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

SUPPORTING INFORMATION FOR

Soluble Polycyclosilane-polysiloxane Hybrid Material and Silicon Thin Film Having Optical Properties at 193 nm and Etch Selectivity

Sung Jin Park,[a] Hyeon Mo Cho,[b,*] Myong Euy Lee,[a,*] Miyoung Kim,[c] Kwenwoo Han,[c] Seunghee Hong,[c] Sanghak Lim,[c] Hansong Lee,[c] Byeonggyu Hwang,[c] Sang Kyun Kim,[c] Sangdeok Shim,[d] Philjae Kang[e] and Moon-Gun Choi[e]

[a] Department of Chemistry & Medical Chemistry, College of Science and Technology, Research & Education center for Advanced Silicon Materials, Yonsei University, Wonju, Republic of Korea. E-mail: melgg@yonsei.ac.kr (M. E. Lee)

[b] University College, Yonsei University, Incheon 406-840, Republic of Korea. E-mail: hyeonmo@yonsei.ac.kr (H. M. Cho)

[c] Process Materials Development Team, Samsung SDI Co. Suwon, Republic of Korea.

[d] Department of Chemistry, Sunchon National University, Sunchon, Republic of Korea.

[e] Department of Chemistry and Molecular Structure Laboratory, Yonsei University, Seoul, 120-749, Republic of Korea.

Table of contents for the Supporting Information:

1. Experimental

1.1. Materials and instruments.

In all reactions in which air-sensitive chemicals were used, the reagents and solvents were dried prior to use. THF, diethylether, benzene, triethylamine and *n*-hexane were distilled from Na/Ph_2CO, and EtOH was distilled from calcium hydride. Other starting materials were purchased as reagent grade and used without further purification. Glassware was flame-dried under nitrogen or argon flushing prior to use. All manipulations were performed using standard Schlenk techniques under a nitrogen or argon atmosphere and using a Glove box (MBraun). ^{1}H, ^{13}C and ^{29}Si NMR spectra were recorded using a Bruker Avance II^{+} BBO 400 MHz S1 spectrometer. The chemical shifts were referenced to internal C_6D_6, $CDCl_3$ or external tetramethylsilane. All solid-state NMR experiments were conducted on NMR instruments (Varian ^{unity}NOVA, USA) using 5 mm and 2.5 mm double resonance MAS probeheads for ^{29}Si and ^{1}H at 14.1 T (^{1}H resonance frequency 600 MHz, wide bore) at room temperature. Mass spectra were recorded on a low-resolution (Agilent Technologies GC/MS: 6890N, 5973N mass selective detector) EI mass spectrometer and a high-resolution (JEOL JMS-600W Agilent 6890 Series) instrument. UV-Vis Spectra were obtained using a Lambda 25 UV-Vis spectrometer (Perkin-Elmer). Gel permeation chromatography (GPC) was performed using Younglin YL 9100 high-performance liquid chromatography (HPLC) with Shodex KF-800 series columns, and a Younglin YL 9170 refractive index (RI) detector with HPLC grade THF as solvent (Burdick & Jacskon). Polystyrene was used as GPC standard, which was purchased from Shodex. IR spectra were recorded on a Perkin Elmer Spectrum one B Fourier transform infrared (FT-IR) spectrophotometer. Spin coating was performed using a Mikasa MS-A150 spin coater. The n (refractive index) and k (extinction coefficient) values were measured by a Ellipsometer VB-400 made by J. A. Woollam Co., Inc. Etch rates against both N_2/O_2 and CF_x plasma were measured using a TCP9400DFM Poly Chamber (Lam Research Corporation). The conditions for N_2/O_2 plasma were 50 mT / 27 MHz 300 W / 2 MHz 0 W / 40 O_2 / 20 N_2 / 500 Ar/ 10 sec and the conditions for CF_x plasma were 200 mT / 27 MHz 600 W / 2 MHz 850 W / 800 Ar / 50 CF_4 / 80 CHF_3 / 10 CH_2F_2 / 20 O_2 / 10 sec. The film mass density was calculated from X-ray reflectivity (XRR) by using a XPert PRO MPD (Panalytical, Nederland). X-ray photoelectron spectroscopy (XPS) measurements were taken by a K-alpha (Thermo U. K.) with a monochromated AI Kα source (1486.6 eV) under ultrahigh vacuum conditions.

1.2. Synthesis of 3.

EtOH (8.6 ml, 0.15 mol) and Et_3N (25.5 ml, 0.18 mol) dissolved in diethylether (100 ml) were slowly added to the mixture of **2** (5.7 g, 12.2 mmol) dissolved in diethylether (300 ml) for 1 h at -78 ^oC. After the mixture had been stirred for 6 h at -78 ^oC and slowly warmed up to room temperature, the solution was stirred for 12 h at that temperature. The $Et_3N^+Cl^-$ salt was removed by filtration and washing with *n*-hexane at argon atmosphere in a Glove box, and volatiles were distilled under vacuum. Two geometric isomers of **3** were obtained as white solid in 25.8% yield and pale green oil in 74.2% yield (5.6 g, 86%). $Me_6Si_6(OEt)_6$ (**3**): ^1H NMR (C_6D_6, 400 MHz): δ 3.57-3.97 (m, 12H, SiO$CH_2$$CH_3$), 1.10-1.29 (m, 18H, SiOCH$_2$$CH_3$), 0.41-0.88 (m, 18H, Si$CH_3$). ^{13}C NMR (C_6D_6, 100 MHz): δ -2.05-1.69 (m, Si-CH_3), 18.91-26.15 (m, Si-OCH$_2$$CH_3$), 58.34-68.15 (m, Si-O$CH_2CH_3$). ^{29}Si NMR (C_6D_6, 79 MHz): δ 2.89-9.79 (m). HRMS: $C_{18}H_{48}O_6Si_6$ 528.2067 (M^+ calcd), 528.2073 (found), 528.2077 (found). MS: *m*/*z* (relative intensity): 528 (M^+, 4.1), 499 (25.0), 455 (10.4), 323 (100), 263 (39.6), 133 (35.4), 89 (20.8). The single crystals of all-*cis* **3** were obtained by recrystallization from *n*-hexane at -20 ^oC. All-*cis* **3**: ^1H NMR (C_6D_6, 400 MHz): δ 3.94 (q, 12H, SiO$CH_2$$CH_3$), 1.27 (t, 18H, SiOCH$_2$$CH_3$), 0.50 (s, 18H, Si$CH_3$). ^{13}C NMR (C_6D_6, 100 MHz): δ -1.56 (Si-CH_3), 19.30 (Si-OCH$_2$$CH_3$), 62.04 (Si-O$CH_2CH_3$). ^{29}Si NMR (C_6D_6, 79 MHz): δ 4.22 (s).

