

Supporting Information

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

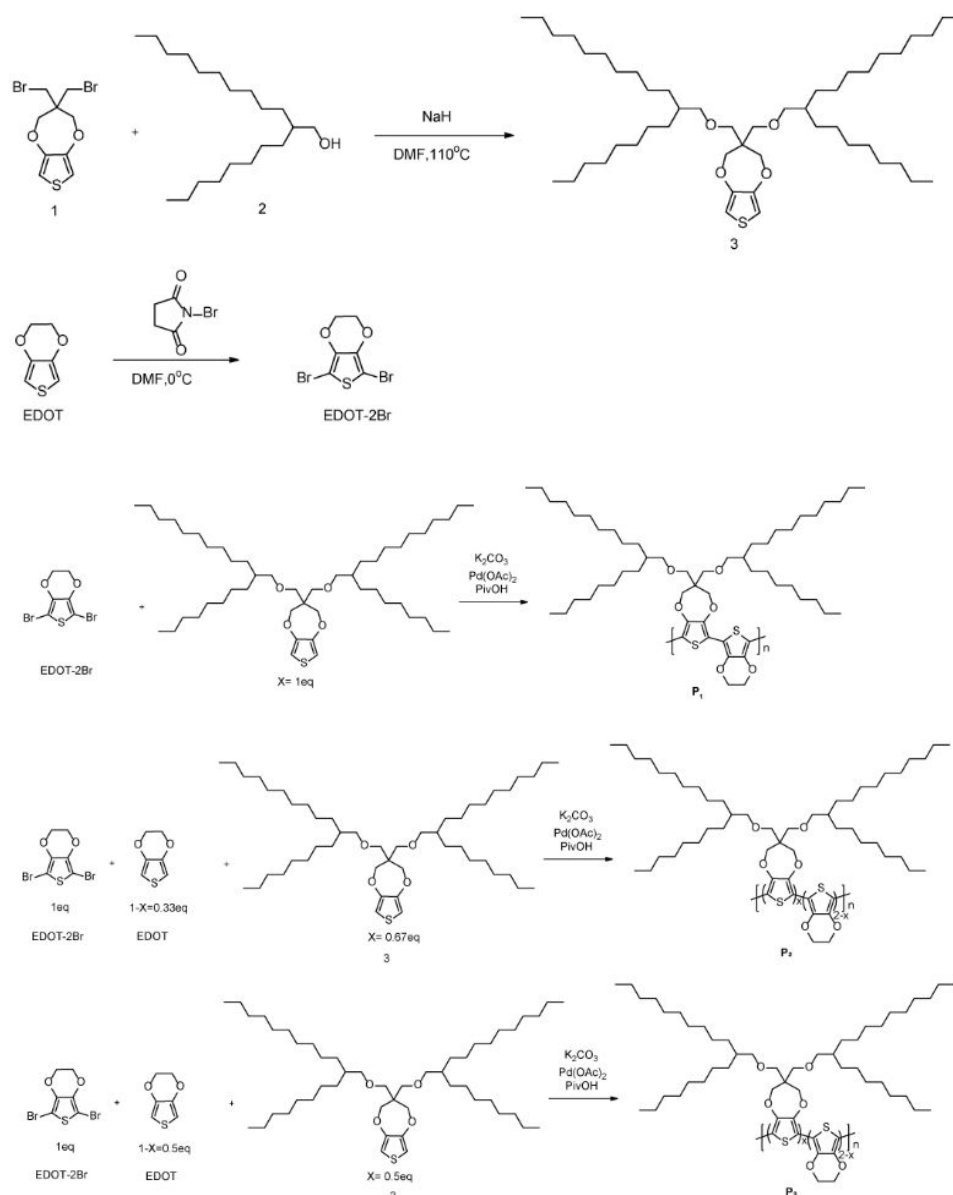
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S1. Synthetic Protocols and ^1H NMR spectrum

1.1 Synthetic Protocols



Scheme S1. Synthetic routes for compound P_1 , P_2 , 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 °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 °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%).

