

## Supporting Information

# Thermally Stable and Solvent-Resistant Conductive Polymer Composites with Cross-linked Siloxane Network

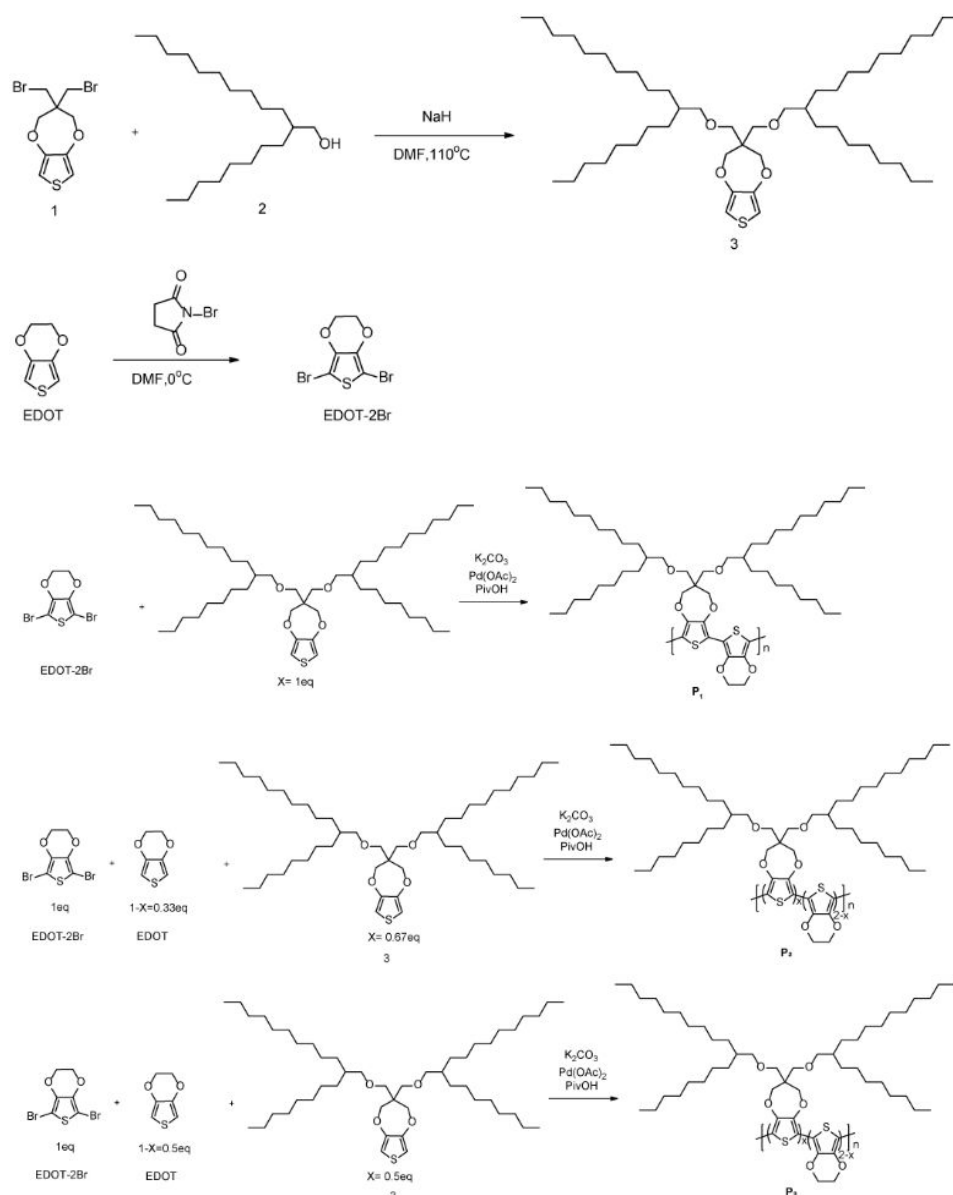
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## S1. Synthetic Protocols and $^1\text{H}$ NMR spectrum

