

# Electronic Supplementary Material

## (ESI) for:

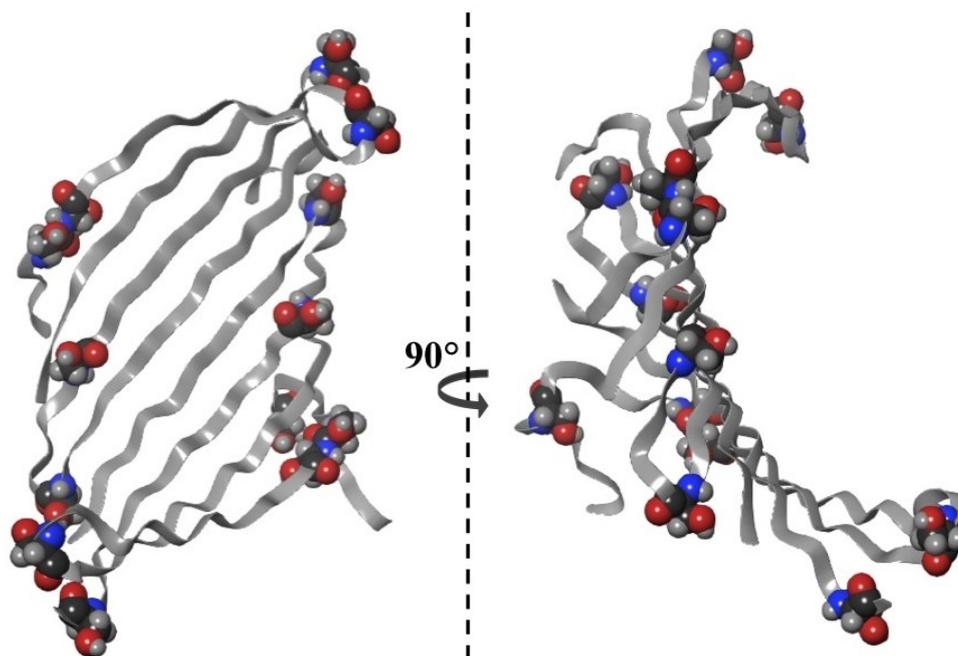
### APTES mediated modular modification of Regenerated Silk Fibroin in water solution

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#### Contents:

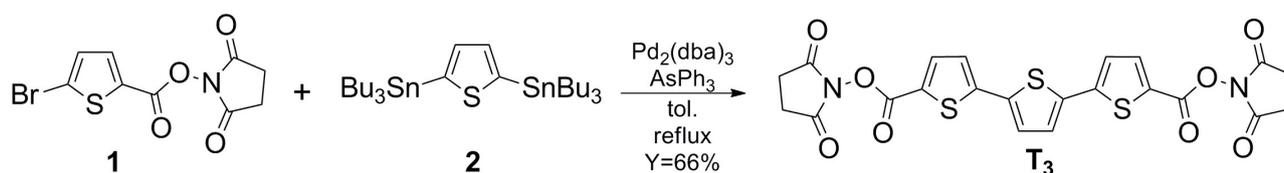
1. Crystal structure of SF
2. Synthesis of T3
3. Photoluminescence spectra of APTES-T3, T3(T3Si in dichloromethane
4. Phase Repartition Tests
5. Stability of SF and SF-APTES-T3 solution
6. Full <sup>1</sup>H-NMR spectra
7. ATR FT-IR spectroscopy
8. Water contact angle measurements
9. Transmittance spectroscopy

## 1. Crystalline structure of SF



**Figure S1.** Available crystal structure of the N-terminal domain of *B. mori* SF with serine residues highlighted in space-filling atoms (from ref. 27 Y.-X. He, N.-N. Zhang, W.-F. Li, N. Jia, B.-Y. Chen, K. Zhou, J. Zhang, Y. Chen, C.-Z Zhou, *J. Mol. Biol.*, 2012, 418, 197).