^1H NMR (300 MHz, CDCl_3) δ (ppm): 6.43 (s, 2H), 4.00 (s, 4H), 3.45 (s, 4H), 3.26 (d, 4H, J=6Hz), 1.26-0.86 (m, 78H).

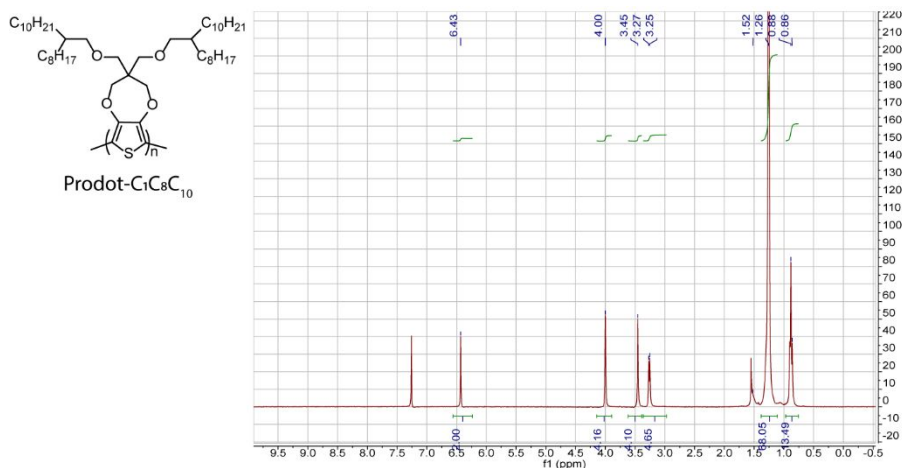


Figure S1. ^1H NMR spectrum of compound 3.

(EDOT-2Br): To a 500 mL flask was charged with a stir bar, EDOT (4.0 g, 28 mmol) and DMF 20mL then cool to 0°C . NBS (10.5 g, 59 mmol) was dissolved into 50 mL DMF and added into the flask dropwise. After stir at 0°C for 50min 100 mL water was added into the flask. Filter and wash with MeOH/water=1/2 solution 50mL to get white solid 8g (95%).

^1H NMR (300 MHz, CDCl_3) δ (ppm): 4.27 (s, 4H).

(Polymer **P**₁): To a Schlenk tube charged with a stir bar, compound 3 (0.777 g, 1.0 mmol), EDOT-2Br (0.3 g, 1.0 mmol), PivOH (31 mg, 0.3 mmol), $\text{Pd}(\text{OAc})_2$ (4.5 mg, 0.02 mmol) and K_2CO_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°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. (0.76g, Y=83%)

^1H NMR (300 MHz, CDCl_3) δ (ppm): 4.38-3.94 (m, 4H), 3.64-3.5 (m, 12H), 1.79-0.83 (m, 78H).

(Polymer **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), Pd(OAc)₂ (4.5 mg, 0.02 mmol) and K₂CO₃ (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 °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%).

(Polymer **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), Pd(OAc)₂ (6.0 mg, 0.027 mmol) and K₂CO₃ (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 °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%)

^1H NMR (300 MHz, CDCl_3) δ (ppm): 4.38-3.95 (m, 12H), 3.58-3.27 (m, 12H), 1.30-0.83 (m, 78H).

