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

Electronic Supplementary Information

Polysiloxane—Poly(vinyl alcohol) Composite Dielectrics for High-Efficiency Low Voltage Organic Thin Film Transistors

Jupeng Cao,[a] Xiaoyun Wei,[a] Yuxuan Che,[b] Aiyuan Li,[a] Yaowu He,[a] Chao He,[a] Yanan Zhu,[a] Xiaolong Chen,[a] Tingting Li,[c] Imran Murtaza,[d] Lijia Yan,[c] Dmitrii F. Perepichka*[b] and Hong Meng*[a]

[a] School of Advanced Materials, Peking University Shenzhen Graduate School, Peking University, Shenzhen, 518055, China.

[b] Department of Chemistry, McGill University, Montreal, H3A 0B8, Canada.

[c] USBT (Nanjing) Organic Optoelectronic Materials Co. Ltd., Nanjing, 210022, China

[d] Faculty of Basic and Applied Sciences, International Islamic University, Islamabad, 44000, Pakistan.

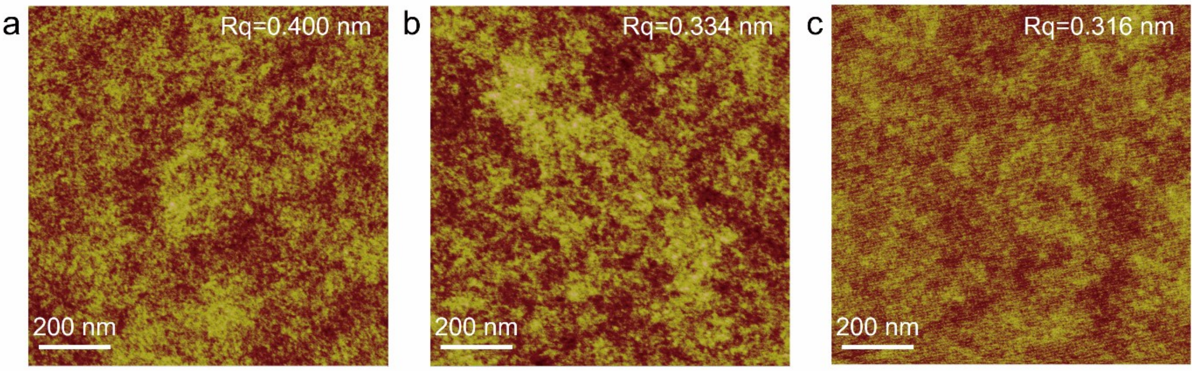

Figure S1. AFM images of composite dielectric film surface. (a), (b) And (c) are based on HPS, HPCPS, and HPFS layer, respectively.

Surface energy

Surface energy was calculated with deionized water and diiodomethane as test liquid by Owens-Wendt Equation:

$$1+\cos\theta=\frac{2\sqrt{\gamma_{s}^{d}\gamma_{lv}^{d}}}{\gamma_{lv}}+\frac{2\sqrt{\gamma_{s}^{p}\gamma_{lv}^{p}}}{\gamma_{lv}} \quad \text{(S1)}$$

Where γ_s, γ_{lv} are the surface energies of the dielectric film and the test liquid, respectively, and θ is the value of the measured contact angle. The superscripts d and p refer to the dispersion and polar components, respectively. The surface energy is composed of polar component (γ_s^p) and dispersion component (γ_s^d) which indicate the permanent dipole and instantaneous dipole moment separately. Table S1 lists the contact angle, surface energy and the dispersion and polar components of the three kinds of dielectric films.

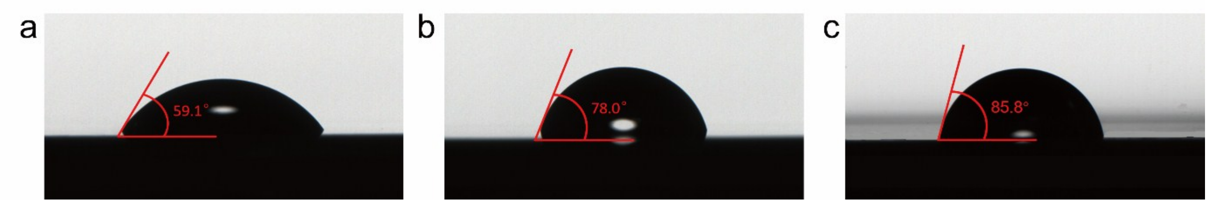

Figure S2. Contact angle images of composite dielectric film surface. (a), (b) And (c) are based on HPS, HPCPS, and HPFS layer, respectively.