### 1.1 Synthetic Protocols

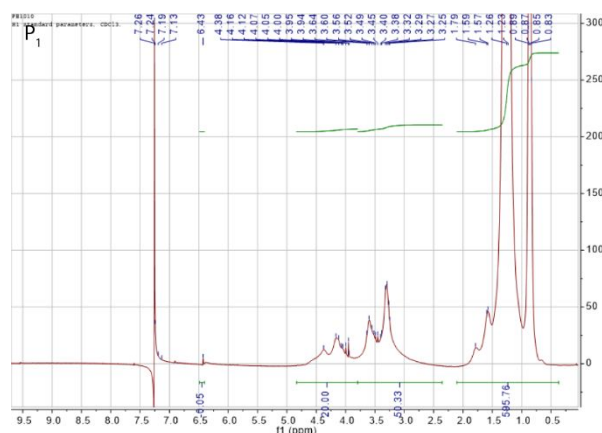


**Scheme S1.** Synthetic routes for compound  $\text{P}_1$ ,  $\text{P}_2$ ,  $\text{P}_3$

(Compound 3): To a 1000 mL flask was charged with a stir bar, 2-Octyl-1-dodecanol (compound 2, 31.4 g, 105.2 mmol) and DMF 180mL. 60% NaH (4 g, 101 mmol) was added slowly, then heat the mixture to  $100^\circ\text{C}$  for 20min. After cool to room temperature added 3,3-bis(bromomethyl)-3,4-dihydro-2H-thieno[3,4-b][1,4]dioxepine (compound 1, 15g, 43.9 mmol) and heat to  $110^\circ\text{C}$  reacted for 18h. Then cool to room temperature and added 540 mL water and 300 mL hexane to extract the product. The hexane layer was collected and rotovap to remove solvent then submitted to silica gel column to purify compound 3. Colorless oil 20g was got. (Y=60%).

$^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm): 6.43 (s, 2H), 4.00 (s, 4H), 3.45 (s, 4H), 3.26 (d, 4H,  $J=6\text{Hz}$ ), 1.26-0.86 (m, 78H).

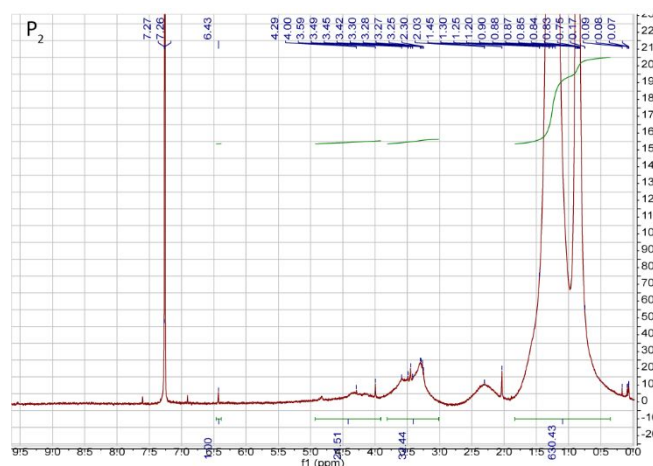




**Figure S2.**  $^1\text{H}$  NMR spectrum of  $\text{P}_1$ .

(Polymer  $\text{P}_2$ ): To a Schlenk tube charged with a stir bar, compound 3 (0.521 g, 0.67 mmol), EDOT-2Br (0.3 g, 1.0 mmol), EDOT (0.047 g, 0.33 mmol), PivOH (31 mg, 0.3 mmol),  $\text{Pd}(\text{OAc})_2$  (4.5 mg, 0.02 mmol) and  $\text{K}_2\text{CO}_3$  (0.36 g, 2.6 mmol). The mixture was vacuum and refilled with nitrogen for three times. Degas DMAc 8 mL was added with syringe and heat to  $140^\circ\text{C}$  for 18h. Then precipitate the solution with 100 mL methanol. Filter and washed with methanol to get solid. The solid was dissolved into 30mL chloroform, 0.5 mL of hydrazine hydrate was added and stirred for 20min. The solution was washed with 30 mL 1N HCl twice, then washed with 30 mL DI water. The solution was added into 200 mL methanol and precipitate the polymer. Solid precipitate from the solution was filter and dry to get the desired polymer. (0.59g, Y=88%).