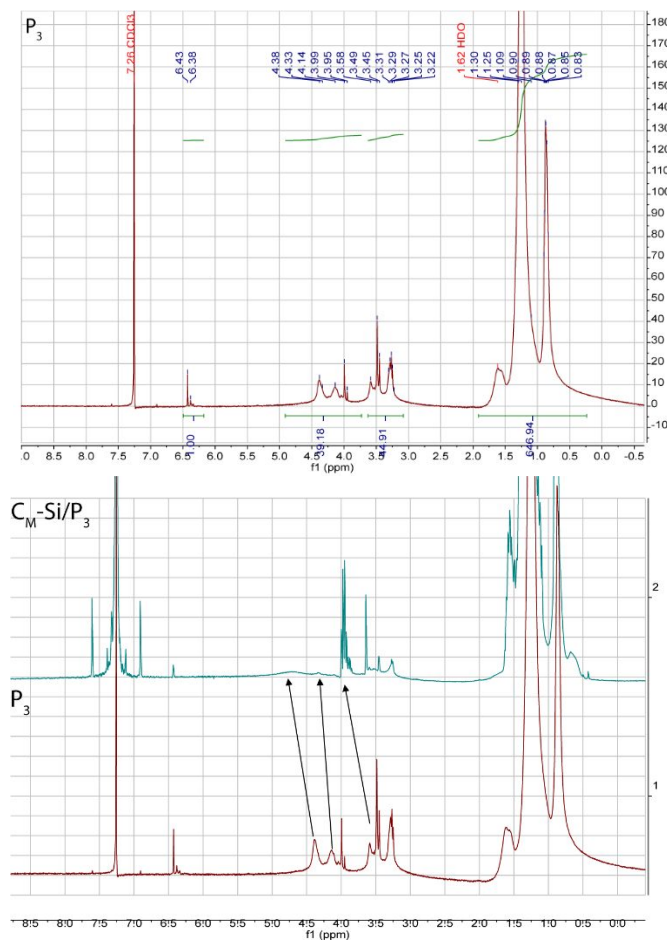


Figure S3. ^1H NMR spectrum of P_3 and $\text{C}_\text{M}\text{-Si/P}_3$.

S2. Additional Tables, Schemes and Figures

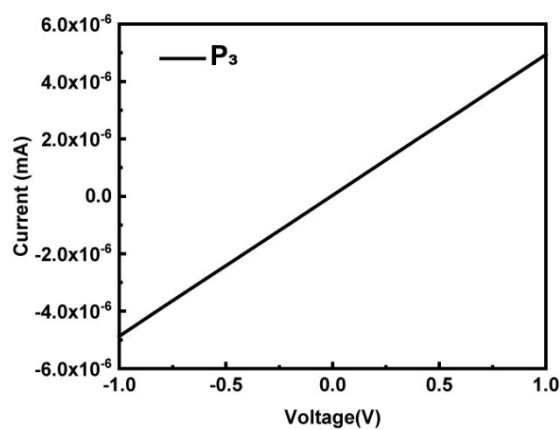


Figure S4 I-V curve of pure P_3 .

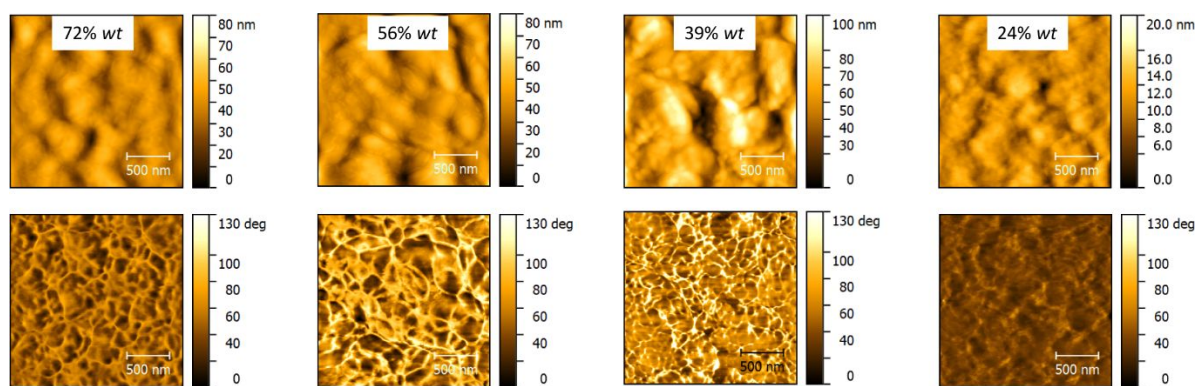


Figure S5 AFM height and phase images of C_6 -Si/ P_3 composites with different content of C_6 -Si.