Table S1. Contact angles, surface energies of HPCPS and HPS films. The surface energy is composed of dispersion and dipole components.

Dielectric	Contact angle [°]		γ_s^p	γ_s^d	γ_s
	DI water	Diiodomethane	[mN m^{-1}]	[mN m^{-1}]	[mN m^{-1}]
HPS	59.1	39.5	16.6	31.1	47.7
HPCPS	78.0	49.8	6.8	29.5	36.3
HPFS	85.8	50.6	3.4	30.9	34.3

Elemental composition

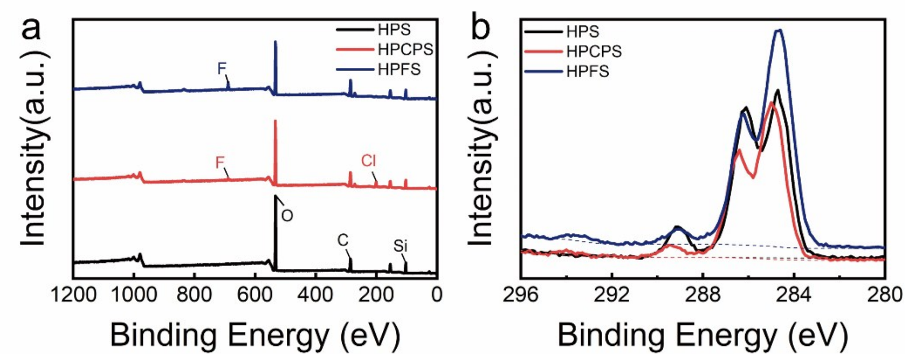

Figure S3. (a) XPS of HPS, HPCPS and HPFS dielectric films, respectively, (b) high solution signal of C1s peak for three dielectrics.

Table S2. The atom ratio of dielectric surface for HPS, HPCPS and HPFS dielectric layers.

Dielectric	Atom Ratio [%]				
	C	O	Si	Cl	F
HPS	41.94	44.98	13.08	-	-
HPCPS	26.26	38.63	16.89	7.76	0.46[a]
HPFS	36.56	36.23	17.01	-	10.20

a) The residual fluorine (<3 mol% vs Si) in the HPCPS is presumably due to trapped fluorinated alcohol. The CPS precursor (trialkoxy-3-chloroprolylsilane) is a mixture of methyl and fluoroalkyl ethers (see Fig. , which are, however, hydrolyzed to the same 3-chloroprolylsiloxane polymer.