$^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm): 4.90-3.90 (m, 8H), 3.59-3.25 (m, 12H), 1.45-0.75 (m, 78H).

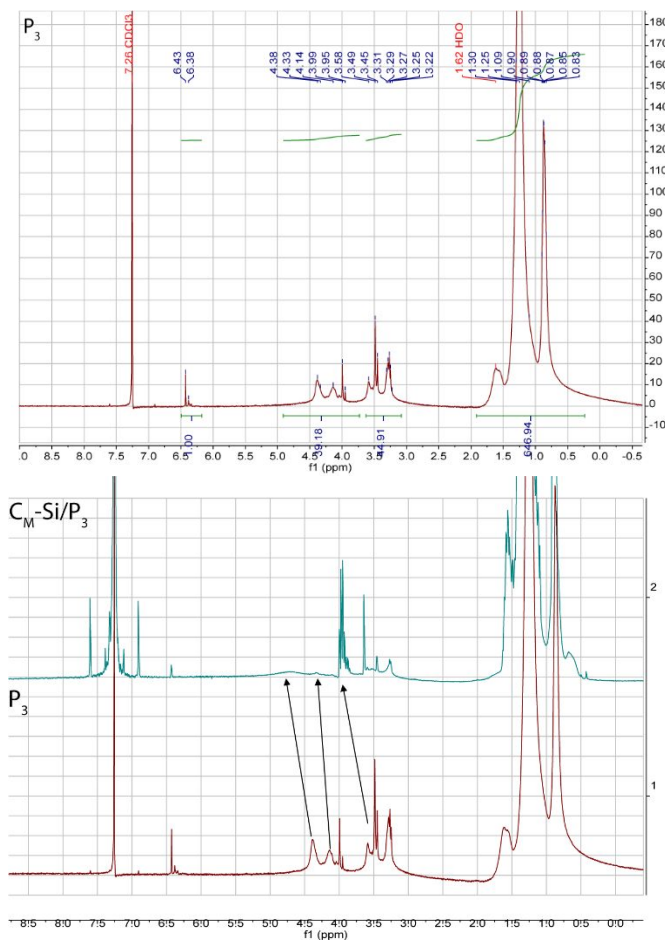


**Figure S3.**  $^1\text{H}$  NMR spectrum of  $\text{P}_2$ .

(Polymer  $\text{P}_3$ ): To a Schlenk tube charged with a stir bar, compound 3 (0.518 g, 0.67 mmol), EDOT-2Br (0.4 g, 1.33 mmol), EDOT (0.095 g, 0.67 mmol), PivOH (41 mg, 0.4 mmol),  $\text{Pd}(\text{OAc})_2$  (6.0 mg, 0.027 mmol) and  $\text{K}_2\text{CO}_3$  (0.48 g, 3.5 mmol). The mixture was vacuum and refilled with nitrogen for three times. Degas DMAc 8 mL was added with syringe and heat to  $140^\circ\text{C}$  for 18h. Then precipitate the solution with 100 mL methanol. Filter and washed with methanol to get solid. The solid was dissolved into 50mL chloroform, 0.5 mL of hydrazine hydrate was added and stirred for 20min. The solution was washed with 40 mL 1N HCl twice, then washed with 40 mL DI water. The solution was added into 250 mL methanol

