO

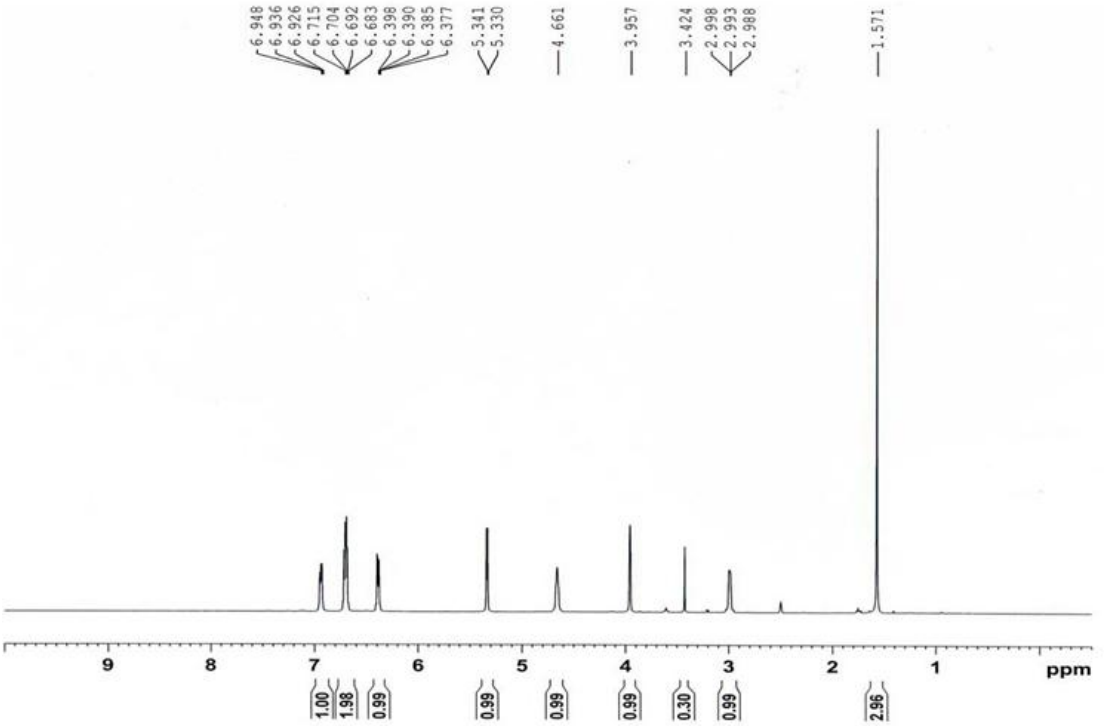

Fig. S7 ^{1}H NMR (400 MHz) spectrum of **5** (*endo* form) in d_6-DMSO

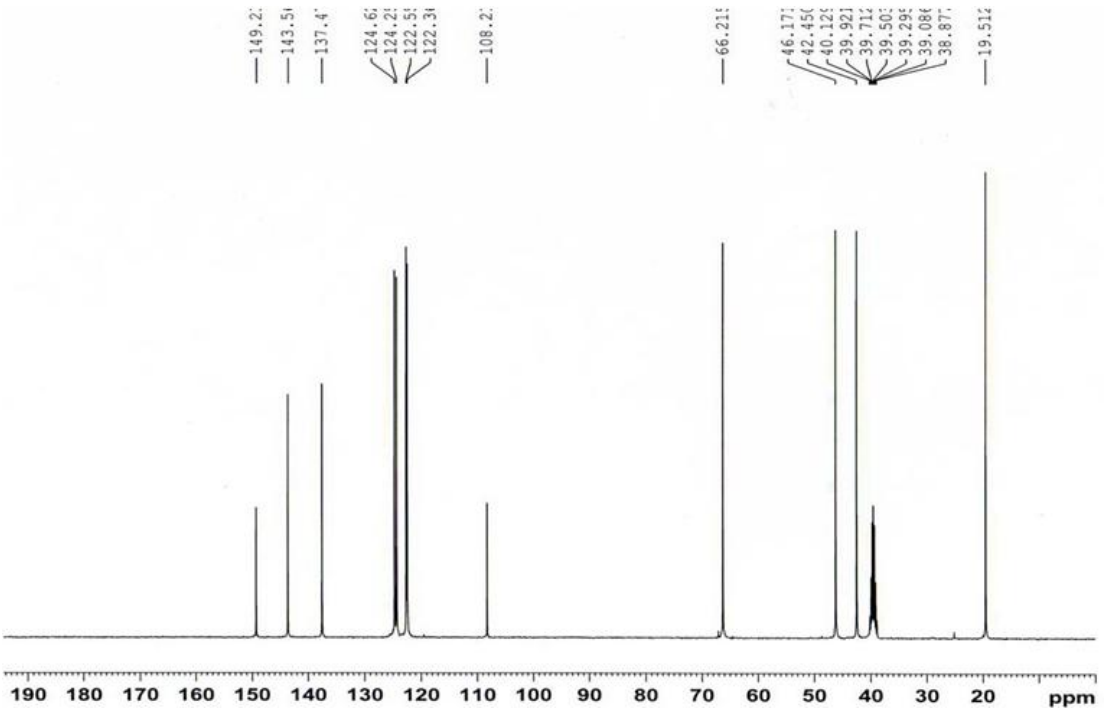

Fig. S8 ^{13}C NMR (100 MHz) spectrum of **5** (*endo* form) in d_6-DMSO

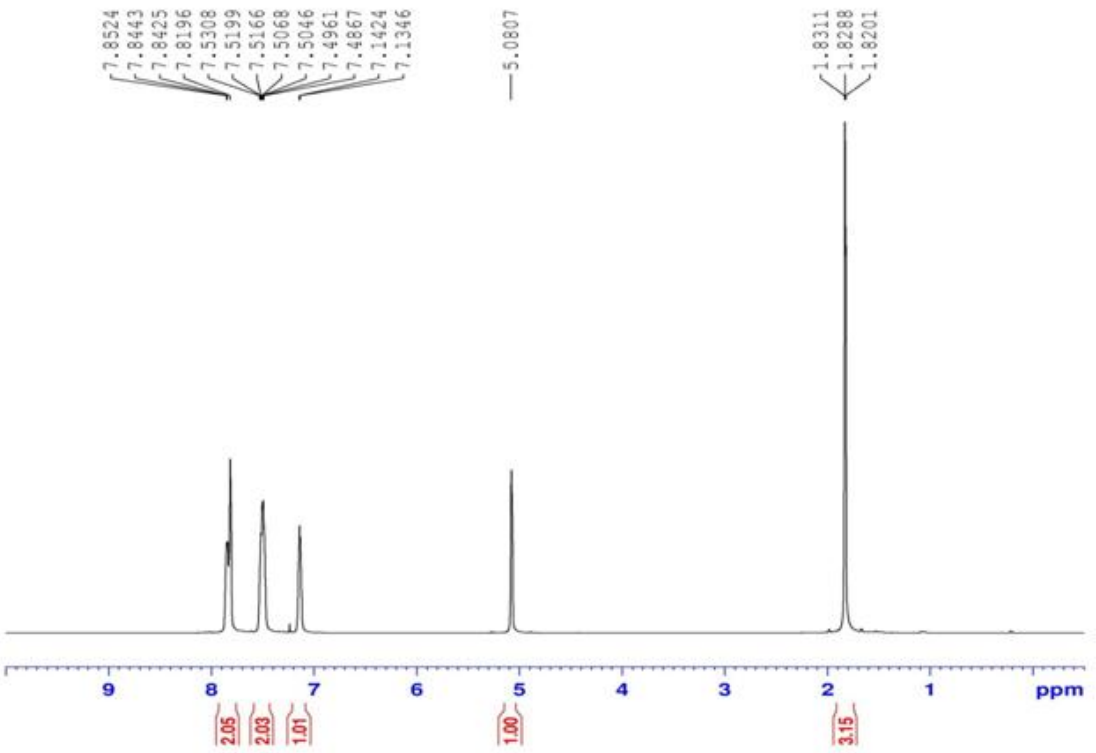