1.3. Synthesis of hybrid of polycyclosilane-polysiloxane compounds and preparation of thin films.

MTMS (methyltrimethoxysilane) was dissolved in PGMEA (propylene glycol monomethyl ether acetate) with 10 wt% concentration. An acid catalyst (100 ppm HNO_3 per H_2O mol) aqueous solution (3 eq H_2O per mol of MTMS) was added. The hydrolysis reaction was carried out for 6 h at room temperature and then H_2O and MeOH were removed by evaporation. Geometric isomers of **3** were dissolved in PGMEA with 10 wt% concentration, which was then added to hydrolyzed MTMS. The hydrolysis and condensation reaction was carried under controlled temperature conditions (r.t.-120 ^oC) for 1-2 weeks to control the molecular weight of hybrid of polysiloxane-polysilicon compounds. The reaction was checked continuously by GPC. By products (EtOH and MeOH) were removed by evaporation and solution diluted in PGMEA to 4 wt% concentration. Thin films of **4a**, **4b** and **4c** were prepared by spin coating on silicon wafers (4 inch or 8 inch) and baking at 200 ^oC for 1 minute using **4a**, **4b** and **4c** solutions, respectively.

2. X-ray Crystallography Detail

Figure S1. ORTEP Diagram of all-*trans* **2**.

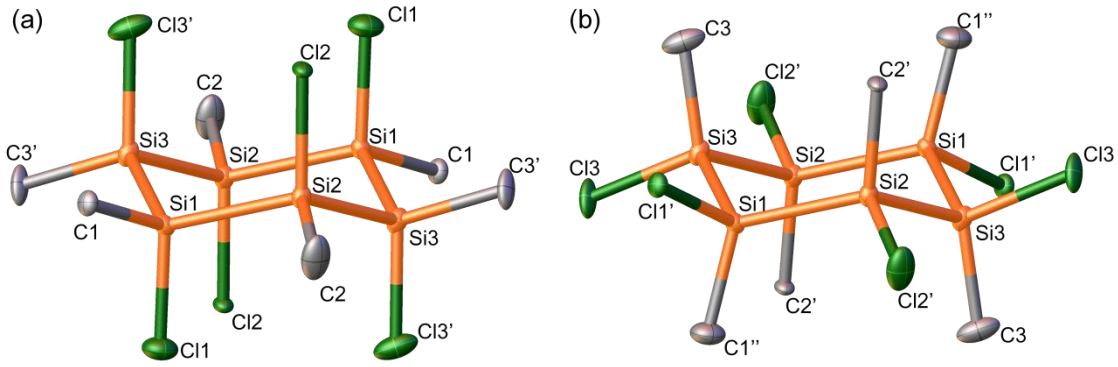

Table S1. Bond lengths [Å] for all-*trans* **2**.

Si1 Si2	2.3359(16)	Si2 C2'	1.904(15)
Si1 Si3	2.3356(16)	Si2 C2	1.878(16)
Si1 Cl1	2.001(4)	Si2 Cl2'	2.002(4)
Si1 C1"	1.869(15)	Si3 Si1	2.3355(16)
Si1 C1	1.887(16)	Si3 Cl3	2.047(4)
Si1 Cl1'	2.064(3)	Si3 C3'	1.879(17)
Si2 Si3	2.3390(16)	Si3 C3	1.868(17)
Si2 Cl2	2.078(3)	Si3 Cl3'	2.030(4)

Table S2. Bond angles [°] for all-*trans* **2**.

Si2 Si1 Si3	112.91(6)	Cl2 Si2 Si1	105.38(15)
Cl1 Si1 Si2	106.74(15)	Cl2 Si2 Si3	108.41(18)
Cl1 Si1 Si3	107.72(18)	C2' Si2 Si1	110.4(8)
C1" Si1 Si2	117.1(8)	C2' Si2 Si3	109.4(9)
C1" Si1 Si3	106.7(9)	C2' Si2 Cl2'	108.4(8)
C1" Si1 Cl1'	104.6(8)	C2 Si2 Si1	105.7(9)
C1 Si1 Si2	110.4(9)	C2 Si2 Si3	117.6(8)
C1 Si1 Si3	111.0(9)	C2 Si2 Cl2	108.2(12)
C1 Si1 Cl1	107.8(7)	Cl2' Si2 Si1	110.85(18)
Cl1' Si1 Si2	106.76(16)	Cl2' Si2 Si3	106.98(14)
Cl1' Si1 Si3	108.19(17)	Si1 Si3 Si2	111.92(6)
Si1 Si2 Si3	110.81(6)		

Table S3. Crystal data and structure refinement for compound all-*trans* **2**.

CCDC no.	984675
Empirical formula	$C_6H_{18}Cl_6Si_6$
Formula weight	471.44
Temperature	100.0 K
Wavelength	0.71073 Å
Crystal system, space group	Monoclinic, C2/c
Unit cell dimensions	a = 17.7183(15) Å alpha = 90.00 °. b = 9.8193(8) Å beta = 109.717(4) °. c = 13.5232(12) Å gamma = 90.00 °.
Volume	2214.8(3) $Å^3$
Z, Calculated density	4, 1.414 Mg/m^3
Absorption coefficient	4.231 mm^{-1}
F(000)	960.0
Crystal size	0.1 × 0.09 × 0.07 mm
Theta range for data collection	4.814 to 52.724°
Limiting indices	$-22 \leq h \leq 20$, $0 \leq k \leq 12$, $0 \leq l \leq 16$
Reflections collected / unique	2316 / 2316[R(int) = 0.0439]
Completeness to theta = 26.362	102.1 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.746 and 0.641
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	2316/103/108
Goodness-of-fit on F^2	1.143
Final R indexes [I>=2σ (I)]	R_1 = 0.0506, wR_2 = 0.1353
Final R indexes [all data]	R_1 = 0.0555, wR_2 = 0.1391
Largest diff. peak and hole	0.82 and -0.53 e.$Å^{-3}$

Figure S2. ORTEP Diagram of all-*cis* **3**.