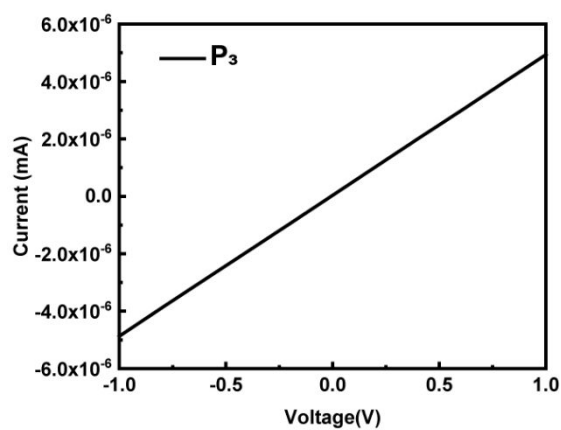
and precipitate the polymer. Solid precipitate from the solution was filter and dry to get the desired polymer. (0.57g, Y=80%)

$^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm): 4.38-3.95 (m, 12H), 3.58-3.27 (m, 12H), 1.30-0.83 (m, 78H).

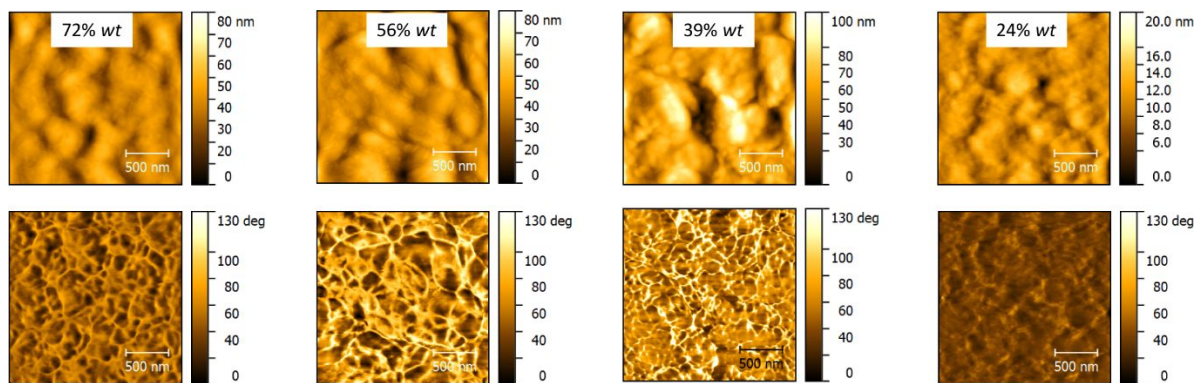


**Figure S3.**  $^1\text{H}$  NMR spectrum of  $\text{P}_3$  and  $\text{C}_\text{M}\text{-Si/P}_3$ .

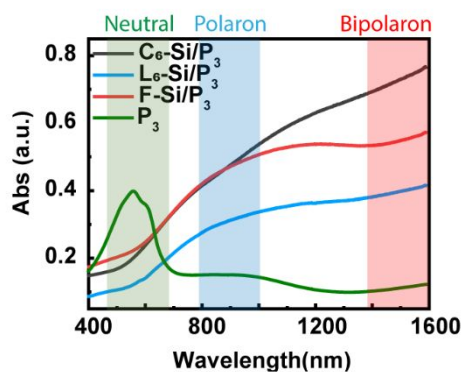
## S2. Additional Tables, Schemes and Figures



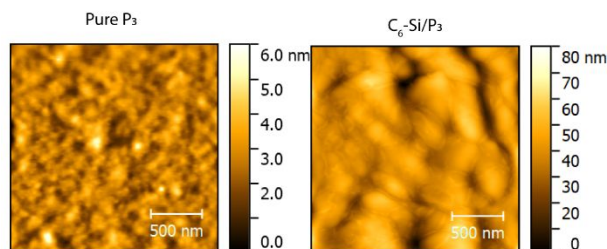
**Figure S4** I-V curve of pure  $\text{P}_3$ .