Fig. S9 ^{1}H NMR (400 MHz) spectrum of **6** in $CDCl_3$

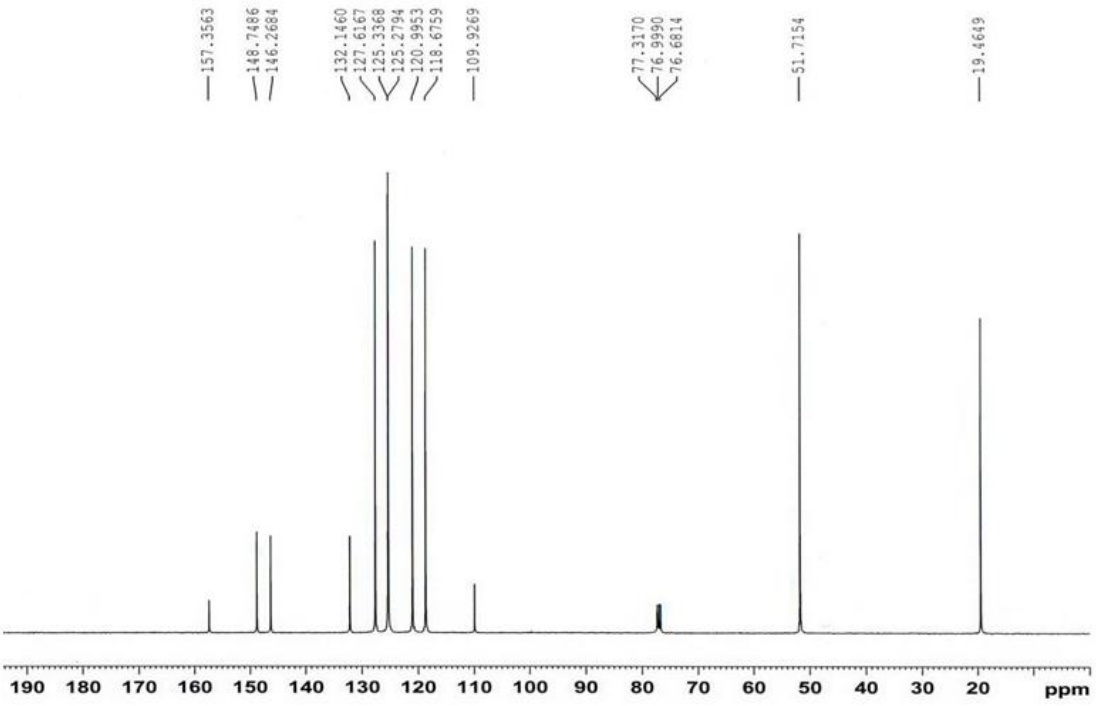

Fig. S10 ^{13}C NMR (100 MHz) spectrum of **6** in $CDCl_3$

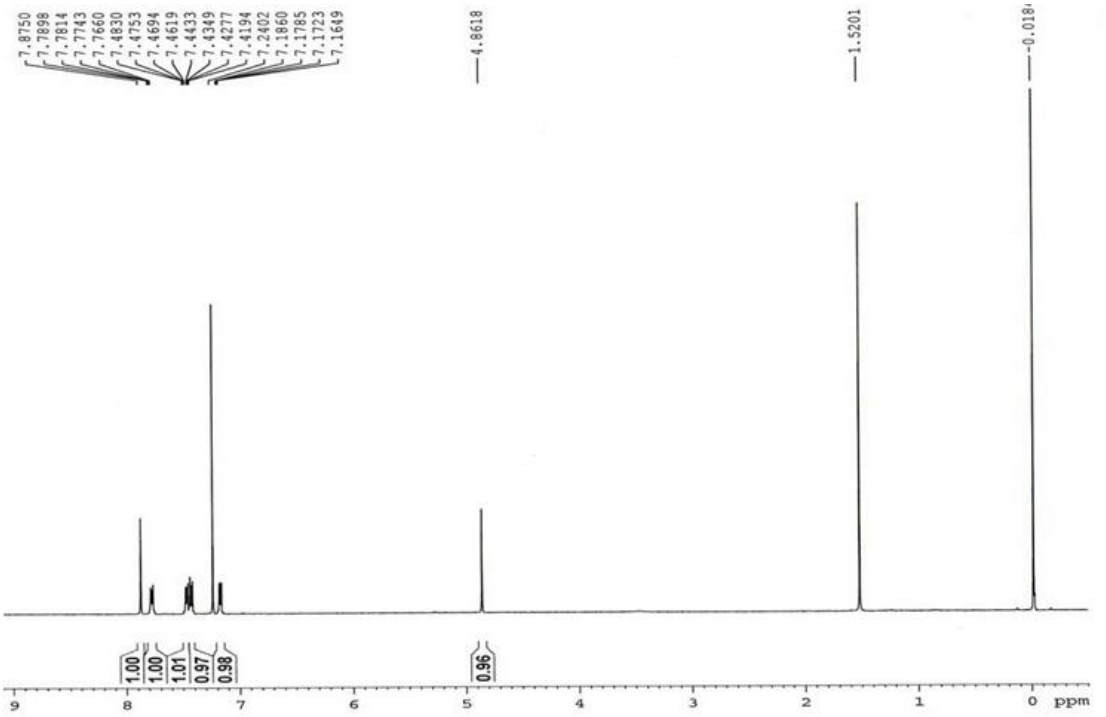

Fig. S11 ^{1}H NMR (400 MHz) spectrum of **1** in $CDCl_3$

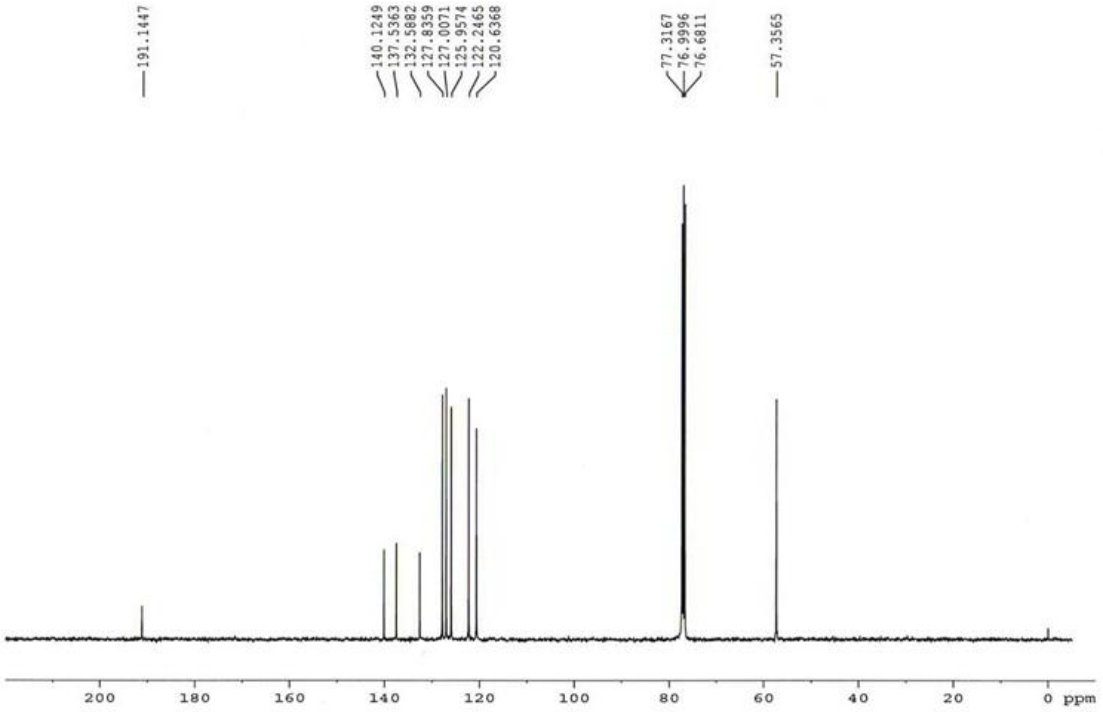