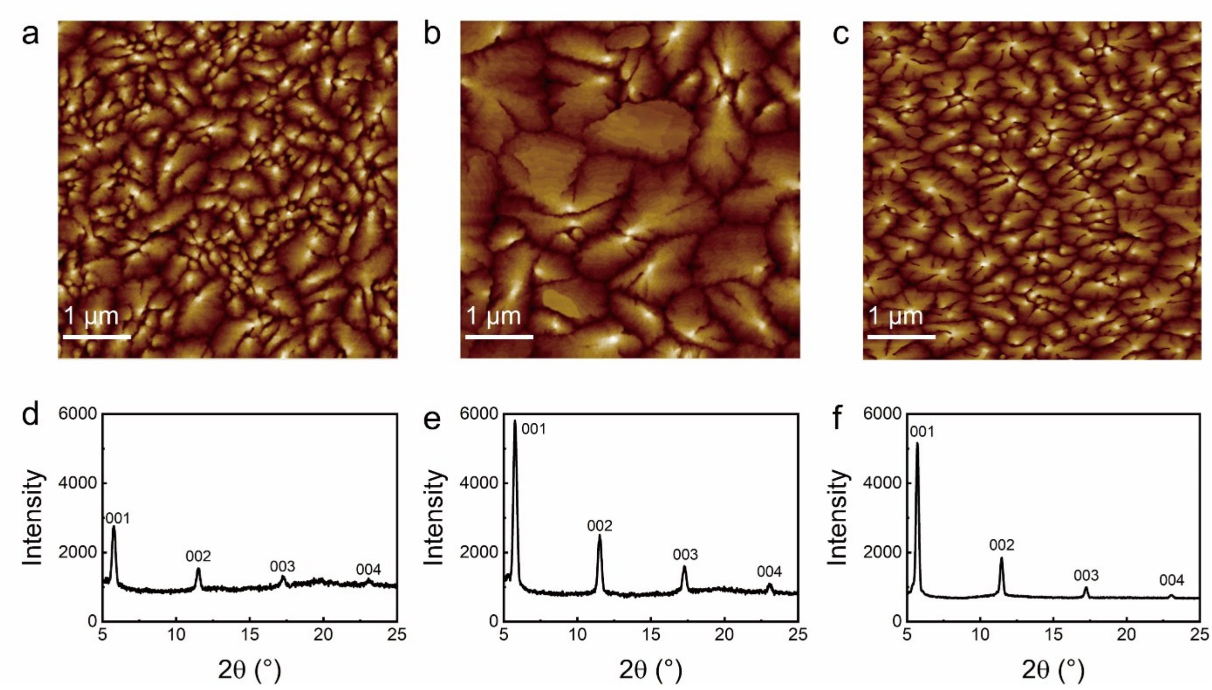

Figure S4. Morphology and crystallinity of 60 nm pentacene films on different dielectrics. (a), (b) and (c) are the AFM images based on HPS, HPCPS and HPFS films, respectively; (d), (e) and (f) are XRD based on HPS, HPCPS and HPFS films, respectively.

Trap density

The trap states density (N_{trap}) of HPCPS and HPS dielectric films were estimated via the following equation[1]:

$$N_{\mathrm{trap}} = \left[\frac{qss\log(e)}{kT} - 1 \right] \frac{C_{\mathrm{i}}}{q} \quad \text{(S2)}$$

Where q is the electrical charge of the carrier, ss is subthreshold slope of transistors, e is mathematical constant, k is Boltzmann's constant, T is the temperature and C_i is the dielectric capacitance. The estimated N_{trap} are listed in Table 1.

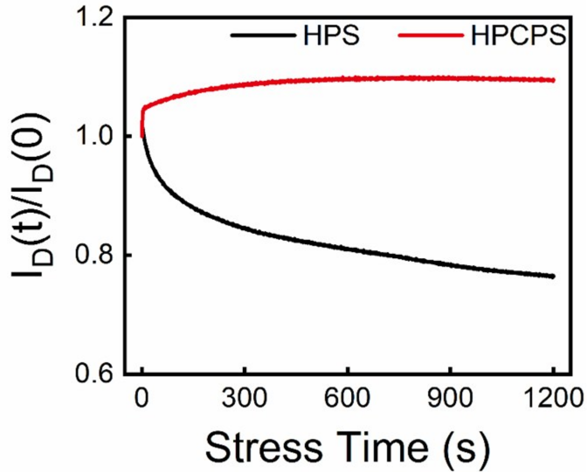

Figure S5. Normalized current variation of HPCPS and HPS-based devices as a function of time under constant biases of $V_{GS} = V_{DS} = -2$ V.

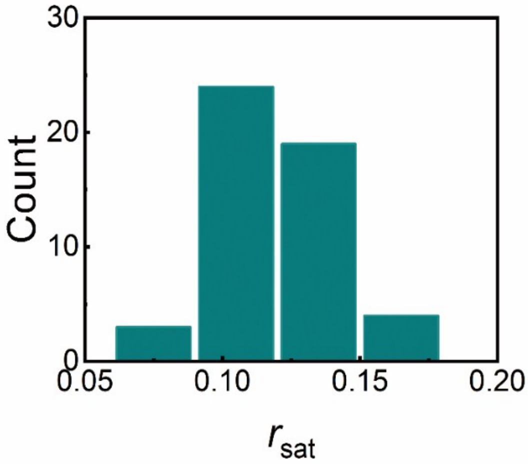

Figure S6. The distribution of reliability factor for 50 C8-BTBT OTTF devices based on HPCPS dielectric.