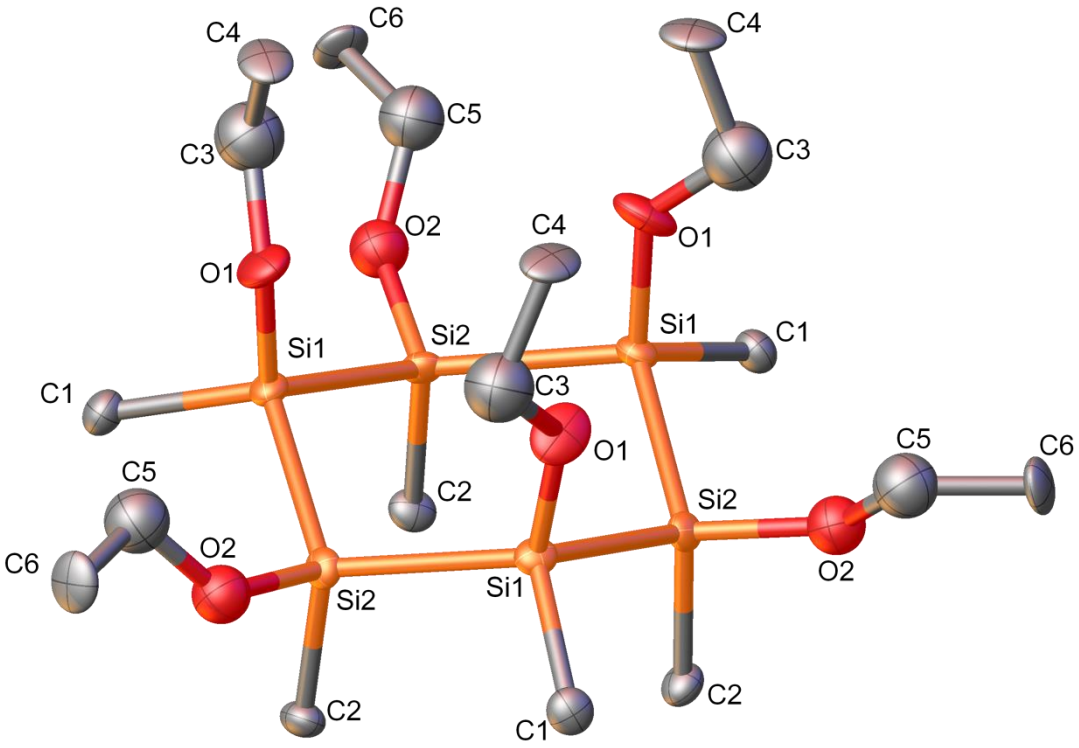

Table S4. Bond lengths [Å] for all-*cis* **3**.

Si1 Si2	2.368(5)	Si2 C2	1.879(13)
Si1 Si2	2.360(5)	O1 C3	1.366(17)
Si1 O1	1.619(13)	O2 C5	1.402(17)
Si1 C1	1.898(13)	C3 C4	1.463(18)
Si2 Si12	2.368(5)	C5 C6	1.38(3)
Si2 O2	1.644(14)		

Table S5. Bond angles [°] for all-*cis* **3**.

Si2 Si1 Si2	109.69(18)	O2 Si2 Si1	109.6(5)
O1 Si1 Si2	105.4(5)	O2 Si2 C2	101.5(6)
O1 Si1 Si2	113.9(5)	C2 Si2 Si1	108.0(4)
O1 Si1 C1	109.0(6)	C2 Si2 Si1	110.2(4)
C1 Si1 Si2	110.6(4)	C3 O1 Si1	133.8(14)
C1 Si1 Si2	108.3(5)	C5 O2 Si2	137.3(15)
Si1 Si2 Si1	112.9(2)	O1 C3 C4	113.2(18)
O2 Si2 Si1	113.9(5)	O2 C5 C6	118(2)

Table S6. Crystal data and structure refinement for compound all-*cis* **3**.

CCDC no.	984676
Empirical formula	$C_{18}H_{48}O_6Si_6$
Formula weight	529.10
Temperature	230.2 K
Wavelength	0.71073 Å
Crystal system, space group	Cubic, I-43d
Unit cell dimensions	a = 23.3514(5) Å alpha = 90.00 °. b = 23.3514(5) Å beta = 90.00 °. c = 23.3514(5) Å gamma = 90.00 °.
Volume	12733.2(5) $Å^3$
Z, Calculated density	16, 1.104 Mg/m^3
Absorption coefficient	0.288 mm^{-1}
F(000)	4608
Crystal size	0.5 × 0.3 × 0.2 mm
Theta range for data collection	2.14 to 24.06°
Limiting indices	$-21 \le h \le 21$, $-21 \le k \le 21$, $-20 \le l \le 21$
Reflections collected / unique	45859 / 901 [R(int) = 0.0719]
Completeness to theta = 24.06	98.8 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.941 and 0.930
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	901/21/95
Goodness-of-fit on F^2	1.060
Final R indexes [I>=2σ (I)]	R_1 = 0.0834, wR_2 = 0.2180
Final R indexes [all data]	R_1 = 0.0902, wR_2 = 0.2289
Largest diff. peak and hole	0.483 and -0.256 e.$Å^{-3}$

3. NMR spectra

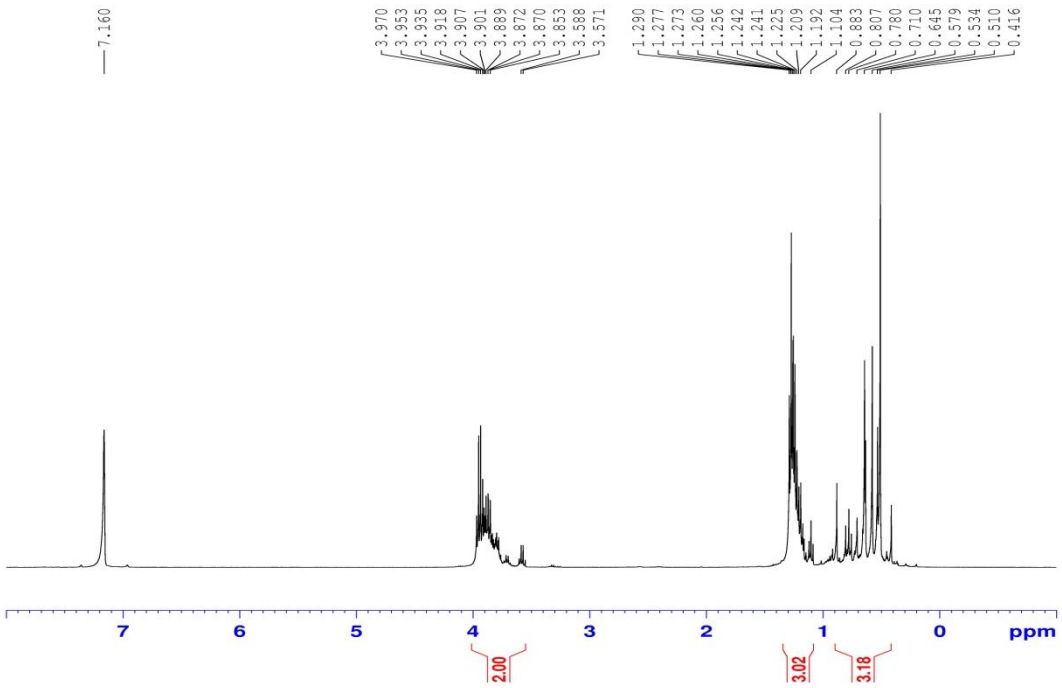

Figure S6. ^{1}H NMR spectrum of **3**.