Fig. S12 ^{13}C NMR (100 MHz) spectrum of **1** in $CDCl_3$

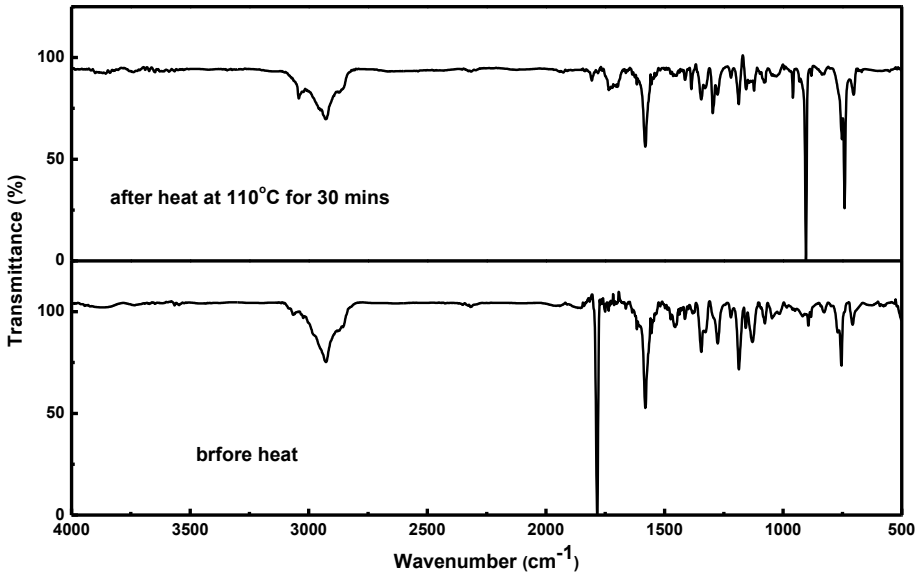

Fig. S13 IR spectra before and after the heating of **1**.

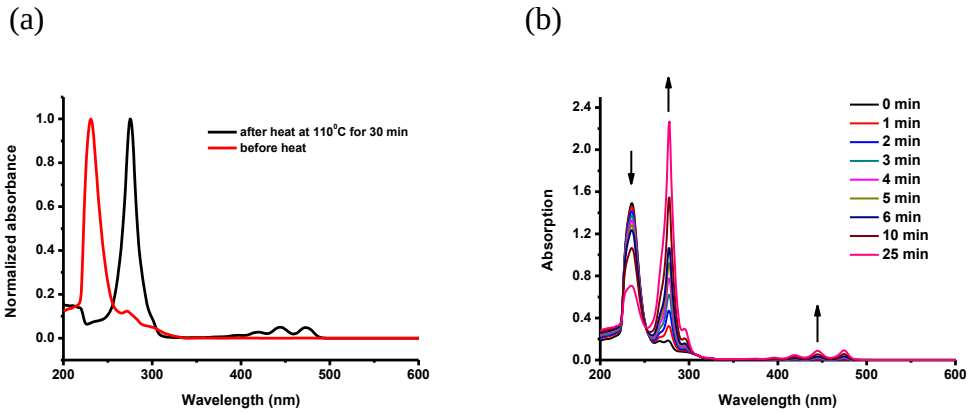

Fig. S14 Absorption spectra of **1** in degassed CH_2Cl_2 obtained with (a) heat and (b) UV irradiation ($\lambda_{ex} \approx 254$ nm) during a period of 0~25 min.

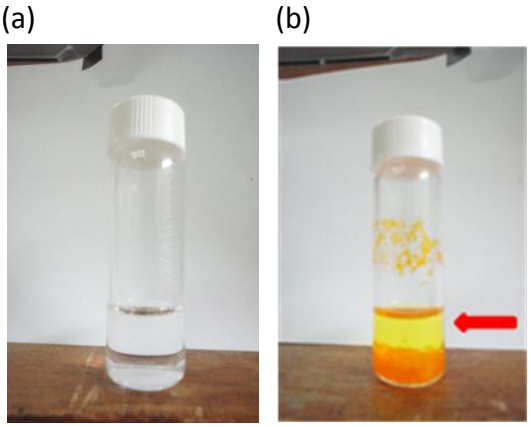

Fig. S15 A toluene solution of **1** (0.6%) (a) before heating and (b) after heated at 110ºC for 15 min. Red arrow indicates the saturated tetracene solution used for spin-coating onto the devices of OFET.

.