## 2. Synthesis of T3



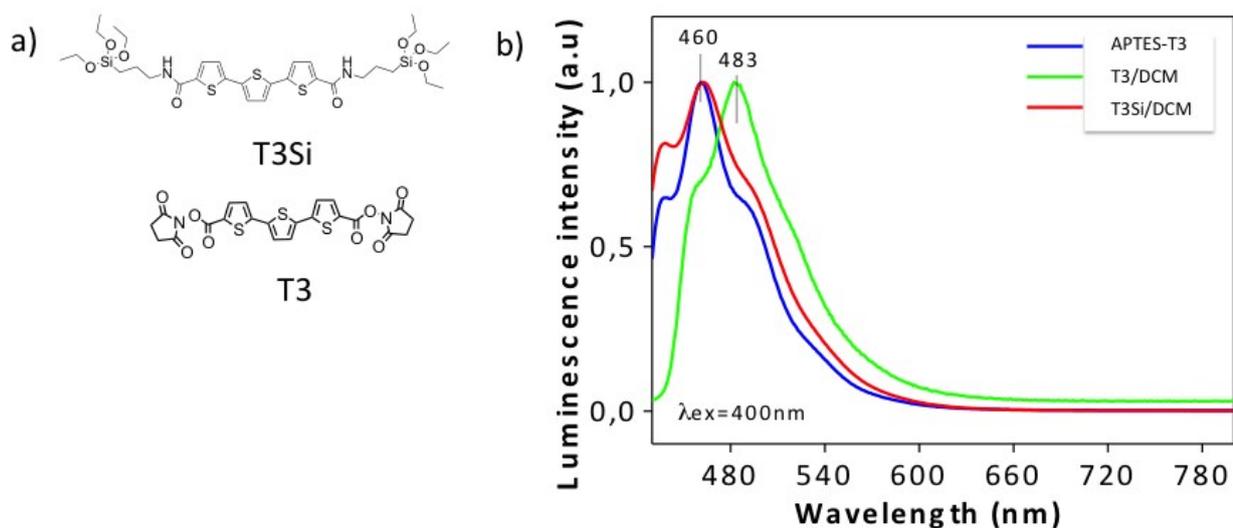
**Scheme S1.** Synthetic route to T3.

To a toluene solution (6 ml) of in situ prepared  $\text{Pd}(\text{AsPh}_3)_4$  (0.02 mmol) and 2,5-dioxopyrrolidin-1-yl-5-bromothiophene-2-carboxylate (**1**, 0.7 mmol)<sup>[ref. G. Barbarella, M. Zambianchi, A. Ventola, E. Fabiano, F. Della Sala, G. Gigli, M. Anni, A. Bolognesi, L. Polito, M. Naldi and M. Capobianco, *Bioconjugate Chem.*, 2006, 17, 58.]</sup>, 2,5-bis(tributylstannyl)thiophene (**2**, 0.35 mmol in 1.5 ml of dry toluene) was added dropwise at reflux temperature. After 18 h, the solvent was filtered and the crude product was purified by flash chromatography on silica gel to provide T3 in 66% yield as a yellow powder.

Characterization: m. p. 259 °C. MS (70 eV, EI):  $m/z$  530 ( $M^+$ ).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ , TMS/ppm):  $\delta$  7.94 (d,  $J = 4.0$  Hz, 2H), 7.31 (s, 2H), 7.26 (d,  $J = 4.0$  Hz, 2H), 2.91 (s, 8H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ , TMS/ppm):  $\delta$

