

Supplementary information

Transition metal silicide surface grafting by multiple functional groups and green optimization by mecanochemistry

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Section 1: Characterization of CrSi₂ particles

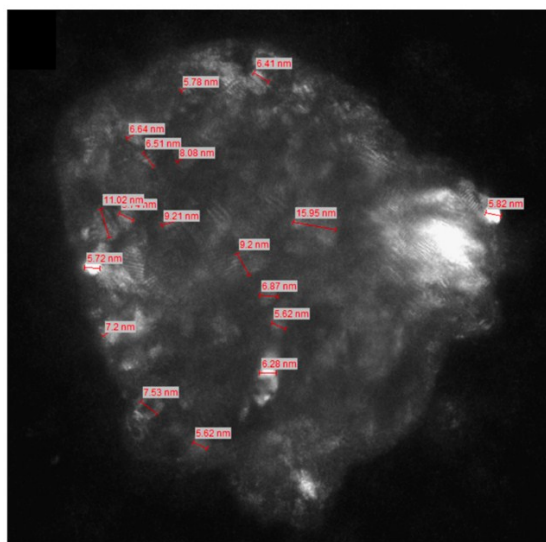


Fig. S1. Dark-field TEM image of CrSi₂ nanoparticles after 4h milling time.

Section 2: X-ray Photoelectron Spectroscopy of grafted CrSi₂ nanocrystallites

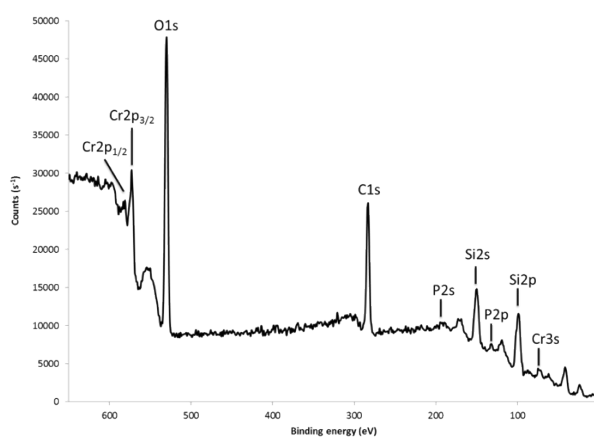


Fig. S1. Survey XPS spectra. Peaks of the different elements present at the surface, highlighting the presence of the grafted molecule dodecylphosphonic acid.

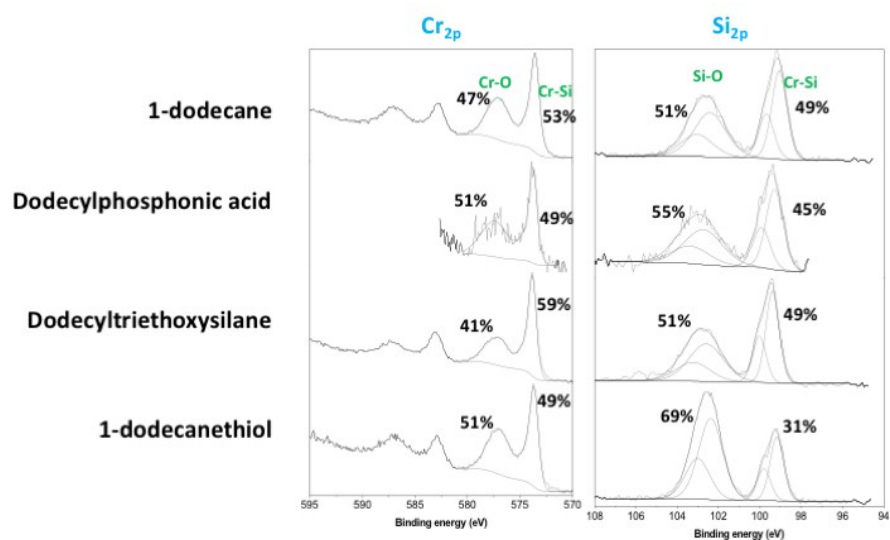


Fig. S2: Narrow-range Cr_{2p} and Si_{2p} XPS spectra. The amount of Cr-O and Si-O bonding compare to Cr-Si bonding are also given.