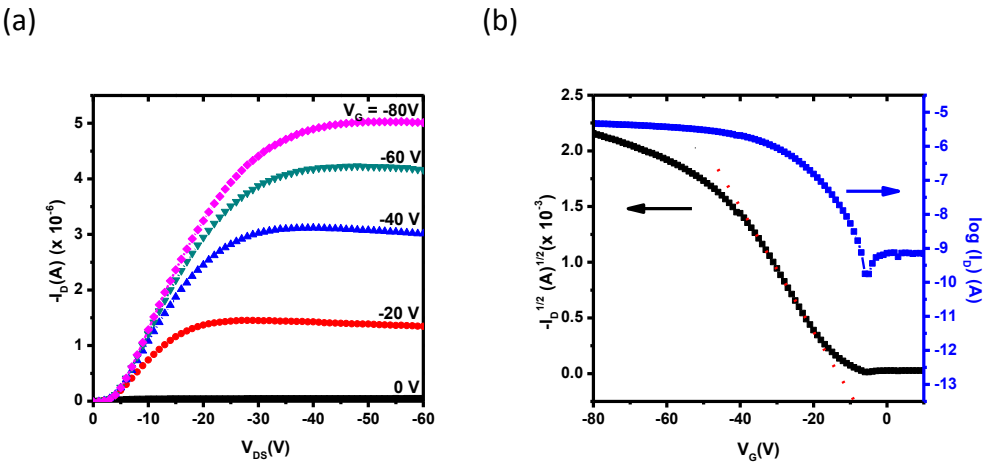

Fig. S16 The FET performance of devices made with a single crystal tetracene on untreated SiO_2/Si wafer. (a) Output characteristics and (b) transfer characteristics measured with V_{DS} = -40V.

Fig. S17 Optical image of a tetracene crystal lying across the S/D electrodes (W = 500 μm, L = 50 μm) on top of a HMDS-pretreated silicon substrate. Scale bar is 50 μm and W/L = 3.84.

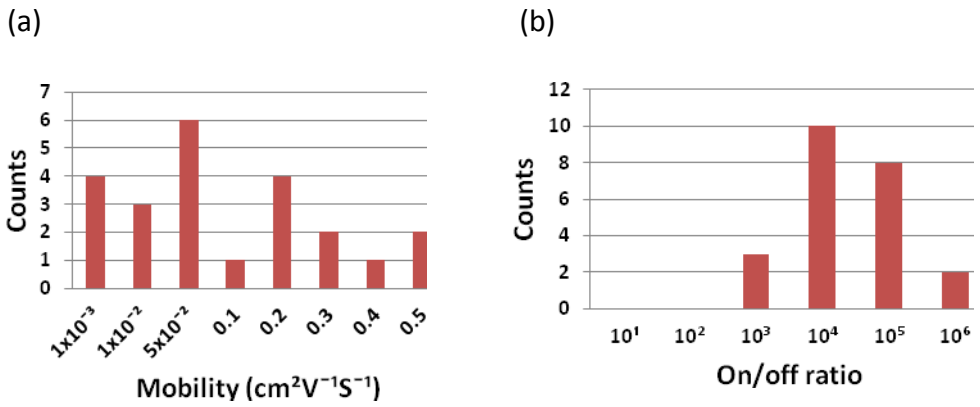

Fig. S18 Histogram of FET performance made with tetracene crystals on HMDS-treated silicon substrates: (a) change mobility, and (b) on/off ratio.

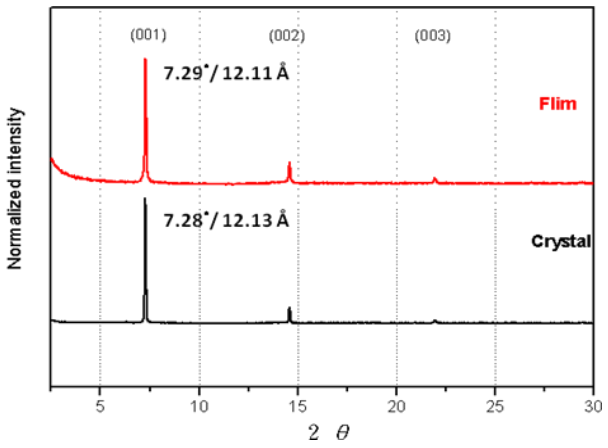

Fig. S19 XRD pattern of the tetracene (a) thin film and (b) single crystal, both revealing an interplanar *d* spacing of 12.11 and 12.13 Å. These spectra match well with the expected (001) spacing of vacuum deposited tetracene films.[15]

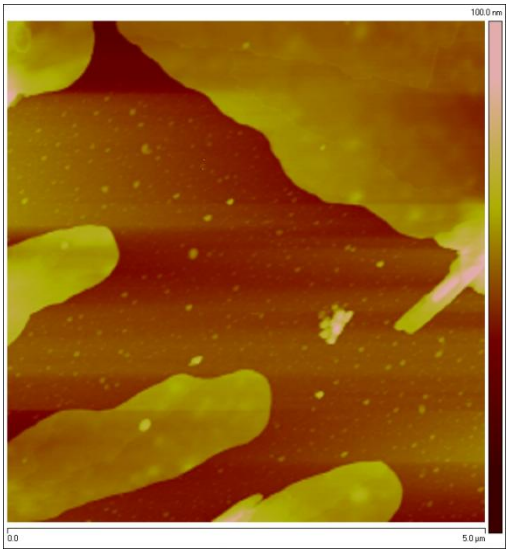

Fig. S20 Atomic-force microscopy image of a tetracene film (5 µm × 5 µm) on a SiO_2/Si substract.