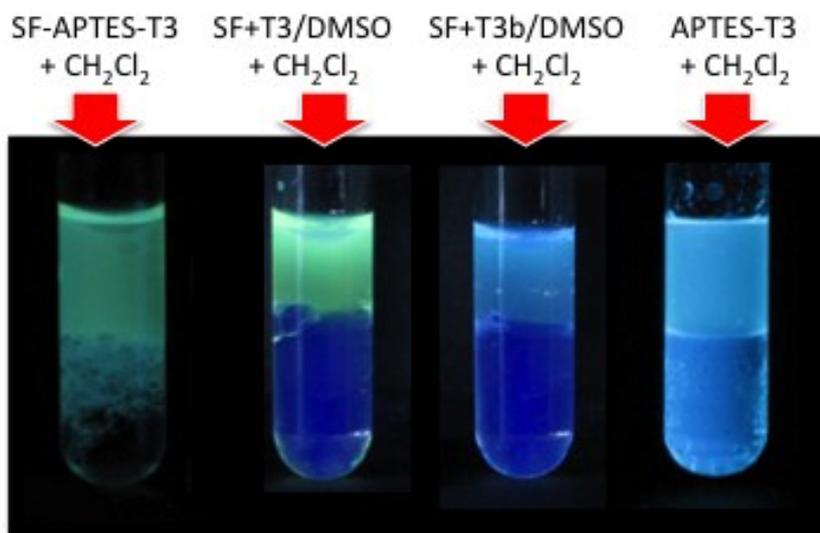
169.0, 157.0, 146.3, 137.5, 136.8, 127.1, 125.1, 124.9, 25.6. Anal. Calcd for  $C_{22}H_{14}N_2O_8S_3$  (529,99): C, 49.80; H, 2.66. Found: C, 49.76; H, 2.59.

### 3. Photoluminescence spectra of APTES-T3, T3, T3Si in dichloromethane



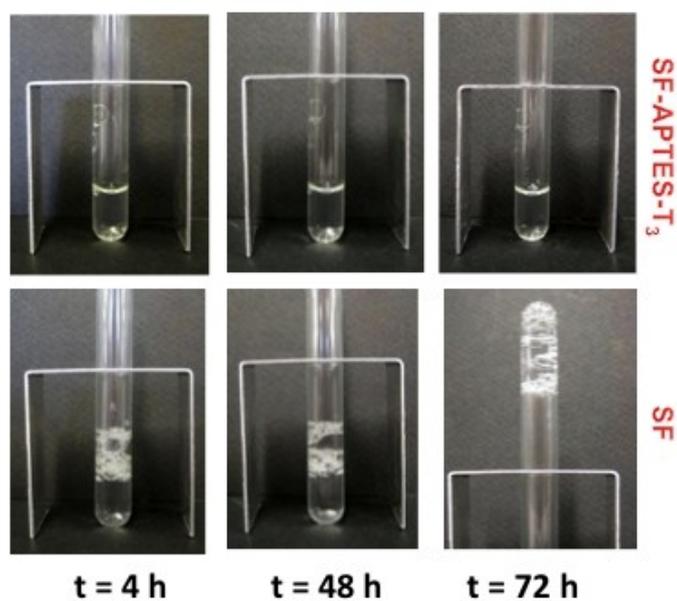
**Figure S2.** a) Molecular structure of T3 and T3Si prepared by coupling APTES with T3, according to an already known procedure [D.Gentili, M. Barbalinardo, I. Manet, M. Durso, M. Brucale, A. Mezzi, M. Melucci and M. Cavallini *Nanoscale*, 2015, 7, 7184], b) photoluminescence spectra of APTES-T3 compared to those of T3 and T3Si in DCM. The spectrum of APTES-T3 is almost superimposable to that of T3Si meaning that after 15 minutes T3 has reacted quantitatively with APTES.

#### 4. Phase Repartition Tests



**Figure S3.** Ripartition test between water and  $\text{CH}_2\text{Cl}_2$  of the different sample investigated.

#### 5. Stability of SF and SF-APTES-T3 solution



**Figure S4.** Stability of the solution of SF and SF-APTES-T<sub>3</sub> at room temperature. Both samples gelate over time. Slower gelation was observed for SF-APTES-T<sub>3</sub>.

#### 6. $^1\text{H-NMR}$ spectra

A SEC eluted fraction of SF-APTES-T<sub>3</sub> (1 ml) was casted on PDMS surface, dried and then dissolved in  $\text{D}_2\text{O}$ .