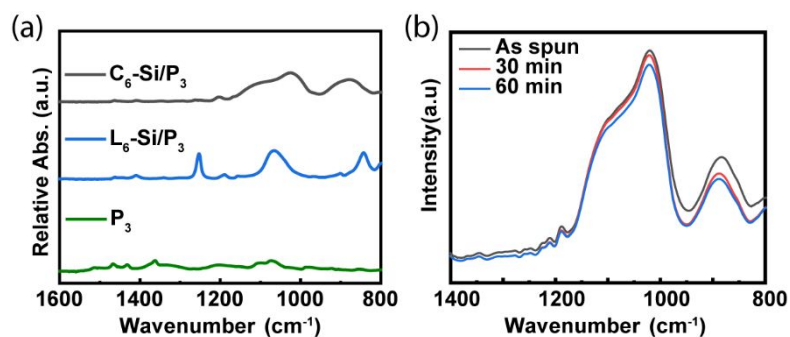
**Figure S5** AFM height and phase images of  $C_6$ -Si/ $P_3$  composites with different content of  $C_6$ -Si.



**Figure S6** Thin films UV-Vis spectra of pure  $P_3$  and different chlorosilanes/ $P_3$  composites at 56% *wt* of the dopants.

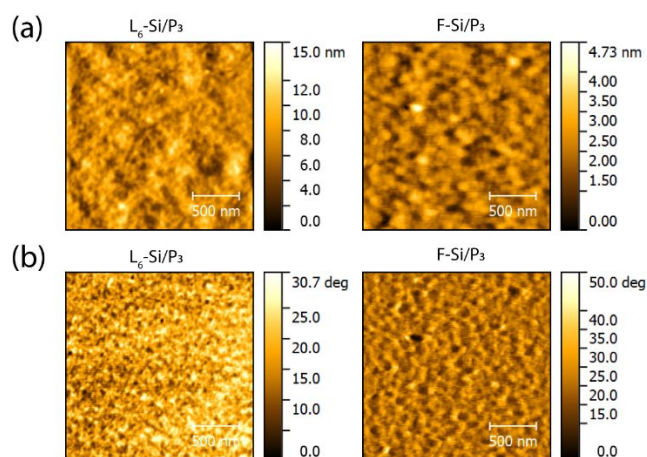


**Figure S7** AFM height images of pure  $P_3$  and 56% *wt*  $C_6$ -Si/ $P_3$ .

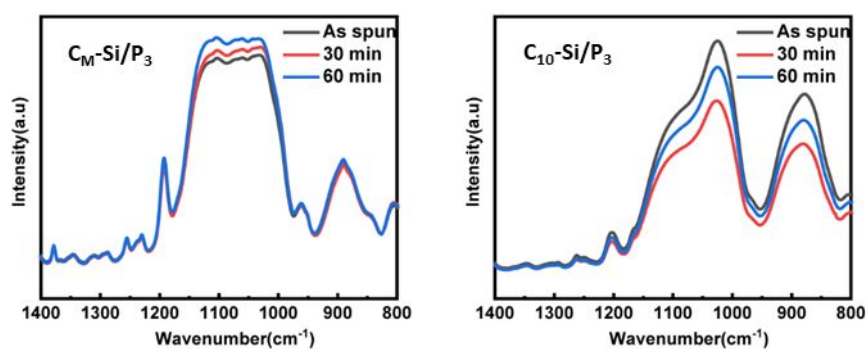


**Figure S8** (a) FTIR spectrum of pure  $P_3$ ,  $C_6$ -Si/ $P_3$  and  $L_6$ -Si/ $P_3$  composites with 56% *wt* of chlorosilanes; (b) FTIR spectrum of 56% *wt*  $C_6$ -Si/ $P_3$  composites before and after annealing at 393 K.