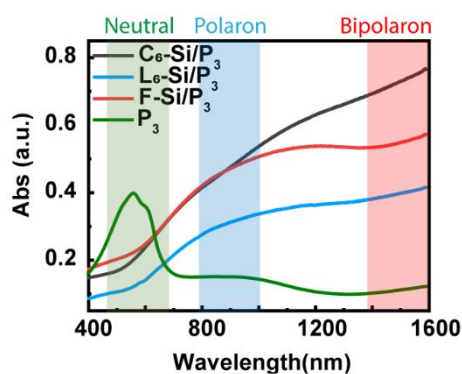


Figure S6 Thin films UV-Vis spectra of pure P_3 and different chlorosilanes/ P_3 composites at 56% *wt* of the dopants.

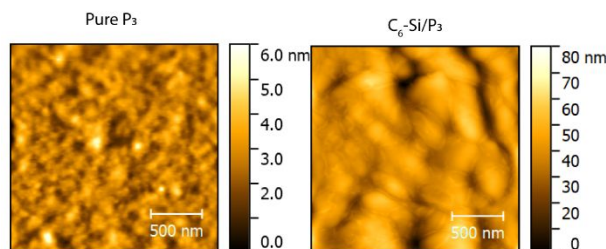


Figure S7 AFM height images of pure P_3 and 56% *wt* C_6 -Si/ P_3 .

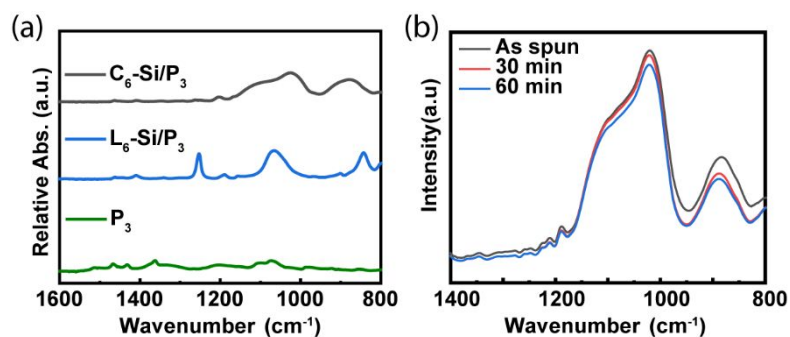


Figure S8 (a) FTIR spectrum of pure P_3 , C_6 -Si/ P_3 and L_6 -Si/ P_3 composites with 56% *wt* of chlorosilanes; (b) FTIR spectrum of 56% *wt* C_6 -Si/ P_3 composites before and after annealing at 393 K.

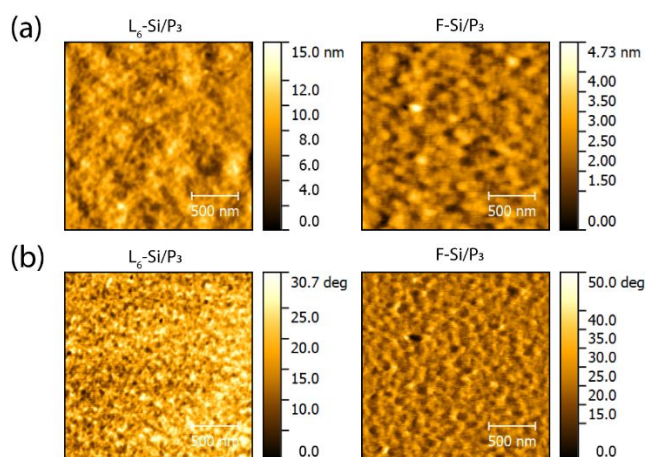


Figure S9 AFM height images a) and phase images b) of 56% wt L_6 -Si/ P_3 and 56% wt F-Si/ P_3 .