Solvent: D2O  
Temp. 25.0 C / 298.1 K  
Operator: lunazzi  
INOVA-600 \*i600\*

Relax. delay 2.000 sec  
Pulse 79.4 degrees  
Acq. time 2.995 sec  
Width 9611.9 Hz  
1024 repetitions  
OBSERVE H1, 599.7291287 MHz  
DATA PROCESSING  
Line broadening 0.2 Hz  
Sq. sine bell 2.995 sec  
Shifted by -2.995 sec  
FT size 131072  
Total time 7 hr, 24 min, 58 sec

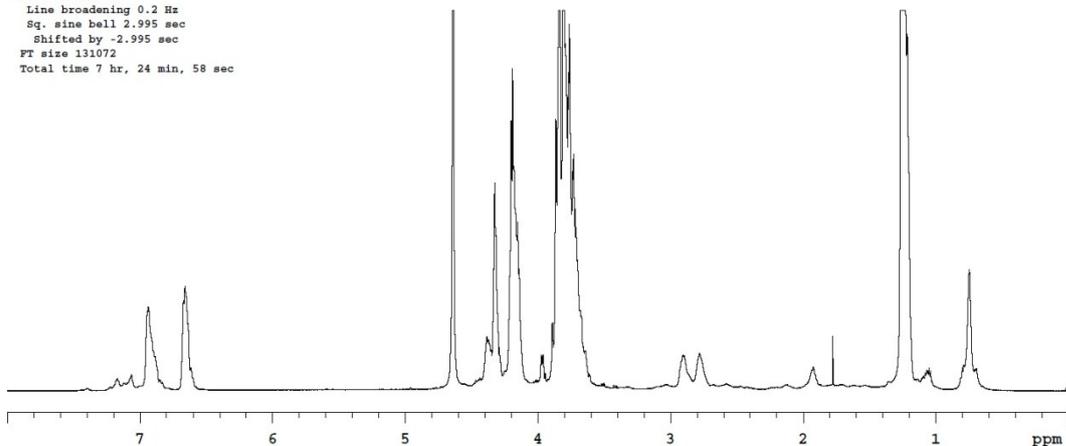


Figure S5.  $^1\text{H}$ -NMR DOSY of SF gz=500.

Solvent: D2O  
Temp. 25.0 C / 298.1 K  
Operator: lunazzi  
INOVA-600 \*i600\*

Relax. delay 2.000 sec  
Pulse 79.4 degrees  
Acq. time 2.995 sec  
Width 9611.9 Hz  
1024 repetitions  
OBSERVE H1, 599.7291287 MHz  
DATA PROCESSING  
Line broadening 0.2 Hz  
Sq. sine bell 2.995 sec  
Shifted by -2.995 sec  
FT size 131072  
Total time 7 hr, 24 min, 58 sec