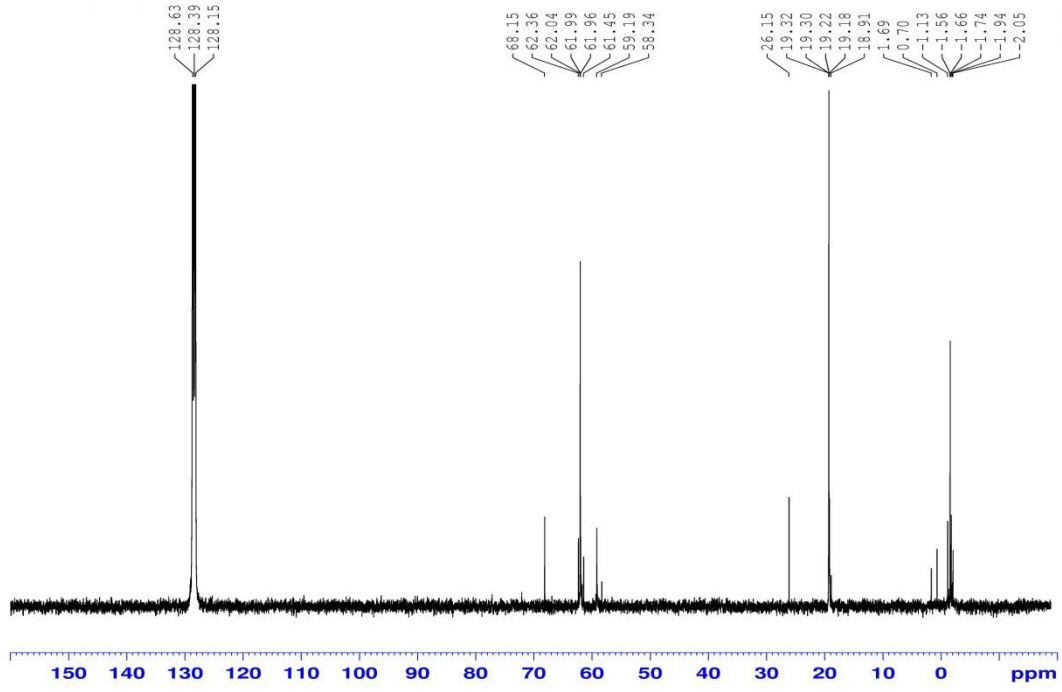

Figure S7. ^{13}C NMR spectrum of **3**.

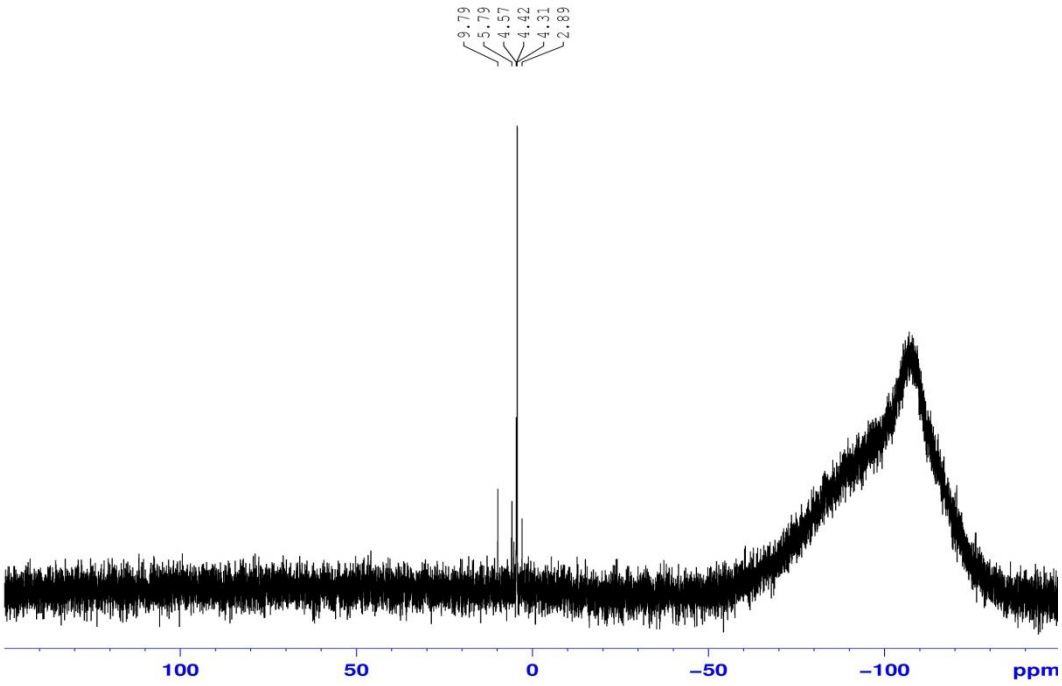

Figure S8. ^{29}Si NMR spectrum of **3**.

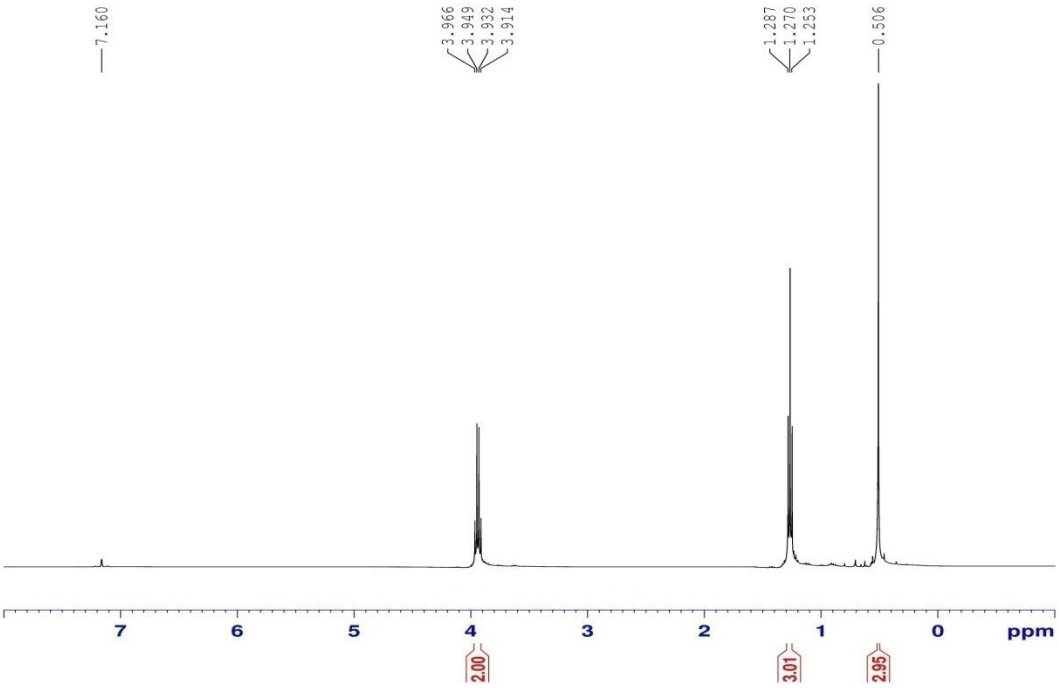

Figure S9. ^{1}H NMR spectrum of all-*cis* **3**.