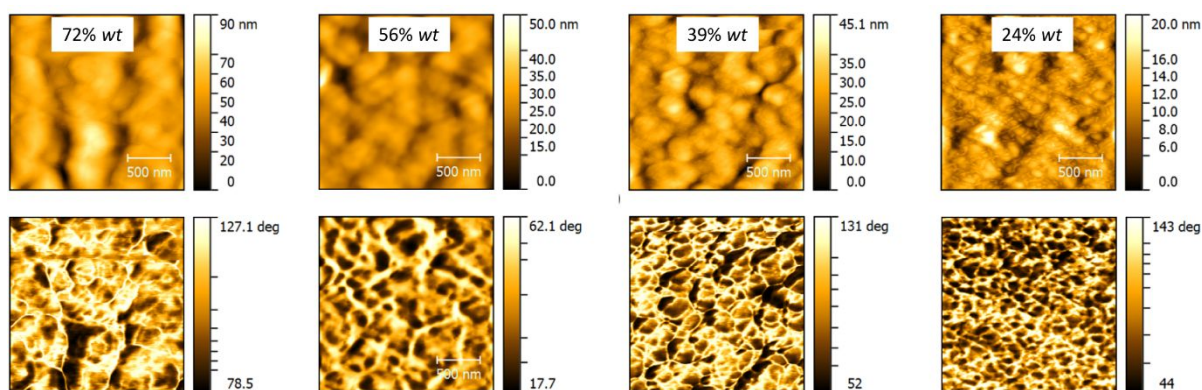




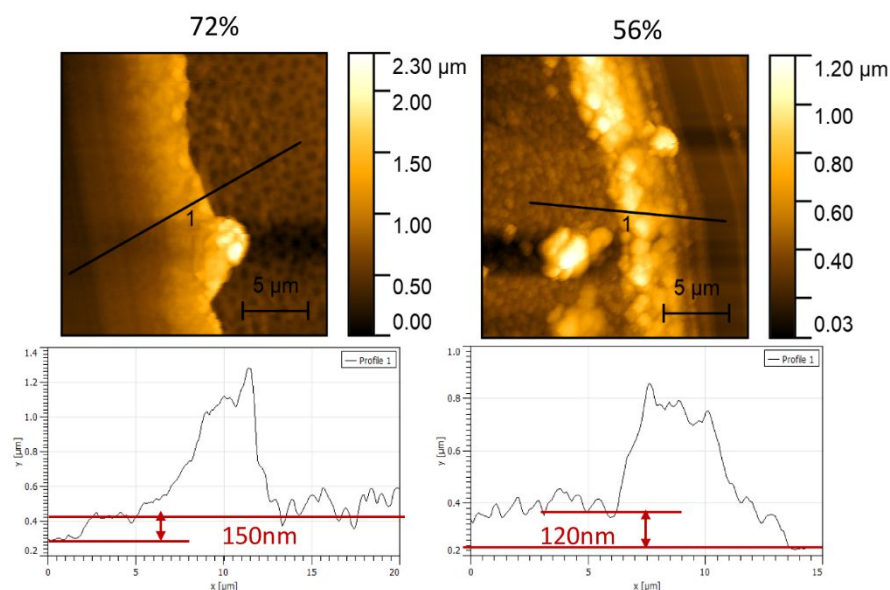
**Figure S9** AFM height images a) and phase images b) of 56% wt  $L_6$ -Si/ $P_3$  and 56% wt F-Si/ $P_3$ .