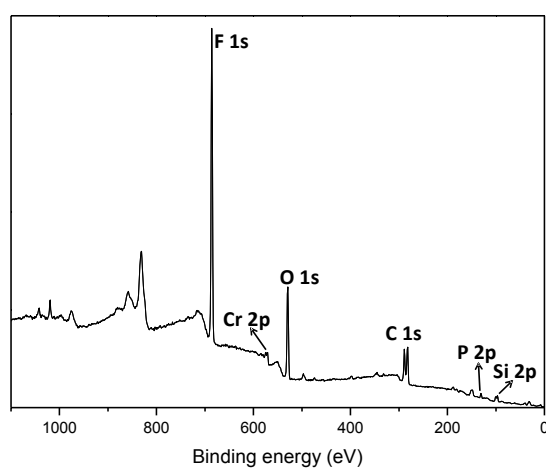


Fig. S3: Survey XPS spectra. Peaks of the different elements present at the surface, highlighting the presence of the grafted molecule H₂O₃P-(CH₂)₂-C₈F₁₇).

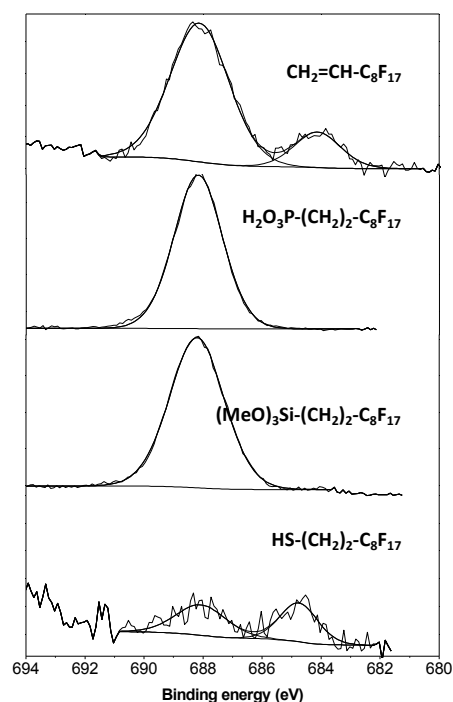
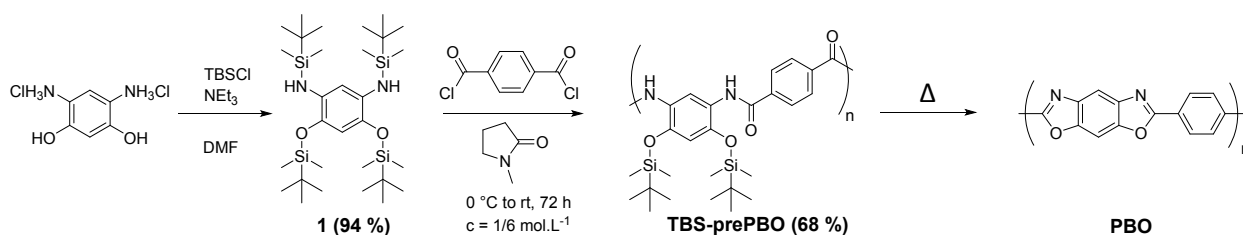


Fig. S4: Narrow-range F_{1s} XPS spectra with C-F bonding at 688eV.

Section 3: Synthesis of poly(p-phenylene-benzobisoxazole)

The poly(p-phenylene-benzobisoxazole) (**PBO**) (Scheme 1), also known as Zylon polymer, is the organic polymer the most thermally stable reported in literature with a decomposition temperature higher than 900K under nitrogen atmosphere ¹.



Scheme 1. Synthesis and thermal steps to conduct to the **PBO** polymer.

The main inconvenient of this polymer is its insolubility in common organic solvents and strong acids should be used to dissolve it. The attempts to increase the solubility by adding aliphatic chains caused a lower decomposition temperature. Fukumaru *et al.* ¹ have proposed the synthesis of a soluble precursor **TBS-prePBO** that enables to form films that are thermally

treated to conduct to the final polymer PBO with decomposition temperature of 670 °C. Hence, in this work, the synthesis of the soluble precursor TBS-prePBO was repeated.

Materials and Methods 4,6-Diaminoresorcinol dihydrochloride, terephthaloyl chloride, and *tert*-butyldimethylsilyl chloride were purchased from TCI and used without further purification. Dry Triethylamine, dry N,N-Dimethylformamide (DMF) and dry N-Methylpyrrolidone (NMP) were purchased from Sigma-Aldrich and used as received. TLC were performed using aluminium sheet covered by SiO₂ Silica gel 60F₂₅₄ (Merck), and column chromatography using Silica gel 60 (particle size 0.063-0.200 mm, Merck). ¹H-NMR (400 MHz) and ¹³C-NMR (101 MHz) were recorded on Bruker Avance 400. Chemical shifts are given in ppm and coupling constants *J* in Hz. The residual signal of the solvent was taken as internal reference standard.