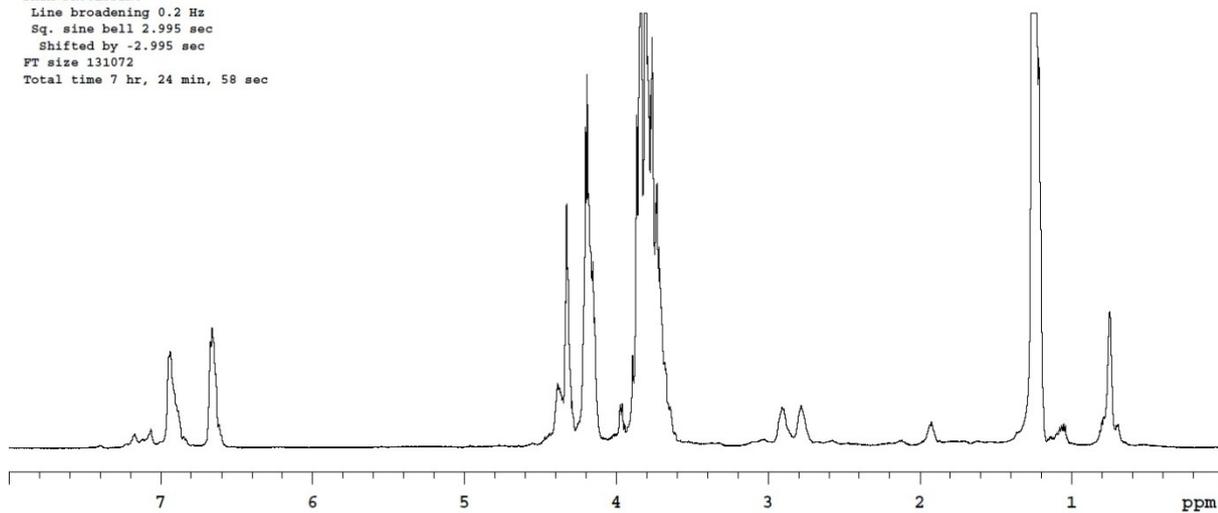


Figure S6. DPGSE  $^1\text{H}$ -NMR of SF ( $\approx 65$  G/cm).

Solvent: D2O  
Temp. 25.0 C / 298.1 K  
Operator: lunazzi  
INOVA-600 "i600"  
  
Relax. delay 2.000 sec  
Pulse 79.4 degrees  
Acq. time 2.995 sec  
Width 9611.9 Hz  
1024 repetitions  
OBSERVE H1, 599.7291287 MHz  
DATA PROCESSING  
Line broadening 0.5 Hz  
Sq. sine bell 2.995 sec  
Shifted by -2.995 sec  
FT size 131072  
Total time 7 hr, 24 min, 58 sec

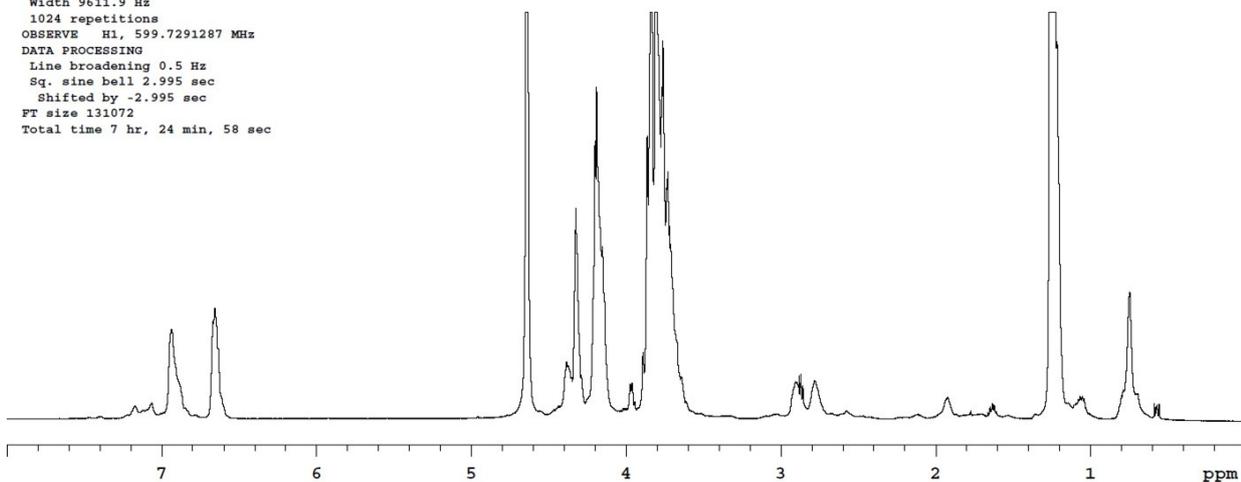


Figure S7. DPGSE  $^1\text{H}$ -NMR of SF-APTES-T3 ( $\approx 1$  G/cm).