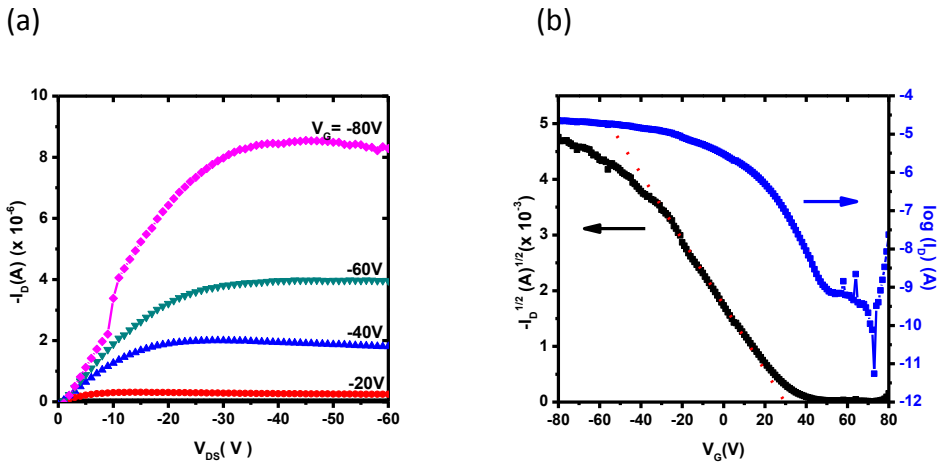

Fig. S21 The FET performance of the devices made with a thin film of tetracene on a SiO_2/Si substrate. (a) Output characteristics and (b) transfer characteristics measured at V_{DS} = -40V.

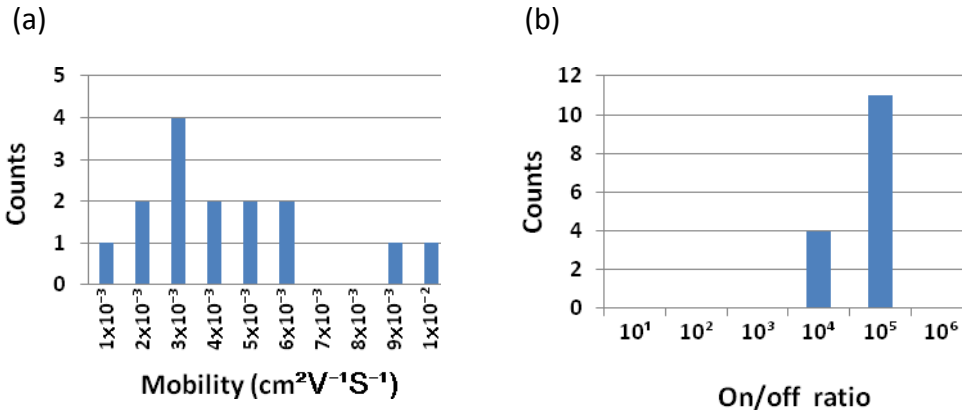

Fig. S22 Histogram of FET performance made with tetracene films on an untreated silicon surface: (a) charge mobility and (b) on/off ratio.

Table S1 X-ray diffraction parameters of the crystal of compounds **1**, **4** and **6**.

Compound	**1**	**4** (*exo*)	**4** (*endo*)	**6**
CCDC Number	847355	847352	847353	847354
Formula	$C_{19}H_{12}O$	$C_{66}H_{54}O_6$	$C_{22}H_{18}O_2$	$C_{22}H_{18}$
FW (amu)	256.29	943.09	314.36	282.36
a (Å)	5.8708(2)	14.3679(10)	8.1278(4)	14.9138(13)
b (Å)	7.6845(3)	12.3365(9)	9.4651(4)	15.2530(12)
c (Å)	28.2976(9)	27.768(2)	10.7576(5)	15.1360(14)
α (deg.)	90	90	102.711(2)	90
β (deg.)	90	101.536(4)	102.324(2)	118.815(4)
Γ (deg.)	90	90	91.986(2)	90
V ($Å^3$)	1276.62(8)	4822.5(6)	785.80(6)	3016.8(5)
Z	4	4	2	8
Space group	P2(1)2(1)2(1)	P2(1)/c	P-1	C2/c
Crystal system	orthorhombic	monoclinic	triclinic	monoclinic
Size (mm^3)	0.30 x 0.10 x 0.07	0.2 x 0.15 x 0.15	0.16 x 0.12 x 0.1	0.12 x 0.1 x 0.1
F(000)	536	1992	332	1200
ρ(Mg/m^3)	1.333	1.299	1.329	1.243
μ (mm^{-1})	0.081	0.082	0.084	0.070
Temp. (K)	200.0(2)	100.0(1)	100.0(1)	100.0(1)
θ(max)	27.50	26.37	26.37	26.37
refl. total, unique	6845, 2886	36505, 9863	11193, 3194	12003, 3090
R_{int}	0.0439	0.0385	0.0245	0.0462
Obsvd refl. ($I > 2\sigma(I)$)	2061	5885	2780	2267
Parameter	181	656	220	201
R_1	0.0389	0.0515	0.0374	0.0609
wR_2	0.0824	0.1173	0.0960	0.1515
GOF	1.026	1.008	1.053	1.066
min/max r_{esd} (e. $Å^{-3}$)	-0.212/0.220	-0.271/0.310	-0.199/0.331	-0.399/0.641