Synthesis of 4,6-Di(*tert*-butyldimethylsilylamino)-1,3-di(*tert*-butyldimethylsiloxy) benzene (1): Under an inert atmosphere (Nitrogen), *tert*-butyldimethylsilyl chloride (21.22 g, 140.8 mmol) and trimethylamine (53 mL, 380 mmol) were added at room temperature to a solution of 4,6-diaminoresorcinol hydrochloride (3.00 g, 14.1 mmol) in DMF (150 mL). The reaction mixture was stirred at room temperature for 6 days. The formed precipitate was isolated by filtration and rinsed several times with water and methanol. The remaining solid was then dried under vacuum overnight, dissolved in chloroform and filtered through Celite. Evaporation of the filtrate under reduced pressure afforded **1** as a light brown powder (7.93 g, 94%). ¹H NMR (400 MHz, CDCl₃) δ 6.28 (s, 1H, Ar-H), 6.24 (s, 1H), 3.64 (s, 2H, NH), 1.00 (s, 18H, C-CH₃), 0.95 (s, 18H, C-CH₃), 0.24 (s, 12H, Si-CH₃), 0.20 (s, 12H, Si-CH₃).

The ¹H NMR spectra of **1** (Fig. S5) was perfectly in agreement with the one previously described.¹

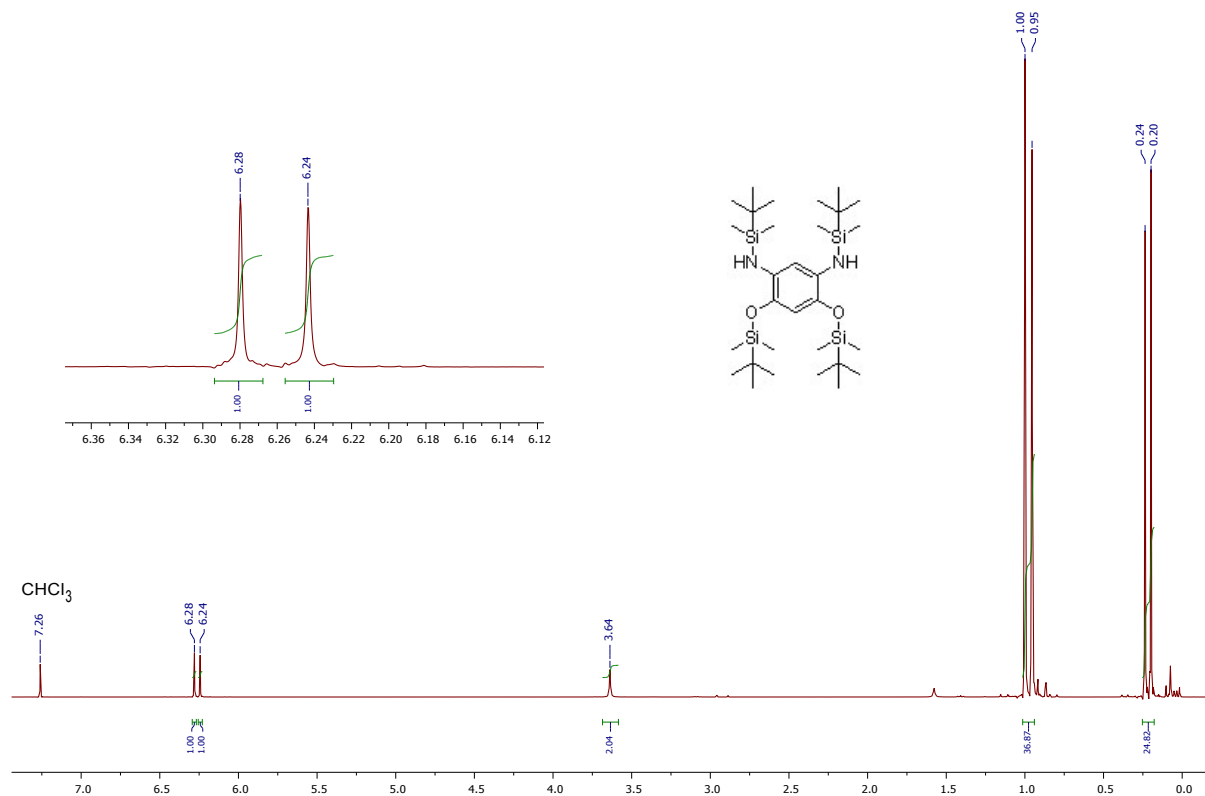


Fig. S5. ^1H NMR spectra of **1** in CDCl_3 .