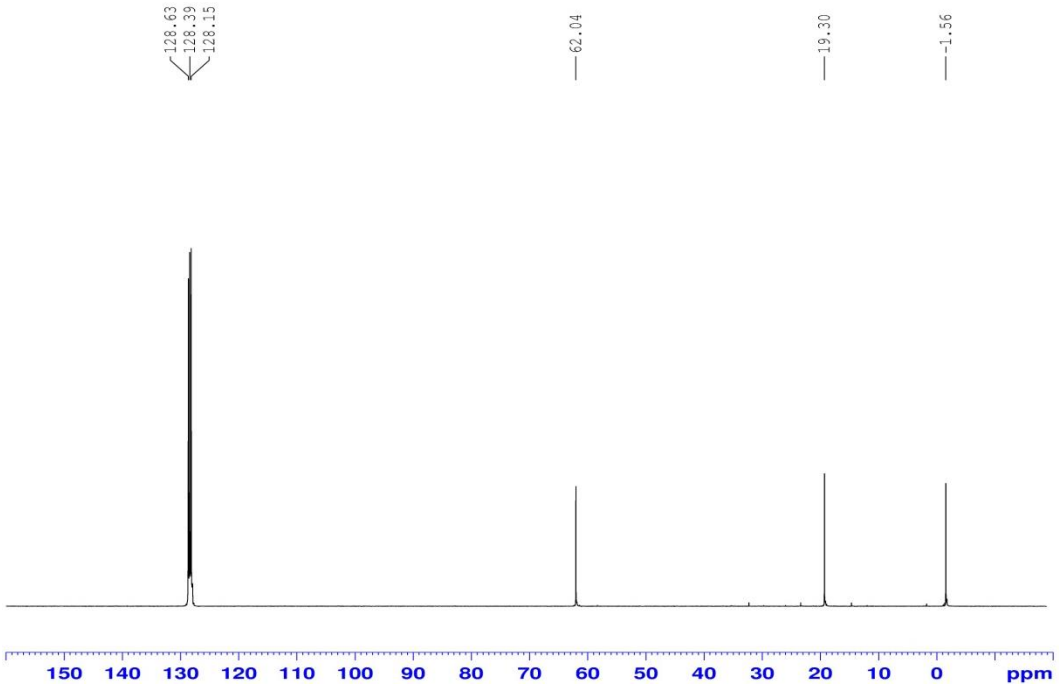

Figure S10. ^{13}C NMR spectrum of all-*cis* **3**.

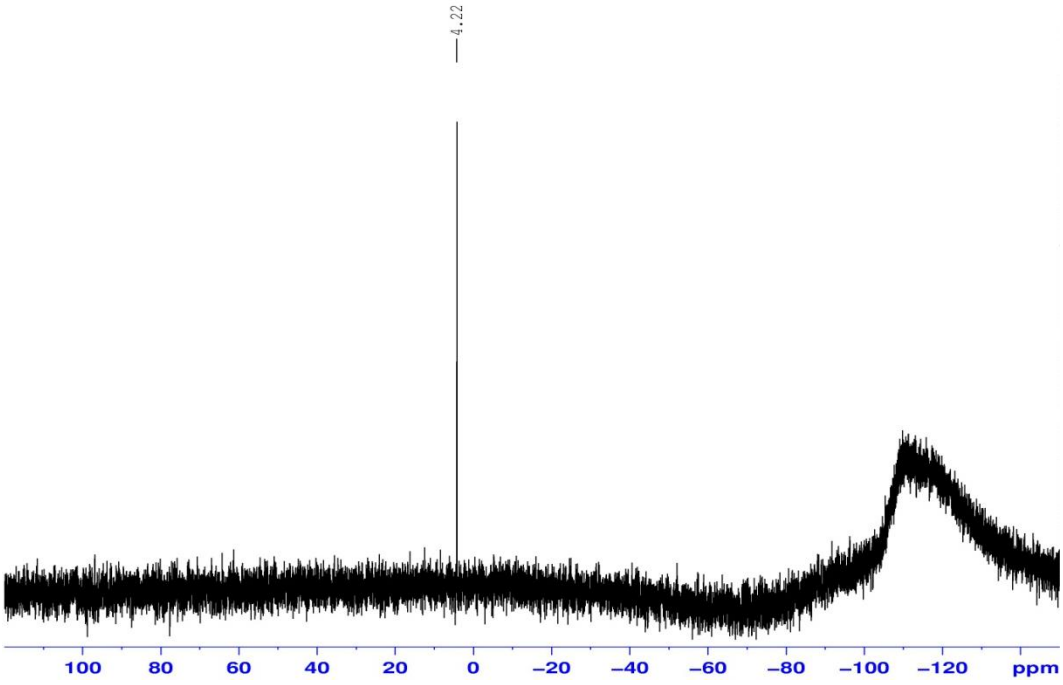

Figure S11. ^{29}Si NMR spectrum of all-*cis* **3**.