Table S2 Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for compound **1**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
O(1)	-891(3)	-964(2)	781(1)	62(1)
C(1)	862(4)	4678(3)	677(1)	47(1)
C(2)	2600(4)	5346(3)	399(1)	53(1)
C(3)	4538(4)	4384(3)	305(1)	53(1)
C(4)	4806(3)	2720(3)	487(1)	49(1)
C(5)	2879(3)	333(3)	1024(1)	46(1)
C(6)	4213(3)	181(2)	1913(1)	41(1)
C(7)	5039(3)	148(2)	2771(1)	43(1)
C(8)	4436(4)	527(3)	3224(1)	47(1)
C(9)	2370(4)	1385(2)	3318(1)	47(1)
C(10)	951(3)	1843(2)	2955(1)	42(1)
C(11)	101(3)	1987(2)	2098(1)	38(1)
C(12)	-409(3)	1933(3)	1179(1)	42(1)
C(13)	248(3)	157(3)	954(1)	47(1)
C(1A)	1139(3)	3037(3)	871(1)	40(1)
C(4A)	3110(3)	2069(3)	776(1)	42(1)
C(5A)	2806(3)	676(2)	1556(1)	40(1)
C(6A)	3617(3)	596(2)	2386(1)	37(1)
C(10A)	1518(3)	1474(2)	2481(1)	36(1)
C(11A)	758(3)	1617(2)	1647(1)	37(1)

Table S3 Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for compound **4** (exo). U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
O(1)	641(1)	-2322(1)	1789(1)	37(1)
O(2)	-80(1)	1936(1)	1657(1)	29(1)
C(1)	-2060(1)	569(2)	2811(1)	26(1)
C(2)	-2693(2)	-115(2)	2975(1)	30(1)
C(3)	-2568(2)	-1235(2)	2981(1)	31(1)
C(4)	-1795(1)	-1693(2)	2831(1)	27(1)
C(4A)	-1150(1)	-1009(2)	2675(1)	22(1)
C(5)	-241(1)	-1230(2)	2497(1)	20(1)
C(5A)	-441(1)	-980(2)	1932(1)	20(1)
C(6)	356(1)	-1391(2)	1705(1)	23(1)
C(6A)	778(1)	-690(2)	1376(1)	19(1)
C(7)	1333(1)	-1162(2)	1075(1)	24(1)
C(8)	1728(1)	-527(2)	760(1)	26(1)
C(9)	1605(1)	586(2)	753(1)	26(1)
C(10)	1069(1)	1065(2)	1054(1)	22(1)
C(10A)	632(1)	432(2)	1359(1)	19(1)
C(11)	-8(1)	952(2)	1648(1)	20(1)
C(11A)	-617(1)	267(1)	1912(1)	20(1)
C(12)	-465(1)	589(2)	2469(1)	20(1)
C(12A)	-1281(1)	104(2)	2664(1)	21(1)
C(13)	320(2)	-216(2)	2685(1)	22(1)
C(14)	1190(2)	-87(2)	2950(1)	26(1)
C(15)	1822(2)	-1030(2)	3130(1)	38(1)
C(16)	1593(2)	1007(2)	3110(1)	38(1)
O(3)	4012(1)	2730(1)	3014(1)	32(1)
O(4)	4095(1)	6950(1)	2930(1)	41(1)
C(17)	2183(1)	6175(2)	4284(1)	25(1)
C(18)	1464(2)	5648(2)	4461(1)	28(1)
C(19)	1409(2)	4528(2)	4460(1)	28(1)
C(20)	2068(1)	3898(2)	4283(1)	23(1)
C(20A)	2795(1)	4423(2)	4117(1)	22(1)
C(21)	3628(1)	4008(2)	3915(1)	21(1)
C(21A)	3419(1)	4284(2)	3349(1)	22(1)