Synthesis of TBS-prePBO (PBO precursor): Under an inert atmosphere (Nitrogen), terephthaloyl chloride (170 mg, 0.84 mmol) was added to a solution of **1** (500 mg, 0.84 mmol) in dry NMP (6 mL) at 0°C . The reaction mixture was then allowed to warm up to room temperature and was stirred at this temperature for 72h. The mixture was poured into 200 mL of methanol producing a precipitate, which was isolated by filtration and rinsed several times with water and methanol. The remaining solid was dried under vacuum affording the TBS-prePBO polymer as a beige powder (301 mg, 68%). ^1H NMR (400 MHz, $\text{DMSO}-d_6$) δ 9.72-9.65 (m, 2H, NH), 8.12-8.07 (m, 4H, Ar-H), 7.68-7.58 (m, 1H, Ar-H), 6.55-6.47 (m, 1H, Ar-H) 0.94-0.87 (m, 18H, C- CH_3), 0.21-0.15 (m, 12H, Si- CH_3).

* : Solvent residual peak (NMP)

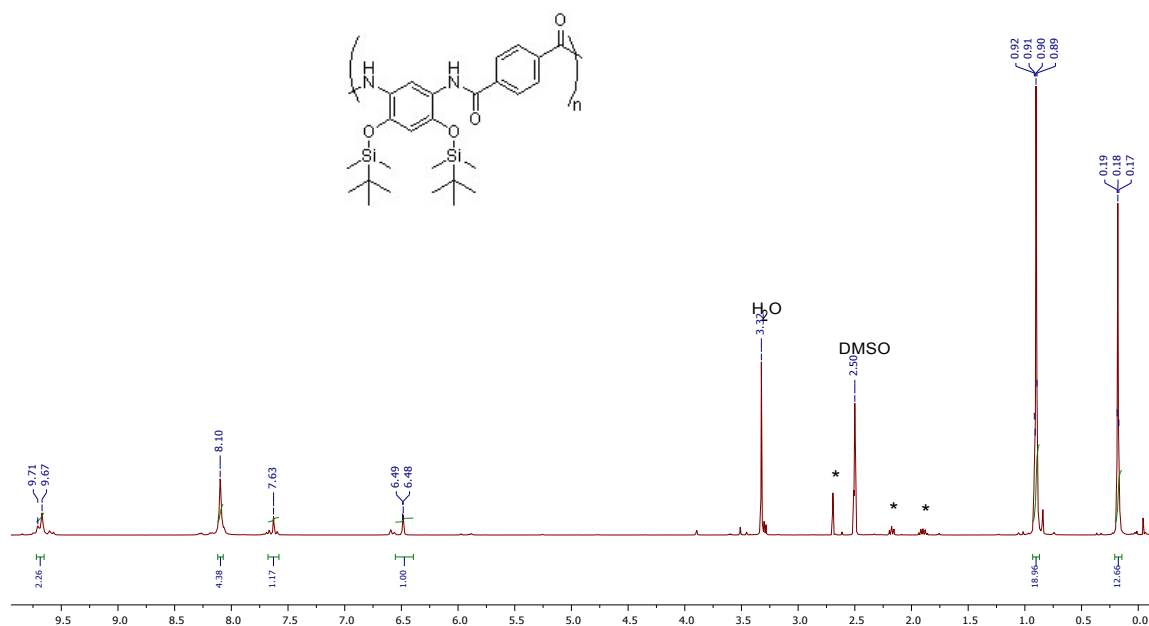


Fig. S6. ¹H NMR spectra of TBS-prePBO in DMSO-d₆.

The ¹H NMR spectra of TBS-prePBO (Fig. S6) was in agreement with the one previously described.¹

To promote air-processed samples, decomposition temperature had to be known so thermogravimetric analysis (TGA) under air atmosphere was conducted on TBS-prePBO (Fig. S7).