Spectroscopic characterization of the CPS precursor

The commercial () sample of CPS monomer was characterized by 1H, 13C, 19F NMR, COSY and HETCOR 2D NMR and GC-MS. Our data unambiguously establishes it structure as mixed methoxy/fluoroalkoxy ester of 3-chloropropylsilyane. The GC-MS shows a fragment at 167 Da [$ClC_3H_6Si(OCH_3)_2^+$] with isotope pattern characteristic of one chlorine atom (also established via Beilstein probe). The fluorinated alkoxy group has three protons: 2H at 4.3 ppm that can be identified as CH_2O-Si and 1H at 5.6 ppm which consists pf two different signals (possibly diastereomers), each with ddd splitting, identified as -CF_2H-. Its exact connectivity could not be fully established (likely a mixture) but – IMPORTANTLY- it is inconsequential for the resulting polymer because it is cleaved from the silicon center during sol-gel hydrolysis. The latter fact is supported by the NMR (Figure S7 bottom) and XPS (Figure S3).

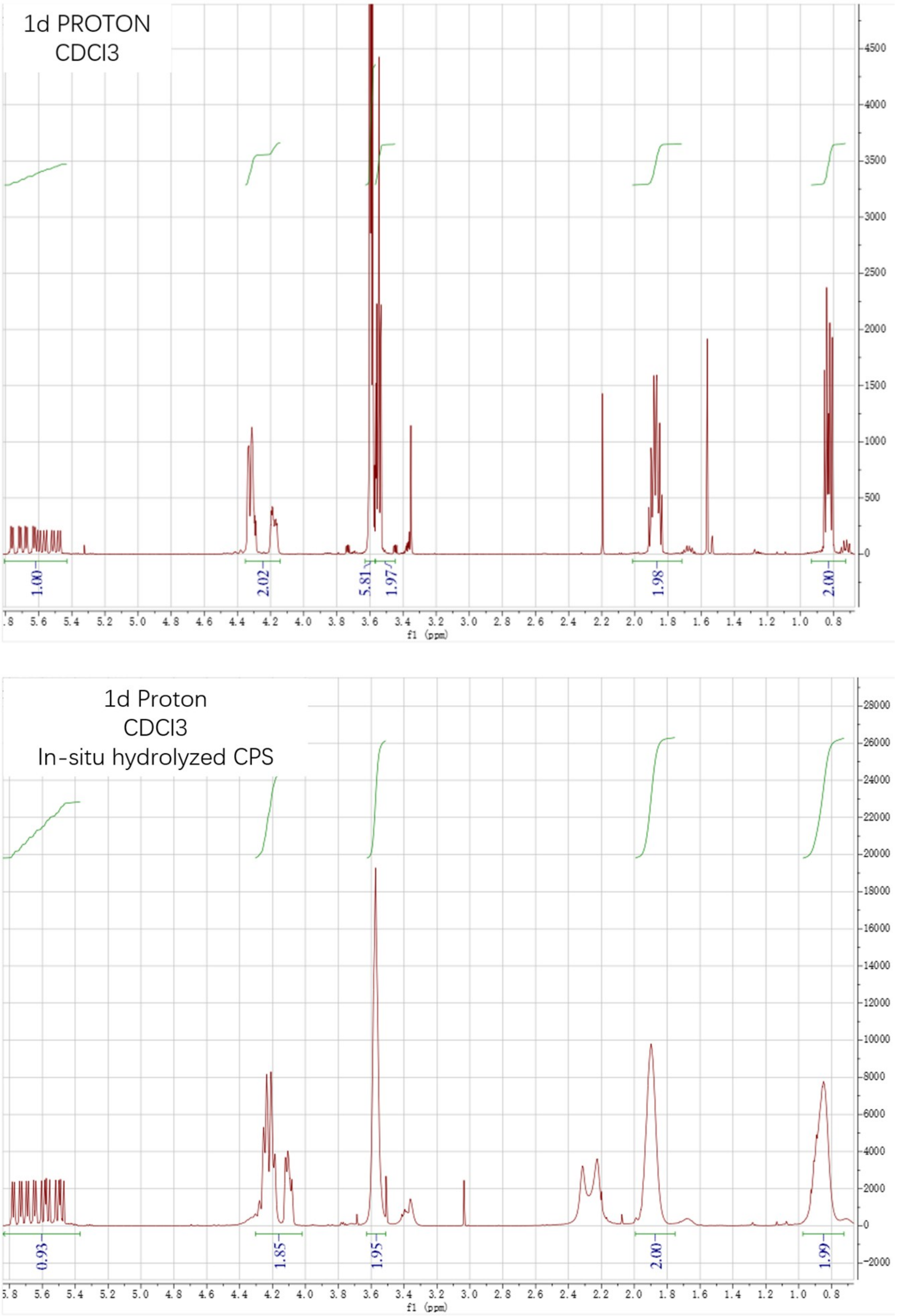

Figure S7. 500MHz ^{1}H NMR in CDCl3 of (top) freshly distilled CPS and (bottom) in-situ hydrolyzed CPS, showing upfield proton signals broadened due to polymerization of the chloropropylsilicate unit. The upfield signals from the free fluoroalkyl alcohol remain sharp.