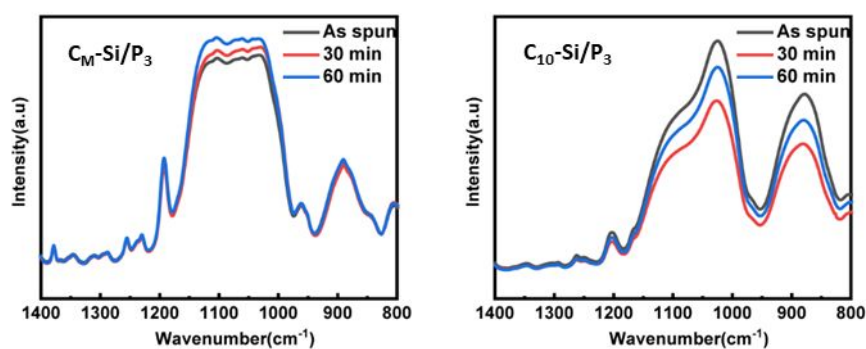


Figure S10 FTIR spectrum of 56% wt C_M -Si/ P_3 composites and C_{10} -Si/ P_3 before and after annealing at 393 K.

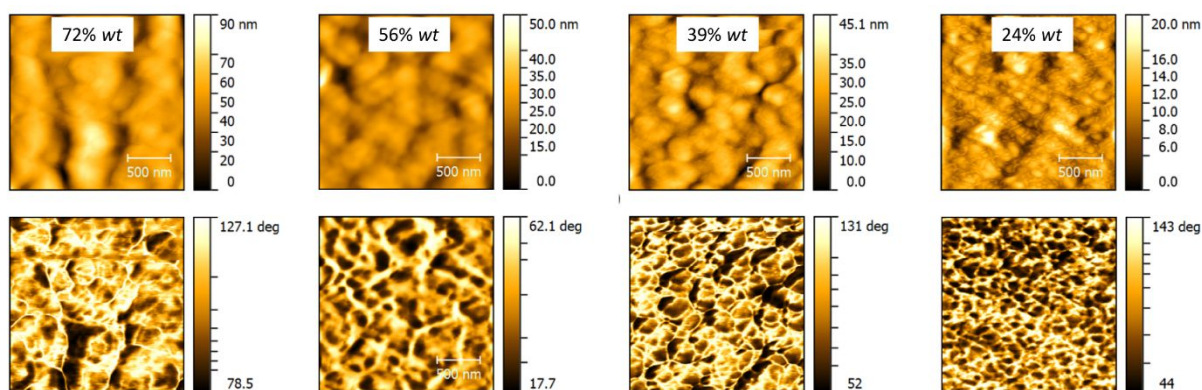


Figure S11 AFM height and phase images of C_M -Si/ P_3 composites with different content of C_M -Si.

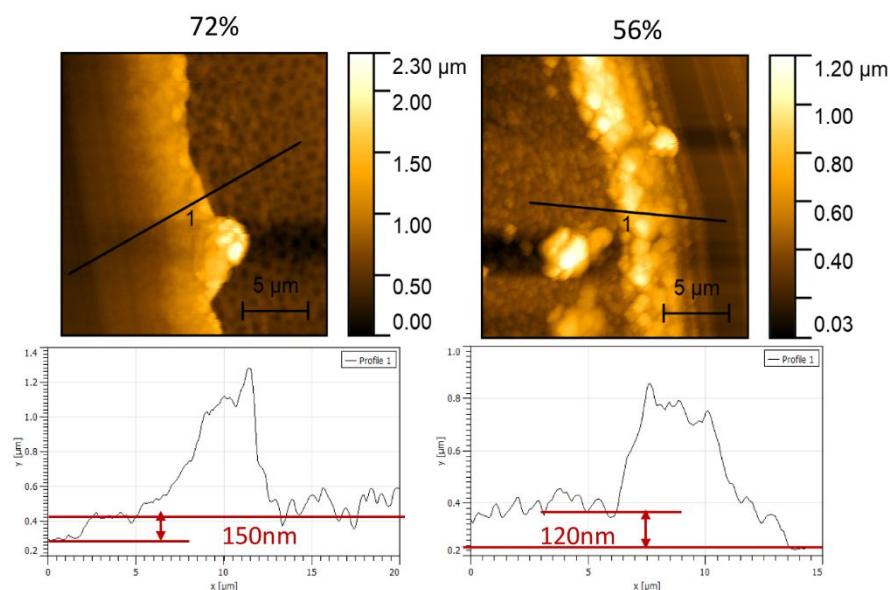


Figure S12 Film thickness of C_M -Si/ P_3 composites with different content of C_M -Si.