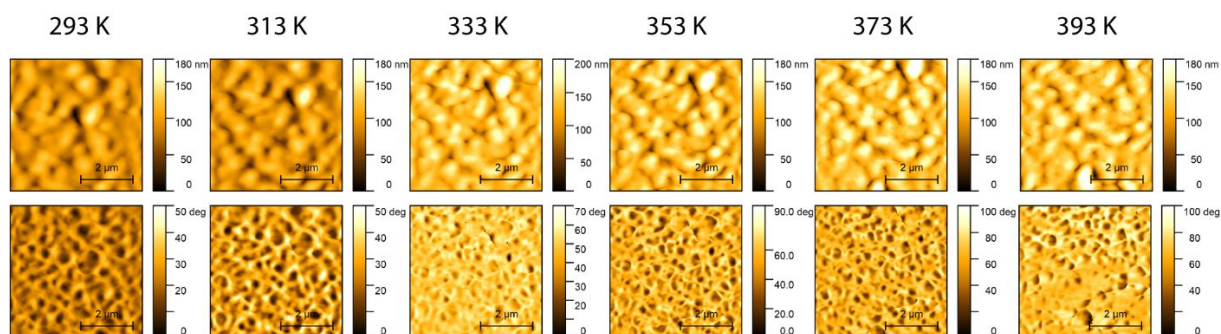
**Figure S10** FTIR spectrum of 56% wt  $C_M$ -Si/ $P_3$  composites and  $C_{10}$ -Si/ $P_3$  before and after annealing at 393 K.



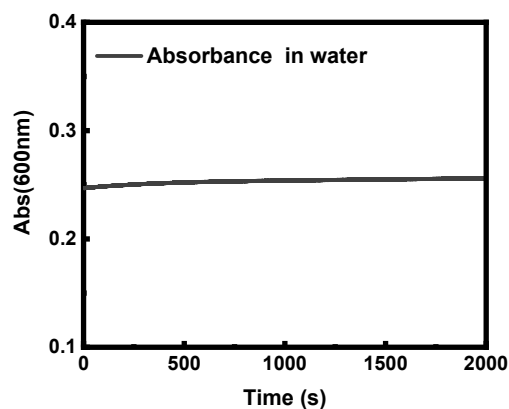
**Figure S11** AFM height and phase images of  $C_M$ -Si/ $P_3$  composites with different content of  $C_M$ -Si.



**Figure S12** Film thickness of  $C_M\text{-Si}/P_3$  composites with different content of  $C_M\text{-Si}$ .

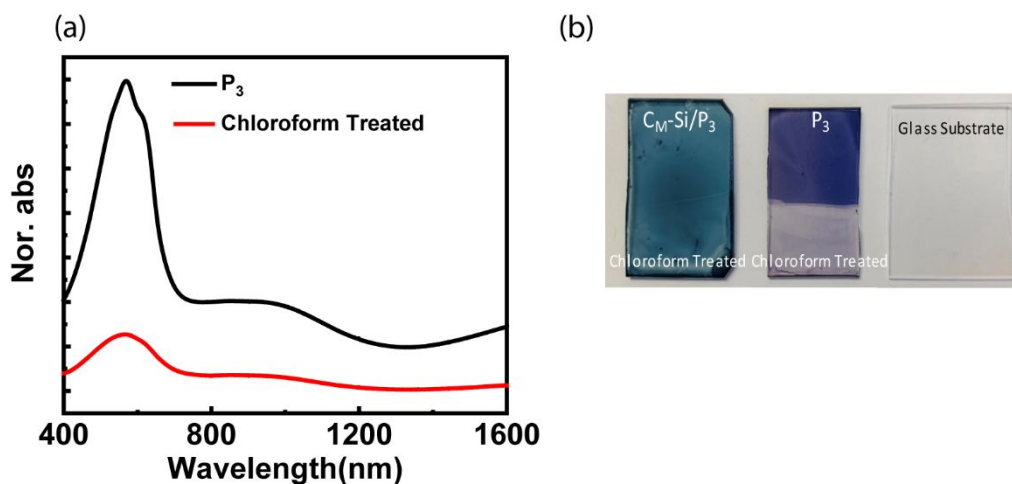


**Figure S13** In-suit temperature dependent AFM height and phase images of  $C_M\text{-Si}/P_3$  composites when increasing temperature from 293K to 393K.