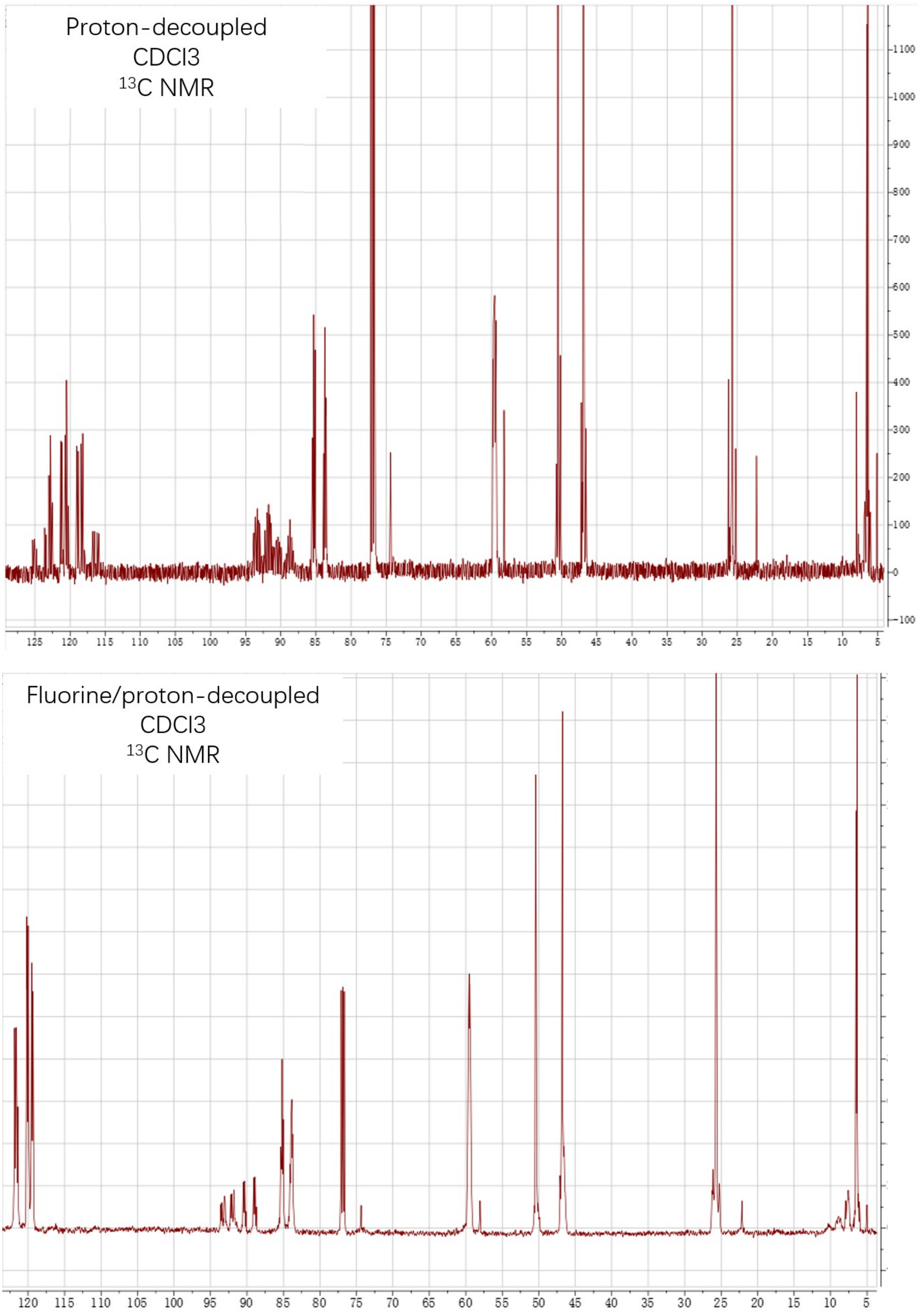

Figure S8. Proton-decoupled (top) and Fluorine/Proton decoupled (bottom) ^{13}C NMR of CPS (125 MHz, in $CDCl_3$).