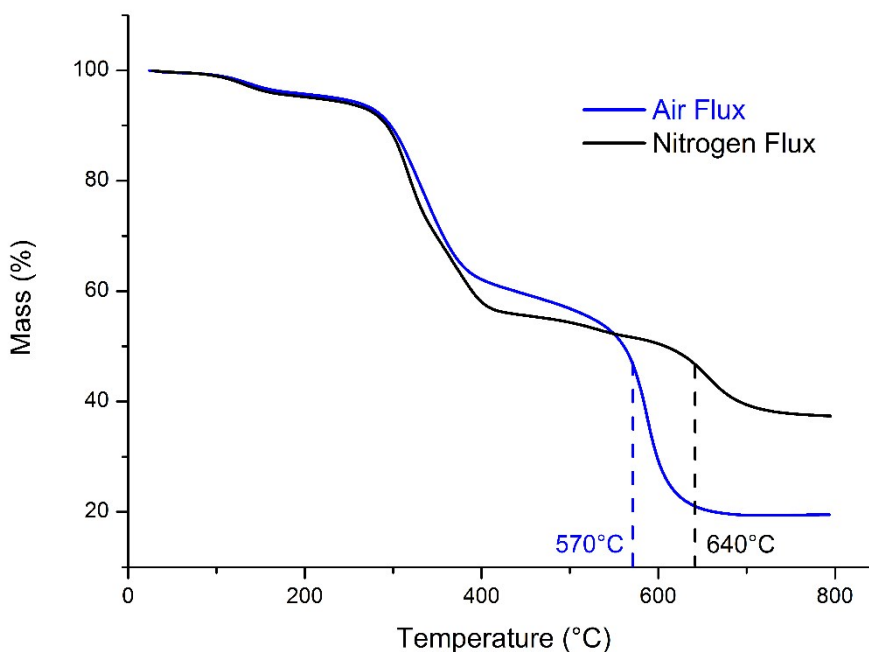


Fig. S7. Thermogravimetric analysis curves of **TBS-prePBO** under air and nitrogen atmosphere.

TGA curves showed a loss of mass from 300 °C to 400 °C that corresponds to the loss of the solubilizing tert-butyldimethylsilyl groups and the water during the cyclisation step to obtain the **PBO** polymer. Then, this last compound was decomposed from 640 °C under nitrogen flux which was in accordance to the literature¹ but was easier decomposed under air at 570 °C.

To use the minimum of energy in the processing steps and not to deteriorate the **PBO**, the films realized with the **TBS-prePBO** will be heated at 400 °C in a furnace under air atmosphere (Fig. S8). Indeed, IR curves (not shown here) showed that the **TBS-prePBO** heated at 500 °C for one hour was decomposed in the presence of the air.

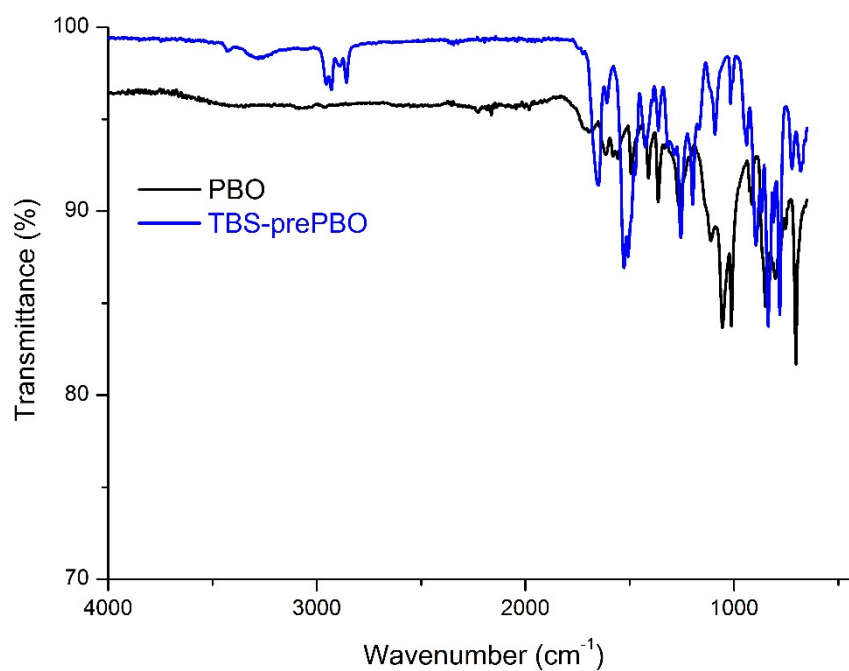


Fig. S8. IR spectra of **TBS-prePBO** and **PBO** films (the latter obtained after a thermal treatment of the **TBS-prePBO** film at 400°C for 1h).

The film obtained after a thermal treatment of the **TBS-prePBO** film at 400°C for 1h presents an IR spectrum analogous to the one described by Fukumaru *et al*, which was assigned to the **PBO** polymer.¹

1. T. Fukumaru, T. Fujigaya and N. Nakashima, *Macromolecules*, 2012, **45**, 4247-4253.