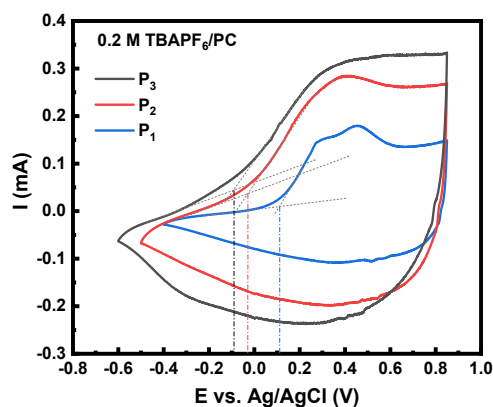


**Figure S14** In-suit UV-Vis absorption at 600 nm of  $C_M\text{-Si}/P_3$  composites in the water.

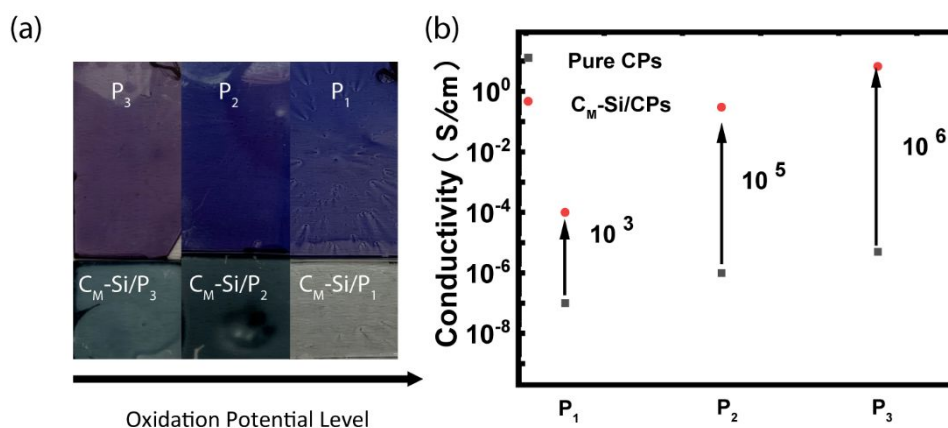




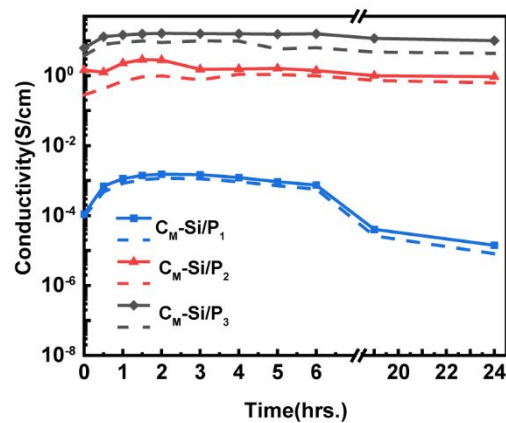
**Figure S15** a) UV-Vis absorptions of pure  $P_3$  film before and after being dipped in chloroform; b) photos of 56 wt%  $C_M$ -Si/ $P_3$  composites and pure  $P_3$  film before and after being dipped in chloroform.



**Figure S16** Cyclic voltammetry (CV) of pure CPs in 0.2 M tetrabutylammonium hexafluorophosphate ( $TBAPF_6$ ) in propylene carbonate (PC) recorded at a scan rate of  $40 \text{ mV s}^{-1}$ . The oxidation potential of  $P_3$ ,  $P_2$  and  $P_1$  is around  $-0.1 \text{ V}$ ,  $-0.02 \text{ V}$  and  $0.1 \text{ V}$ , respectively.



**Figure S17** a) Photographs of CPs films and  $C_M$ -Si/CPs composites; b) conductivity comparison of CPs films and  $C_M$ -Si/CPs composites.



**Figure S18** Conductivities of 56 wt % C<sub>M</sub>-Si/CPs composites with different CPs when baked at 353K under ambient conditions after 24 hours, measured by two-probe and four. The lines with symbols refer to the result measured by two-probe method and the dashed lines refer to four-probe method results.