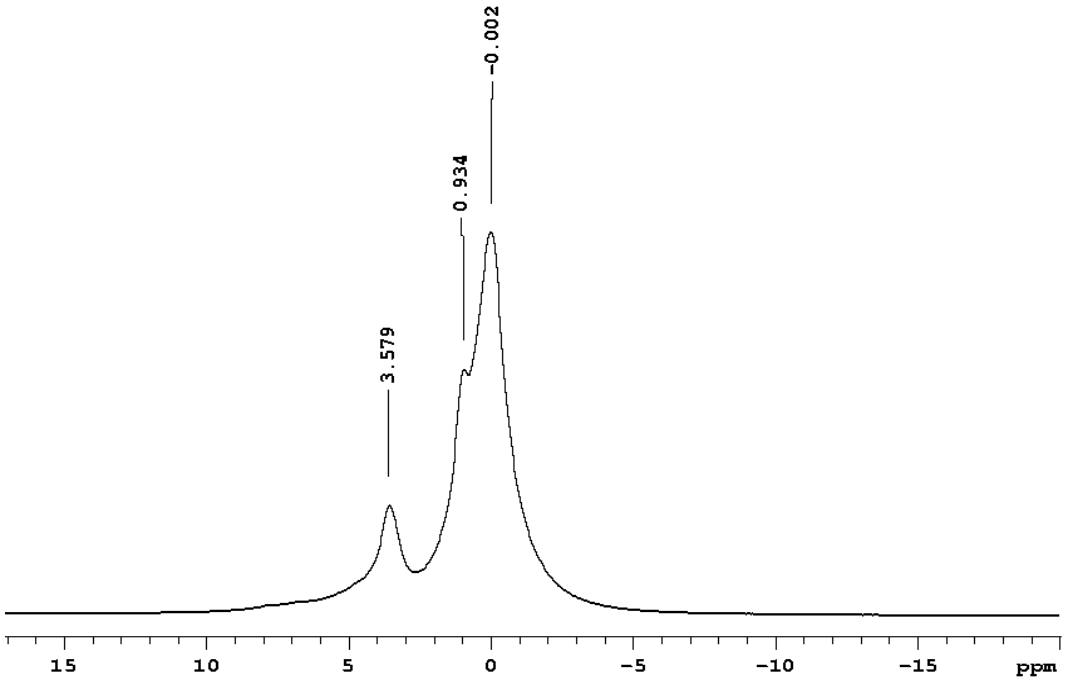

Figure S12. ^{1}H CP/MAS NMR spectrum of film **4a**.

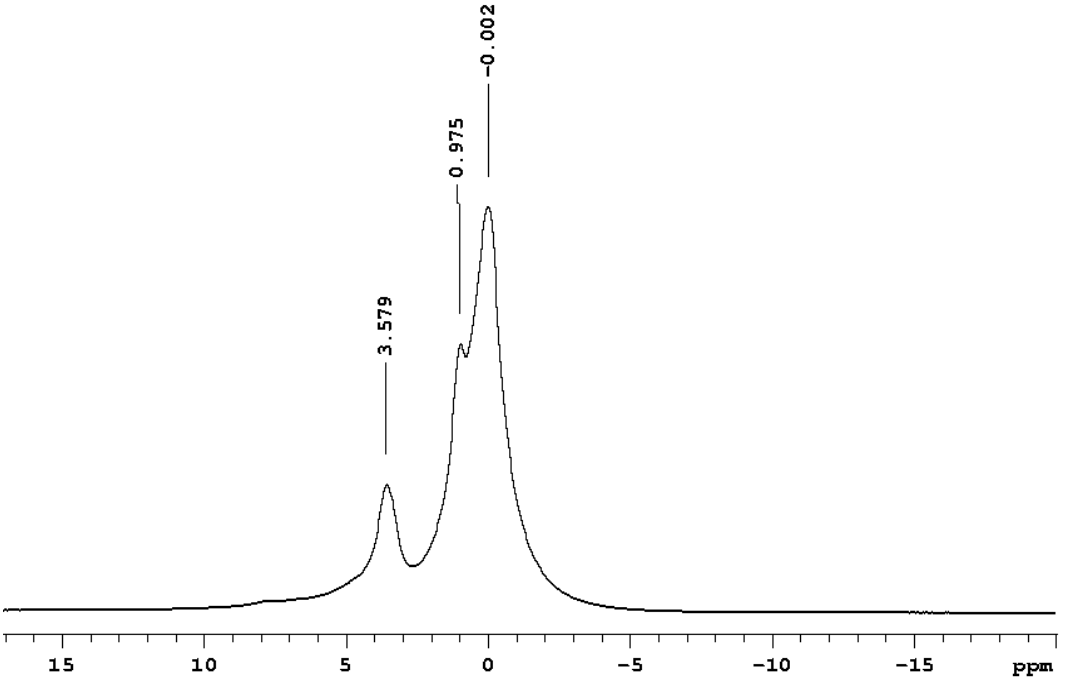

Figure S13. ^{1}H CP/MAS NMR spectrum of film **4b**.

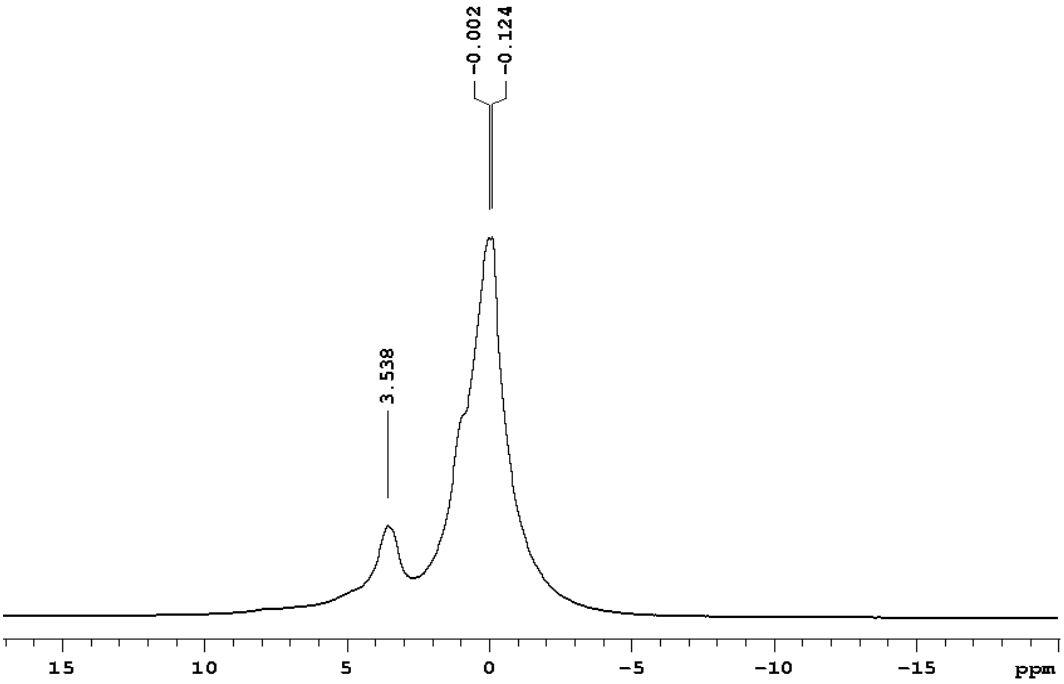

Figure S14. ^{1}H CP/MAS NMR spectrum of film **4c**.