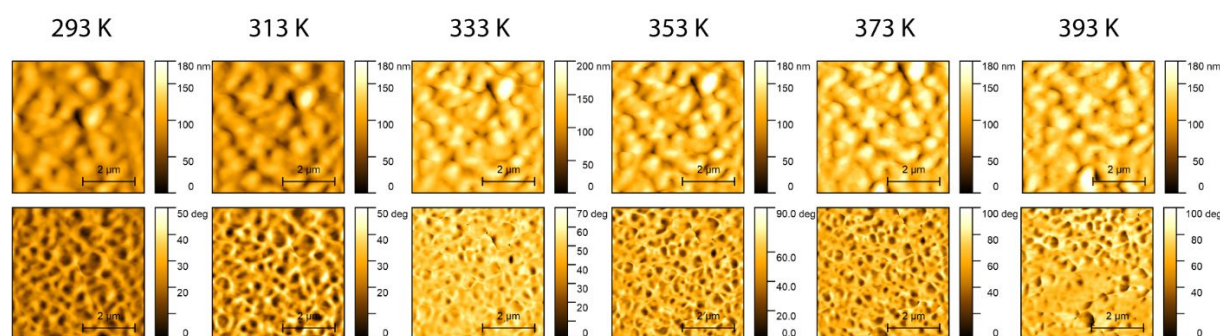


Figure S13 In-suit temperature dependent AFM height and phase images of C_M -Si/ P_3 composites when increasing temperature from 293K to 393K.

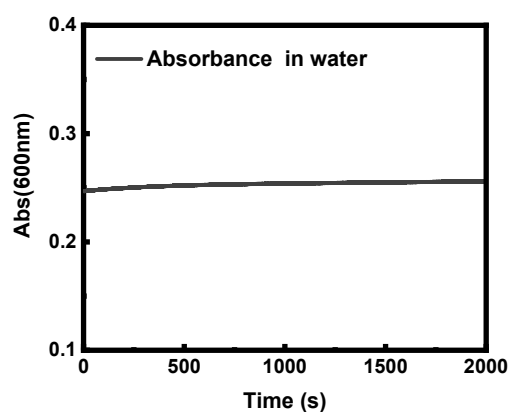


Figure S14 In-suit UV-Vis absorption at 600 nm of C_M -Si/ P_3 composites in the water.

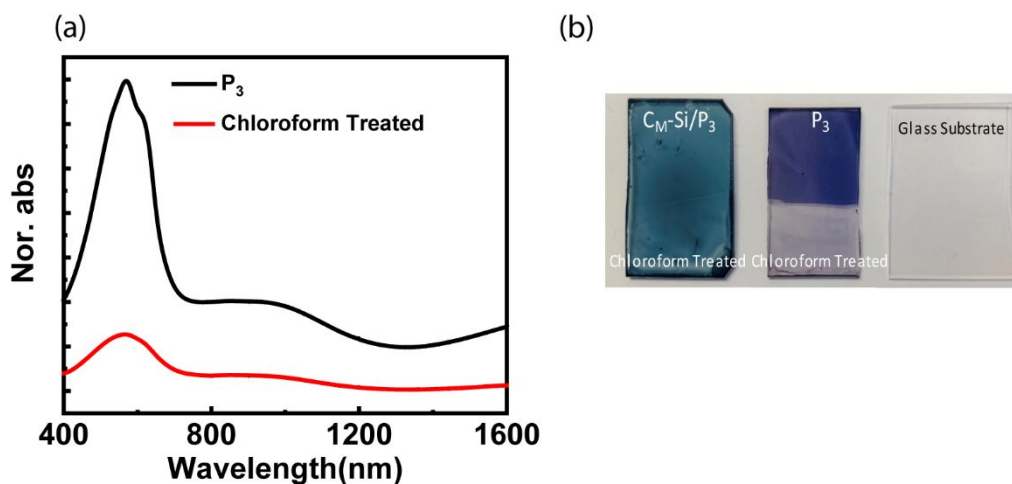


Figure S15 a) UV-Vis absorptions of pure P_3 film before and after being dipped in chloroform; b) photos of 56 wt% C_M -Si/ P_3 composites and pure P_3 film before and after being dipped in chloroform.