Solvent: D2O  
Temp. 25.0 C / 298.1 K  
Operator: lunazzi  
INOVA-600 "i600"  
  
Relax. delay 2.000 sec  
Pulse 79.4 degrees  
Acq. time 2.995 sec  
Width 9611.9 Hz  
1024 repetitions  
OBSERVE H1, 599.7291287 MHz  
DATA PROCESSING  
Line broadening 0.5 Hz  
Sq. sine bell 2.995 sec  
Shifted by -2.995 sec  
FT size 131072  
Total time 7 hr, 24 min, 58 sec

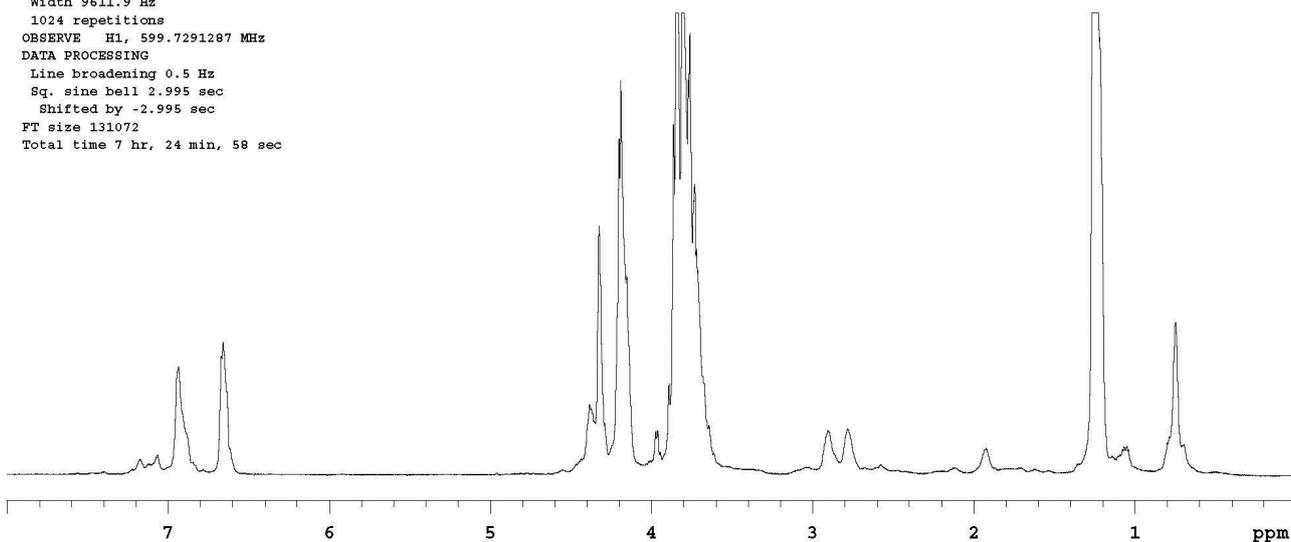


Figure S8. DPGSE  $^1\text{H}$ -NMR of SF-APTES-T3 ( $\approx 65$  G/cm)

## 7. ATR FT-IR spectroscopy

ATR spectra of SF films were performed by means of a FT-IR Bruker Vertex 70 interferometer equipped with a diamond crystal single reflection Platinum ATR accessory. Free-standing silk films for IR characterization were prepared by drop-casting and slow-drying approach. Specifically, 1 mL of SF solutions was casted on support/mold of polydimethylsiloxane (PDMS) left dried, and piled off from the PDMS substrate.

The curve-fitting of overlapping bands of the infrared spectra covering the amide I and II regions ( $1500\text{--}1700\text{ cm}^{-1}$ ) were performed by using the Levenberg–Marquardt algorithm implemented in the OPUS 2.0 software.