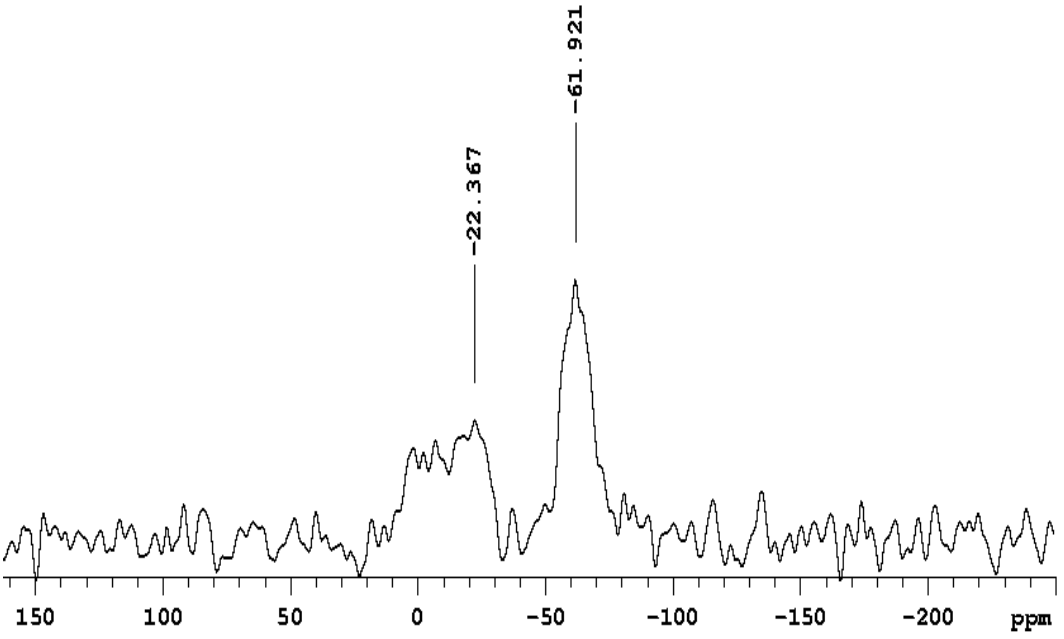

Figure S15. ^{29}Si CP/MAS NMR spectrum of film **4a**.

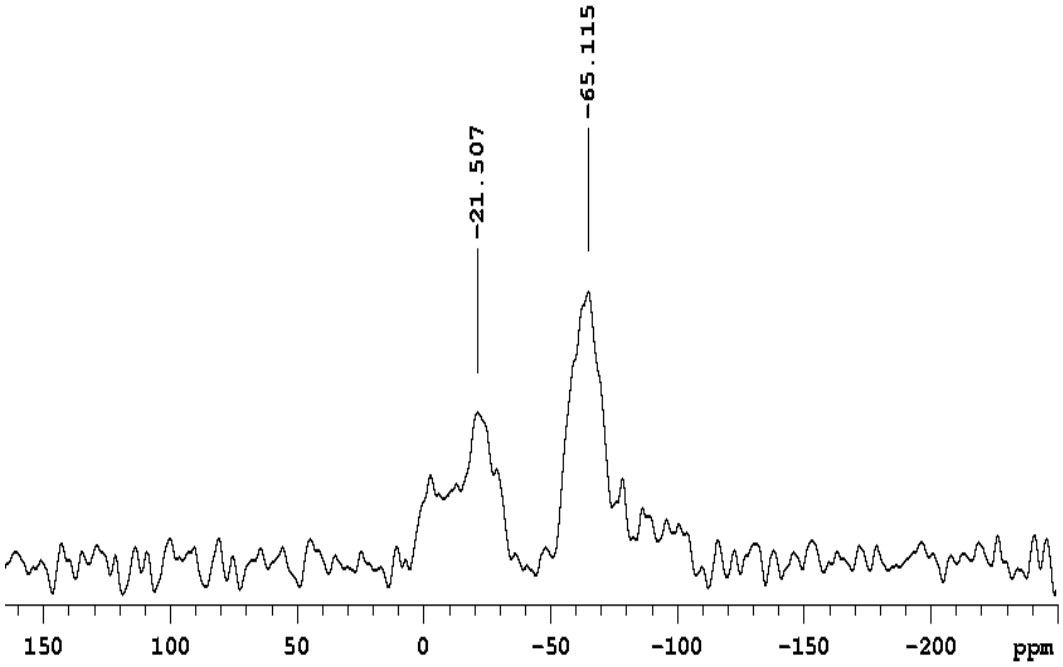

Figure S16. ^{29}Si CP/MAS NMR spectrum of film **4b**.

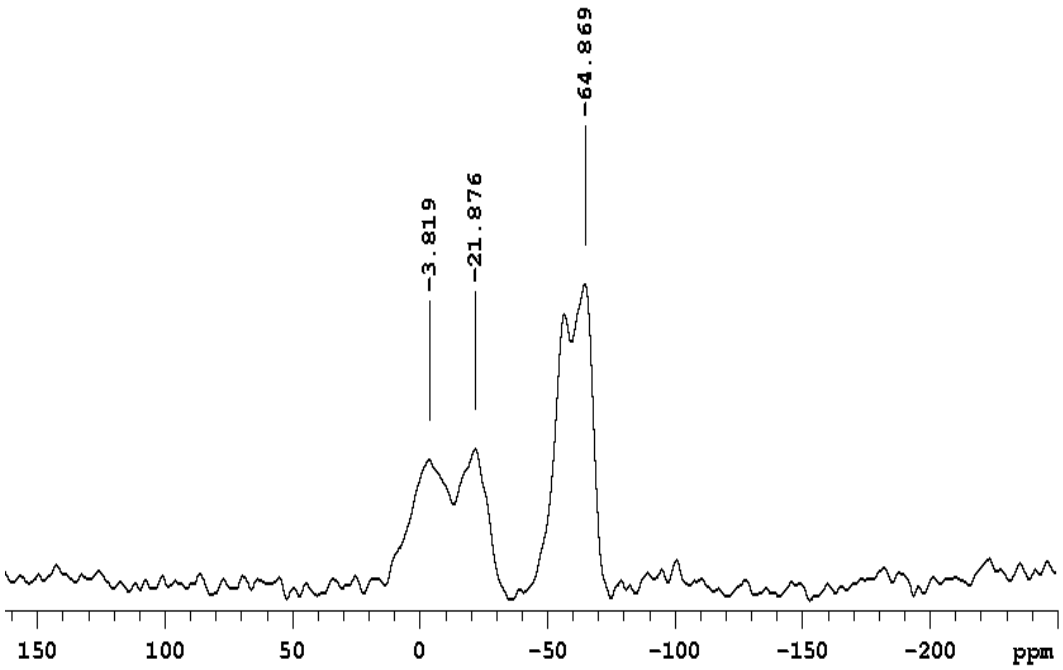

Figure S17. ^{29}Si CP/MAS NMR spectrum of film **4c**.