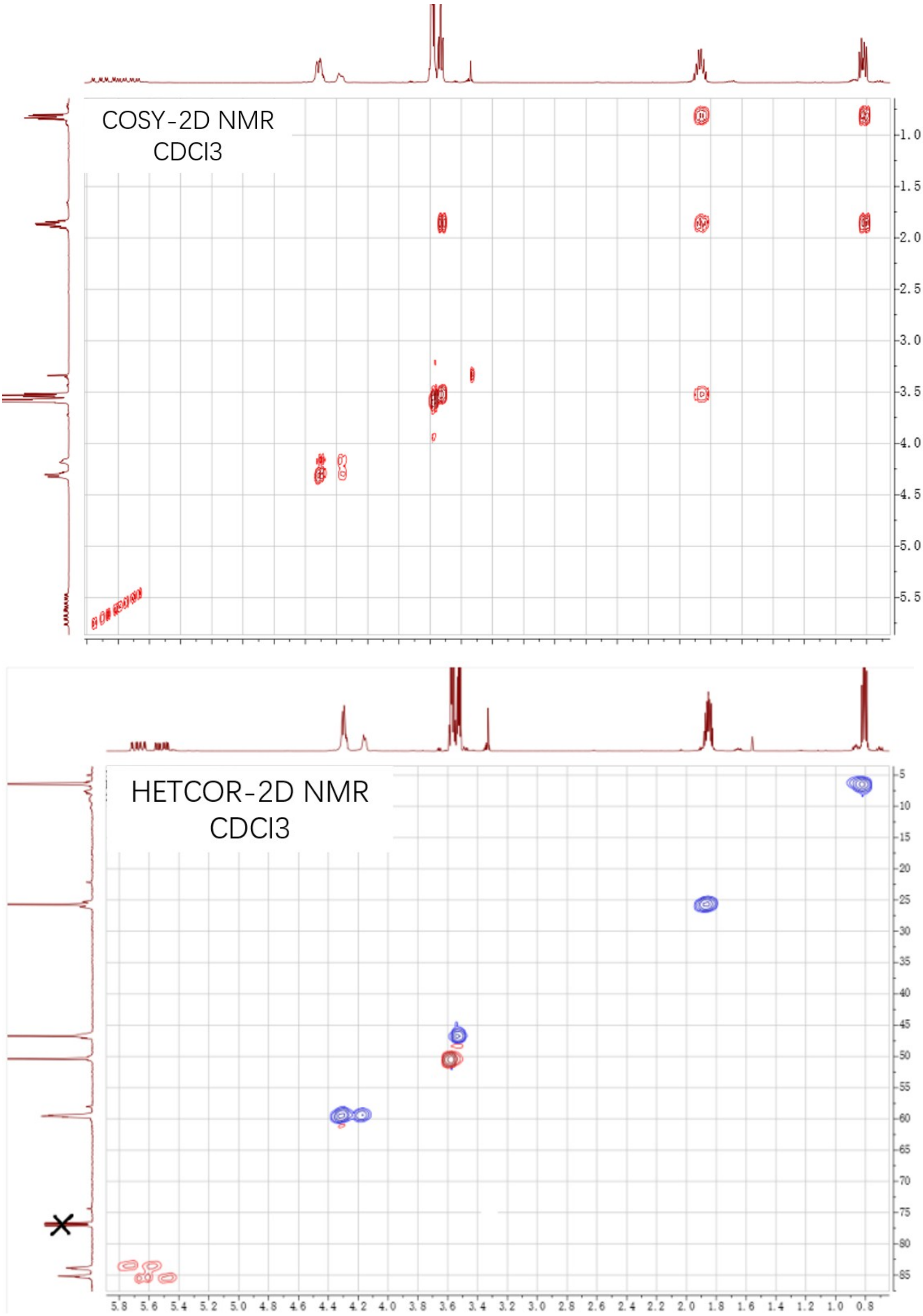

Figure S9. 2D NMR of CPS in $CDCl_3$ proving the connectivity of the chloropropylsilyl group: COSY (top) and HETCOR (bottom).