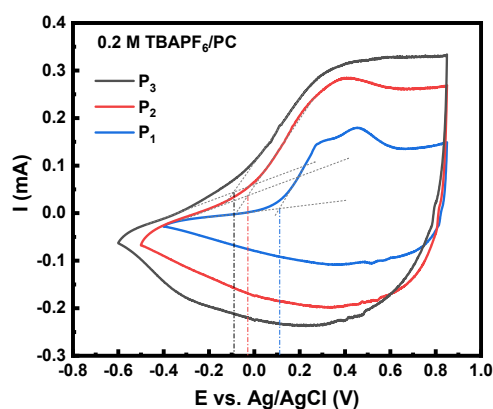


Figure S16 Cyclic voltammetry (CV) of pure CPs in 0.2 M tetrabutylammonium hexafluorophosphate ($TBAPF_6$) in propylene carbonate (PC) recorded at a scan rate of 40 mV s^{-1} . The oxidation potential of P_3 , P_2 and P_1 is around -0.1 V , -0.02 V and 0.1 V , respectively.

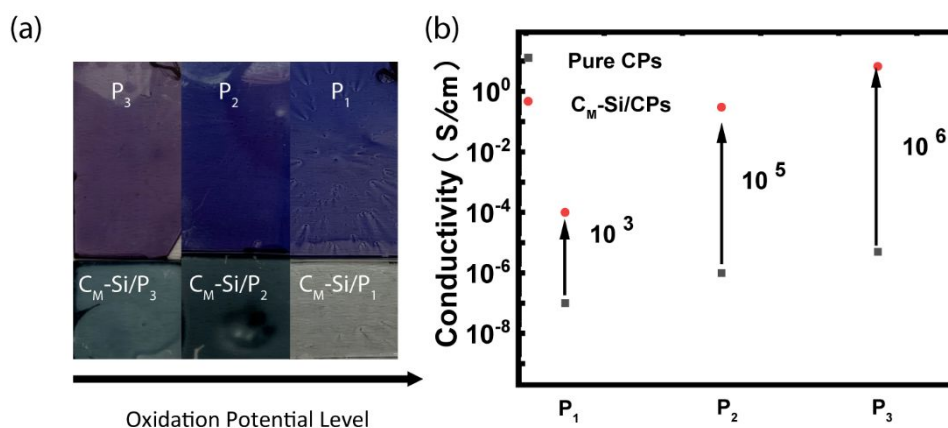


Figure S17 a) Photographs of CPs films and C_M -Si/CPs composites; b) conductivity comparison of CPs films and C_M -Si/CPs composites.

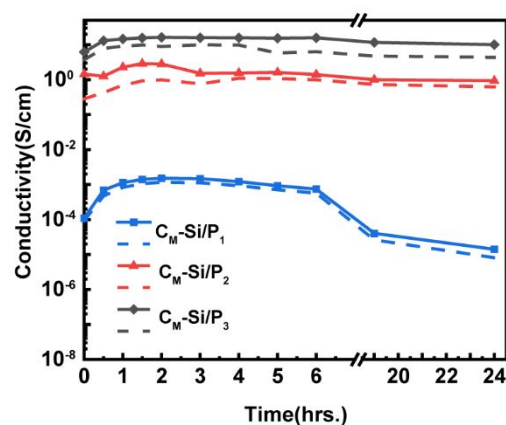


Figure S18 Conductivities of 56 wt % C_M -Si/CPs composites with different CPs when baked at 353K under ambient conditions after 24 hours, measured by two-probe and four. The lines with symbols refer to the result measured by two-probe method and the dashed lines refer to four-probe method results.