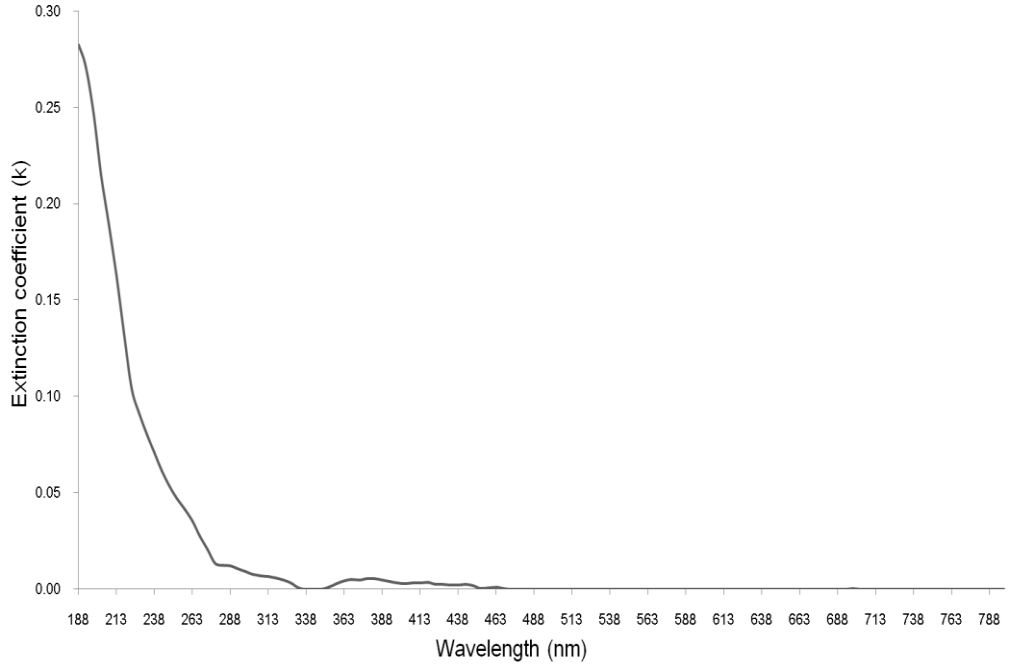

Figure S18. Extinction coefficient (k) spectrum of film **4a**.

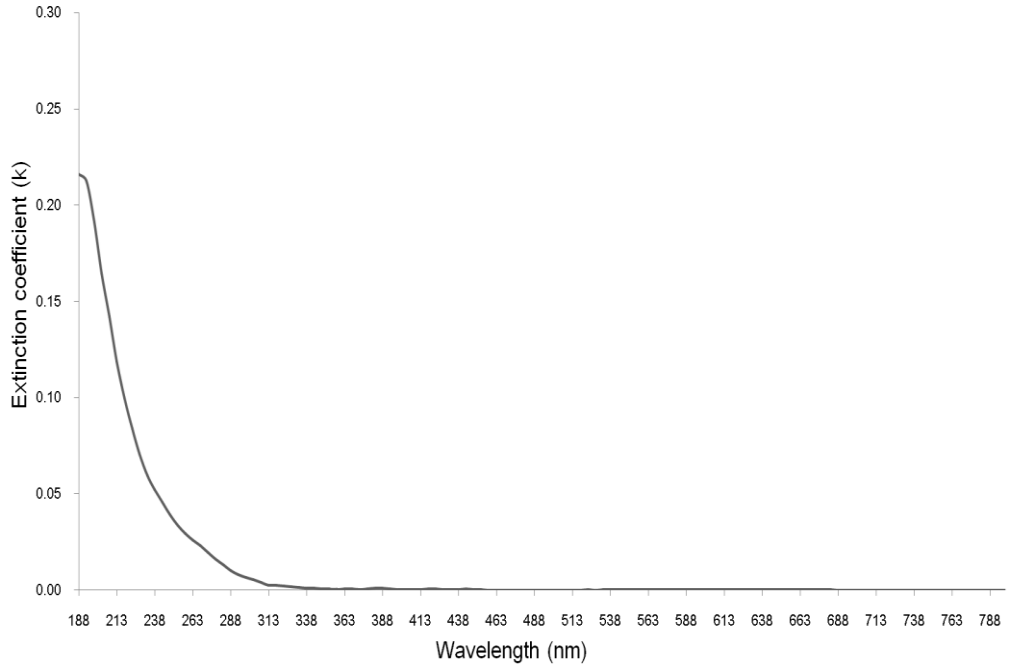

Figure S19. Extinction coefficient (k) spectrum of film **4b**.

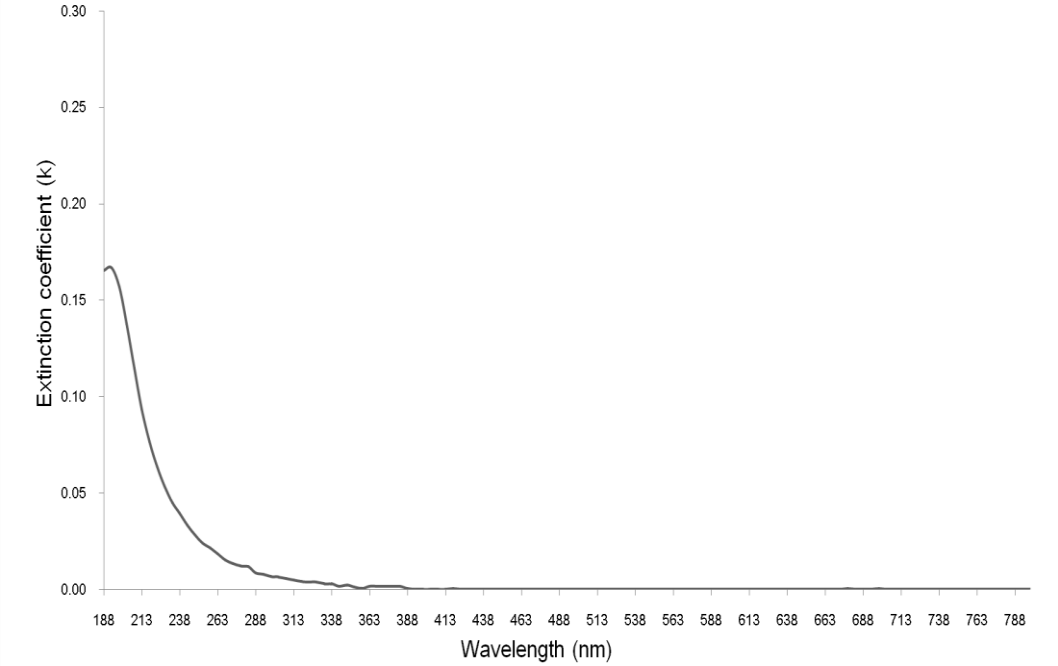

Figure S20. Extinction coefficient (k) spectrum of film **4c**.