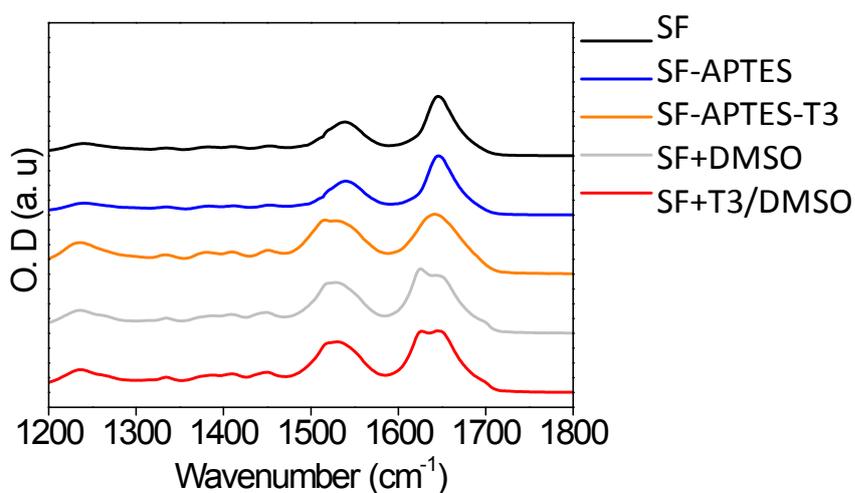


Figure S9. ATR spectra of the SF and modified SF films.

## 8. Water contact angle measurements

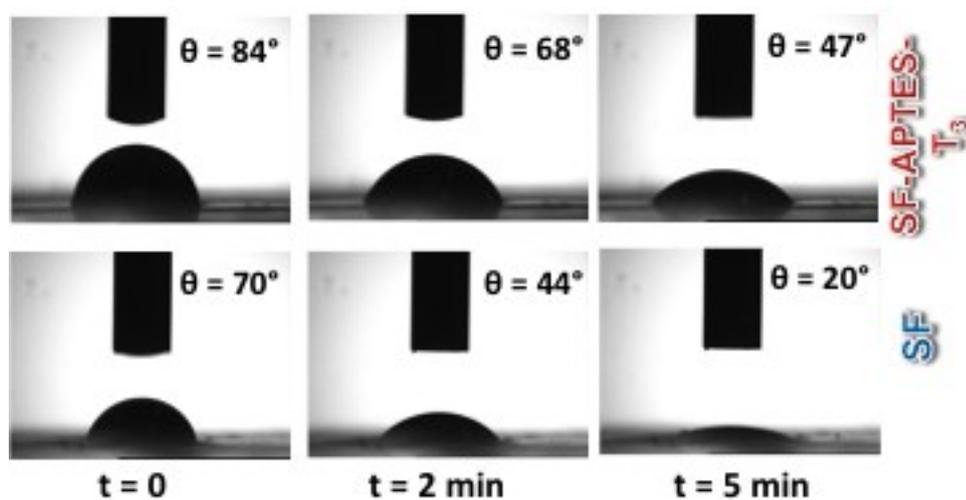
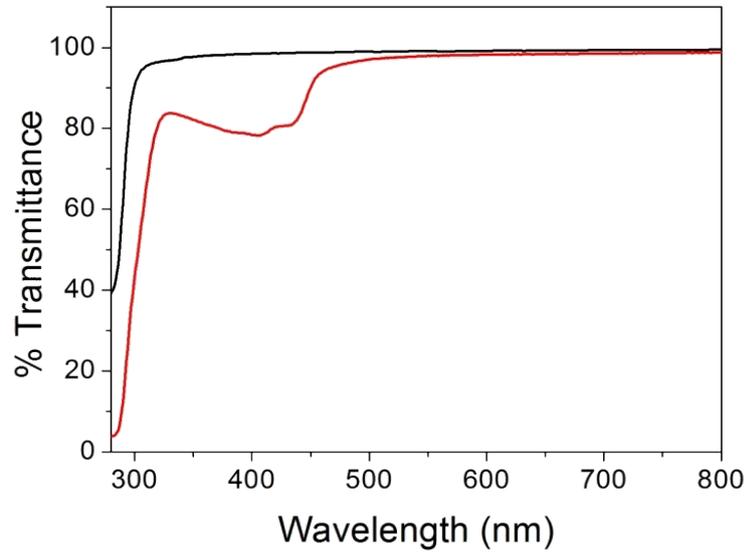


Figure S10. Water contact angle evolution over 5 minutes for SF-APTES-T3 and SF.

## 9. Transmittance spectroscopy



**Fig. S11.** Transmittance spectra of SF film (black curve) and SF-APTES-T3 film (red curve).