C(22)	4138(1)	3685(2)	3121(1)	24(1)
C(22A)	5019(1)	4255(2)	3062(1)	25(1)
C(23)	5808(2)	3659(2)	3001(1)	32(1)
C(24)	6630(2)	4184(2)	2952(1)	43(1)
C(25)	6664(2)	5300(2)	2946(1)	44(1)
C(26)	5873(2)	5902(2)	2984(1)	37(1)
C(26A)	5047(2)	5380(2)	3051(1)	27(1)
C(27)	4193(2)	6031(2)	3088(1)	27(1)
C(27A)	3464(1)	5543(2)	3345(1)	22(1)
C(28)	3714(1)	5838(2)	3909(1)	22(1)
C(28A)	2849(1)	5552(2)	4115(1)	22(1)
C(29)	4351(1)	4887(2)	4107(1)	22(1)
C(30)	5237(2)	4844(2)	4358(1)	24(1)
C(31)	5726(1)	3786(2)	4509(1)	34(1)
C(32)	5835(1)	5839(2)	4498(1)	33(1)
O(5)	1326(1)	2816(1)	179(1)	33(1)
O(6)	1505(1)	7157(1)	194(1)	33(1)
C(33)	4532(1)	5974(2)	1327(1)	25(1)
C(34)	5106(1)	5374(2)	1694(1)	29(1)
C(35)	5058(1)	4256(2)	1694(1)	29(1)
C(36)	4439(1)	3700(2)	1327(1)	25(1)
C(36A)	3888(1)	4296(2)	958(1)	23(1)
C(37)	3196(1)	3976(2)	495(1)	23(1)
C(37A)	2172(1)	4317(2)	566(1)	20(1)
C(38)	1460(1)	3793(2)	164(1)	23(1)
C(38A)	969(1)	4440(2)	-261(1)	21(1)
C(39)	429(1)	3910(2)	-665(1)	24(1)
C(40)	-43(1)	4498(2)	-1064(1)	26(1)
C(41)	18(1)	5619(2)	-1062(1)	27(1)
C(42)	538(1)	6153(2)	-662(1)	24(1)
C(42A)	1020(1)	5574(2)	-259(1)	20(1)
C(43)	1558(1)	6170(2)	172(1)	22(1)
C(43A)	2223(1)	5577(2)	571(1)	21(1)
C(44)	3266(1)	5810(2)	501(1)	22(1)
C(44A)	3931(1)	5426(2)	959(1)	23(1)
C(45)	3384(1)	4884(2)	157(1)	22(1)
C(46)	3595(1)	4880(2)	-288(1)	25(1)
C(47)	3696(2)	3844(2)	-556(1)	38(1)

C(48)	3779(2)	5899(2)	-549(1)	36(1)

Table S4 Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for compound **4** (endo). U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
O(1)	2865(1)	5916(1)	4416(1)	27(1)
O(2)	4892(1)	10895(1)	8099(1)	31(1)
C(1)	1872(2)	8462(1)	9042(1)	19(1)
C(2)	201(2)	7867(1)	8635(1)	22(1)
C(3)	-257(2)	6588(2)	7675(1)	22(1)
C(4)	944(2)	5857(1)	7091(1)	19(1)
C(4A)	2613(2)	6424(1)	7521(1)	17(1)
C(5)	4232(2)	5901(1)	7163(1)	17(1)
C(5A)	4810(2)	6993(1)	6399(1)	17(1)
C(6)	3459(2)	7042(1)	5210(1)	19(1)
C(6A)	2869(2)	8468(1)	5009(1)	20(1)
C(7)	1743(2)	8499(2)	3835(1)	25(1)
C(8)	1171(2)	9802(2)	3618(1)	29(1)
C(9)	1697(2)	11085(2)	4566(2)	29(1)
C(10)	2799(2)	11066(2)	5732(1)	25(1)
C(10A)	3399(2)	9760(1)	5964(1)	20(1)
C(11)	4565(2)	9785(1)	7241(1)	20(1)
C(11A)	5355(2)	8421(1)	7476(1)	17(1)
C(12)	4969(2)	8009(1)	8729(1)	17(1)
C(12A)	3070(2)	7721(1)	8483(1)	16(1)
C(13)	5453(2)	6448(1)	8493(1)	17(1)
C(14)	6546(2)	5784(1)	9228(1)	19(1)
C(15)	6838(2)	4212(1)	8807(1)	25(1)
C(16)	7576(2)	6550(2)	10558(1)	25(1)

Table S5 Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å^{2}x 10^3) for compound **6**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
C(1)	3836(2)	-1608(1)	2744(2)	25(1)
C(2)	3633(2)	-1618(2)	3538(2)	27(1)
C(3)	2942(2)	-1012(2)	3583(2)	29(1)
C(4)	2456(2)	-398(2)	2830(2)	26(1)
C(4A)	2664(2)	-399(1)	2022(2)	24(1)
C(5)	2239(2)	163(1)	1077(2)	21(1)
C(5A)	3132(2)	700(1)	1135(2)	18(1)
C(6)	3304(2)	1578(1)	1171(2)	19(1)
C(6A)	4207(2)	1885(1)	1172(2)	20(1)
C(7)	4425(2)	2792(1)	1191(2)	24(1)
C(8)	5301(2)	3073(2)	1200(2)	28(1)
C(9)	6001(2)	2469(2)	1179(2)	26(1)
C(10)	5808(2)	1587(1)	1147(2)	22(1)
C(10A)	4914(2)	1270(1)	1145(2)	18(1)
C(11)	4703(2)	355(1)	1102(2)	17(1)
C(11A)	3830(2)	88(1)	1095(2)	16(1)
C(12)	3361(2)	-821(1)	1006(2)	19(1)
C(12A)	3336(2)	-992(2)	1978(2)	23(1)
C(13)	2226(2)	-573(2)	350(2)	23(1)
C(14)	1476(2)	-888(2)	-499(2)	26(1)
C(15)	406(2)	-547(2)	-984(2)	32(1)
C(16)	1629(2)	-1640(2)	-1046(2)	30(1)