

Supporting Information for

Responsive Periodic Mesoporous Polydiacetylene/Silica Nanocomposites

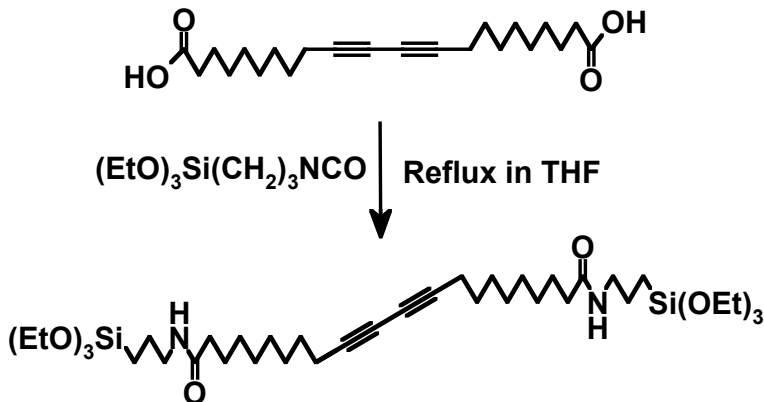
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1. Synthesis and Characterization of the bridged silsesquioxane

Synthesis of diacetylene-bridged silsesquioxane¹: 10, 12-docosadiyndioic acid was filtered using membranes with a pore diameter of 20 nm to remove any PDA present prior to use. Purified monomer (1 g, 2.8 mmol) was then dissolved in THF (20 mL, anhydrous) under a nitrogen atmosphere. *n*-isocyanatopropyltriethoxysilane (1.385 g, 5.6 mmol) was slowly added at room temperature followed by 24 h reflux. After cooling to room temperature, evaporation of solution produced a colorless viscous liquid. The overall yield was more than 89% with high purity, confirmed by NMR (GE Omega PSG500 500 MHz) and IR (Thermo Nicolet NexusTM 670 Fourier transform infrared) spectroscopic analysis.



Scheme 1. Synthesis of the precursor

Characterization: FTIR (CHCl₃): $\bar{\nu}$ =1568 ($\bar{\nu}_{\text{NH}}$), 1644 ($\bar{\nu}_{\text{CO}}$), 3440 cm⁻¹ ($\bar{\nu}_{\text{NH}}$); ¹H NMR (500 MHz, CDCl₃, TMS): δ =0.59 (t, 4 H; CH₂Si), 1.19 (t, 9 H; CH₃), 1.57 (qt, 4 H; CH₂), 3.11 (m, 4 H; NCH₂), 3.70 (qd, 12 H; OCH₂), 5.10 (m, 2 H; NH); ¹³C NMR (500 MHz, CDCl₃): δ =7.9 (CH₂Si), 18.5 (CH₃), 23.0 (CH₂), 42.0 (CH₂N), 58.5 (CH₂O), 77.2 (C=C), 155.0 ppm (CO).

2. Synthesis and Characterization of PDA-PMO

Synthesis: PDA/silica nanocomposites films were prepared under acid condition. Replicating a typical synthesis of mesoporous nanocomposite films, the diacetylene-bridged silsesquioxane (320 mg) was dissolved in THF (4 mL) followed by addition of 14.6mg CTAB (in 0.1 mL 0.1N HCl). The films were then prepared by coating the precursor solutions on glass slides, followed by evaporation of the solvents. Successive surfactant removal was conducted by refluxing the colorless solid in methanol and concentrated HCl (~0.1g solid in 2 g 36% HCl and 14 g methanol). Polymerization was achieved upon exposure to ultraviolet light (254 nm) from several minutes to an hour, giving a blue color nanocomposite.

Characterization: XRD was performed on a Phillips Xpert X-ray diffractometer (Cu K α radiation at λ =0.1542 nm). Optical absorption was measured using a BeckmanTM DU 640B Ultraviolet-visible (UV-vis) spectrophotometer. Chromatic response (CR) was calculated using $[B_0-B]/B_0$, where $B_0 = A_{\text{blue}}/[A_{\text{blue}}+A_{\text{red}}]$, A is the absorbance maximum of the blue or the red form, ^[16] and $B_{(0)} = A_{652}/[A_{652}+A_{554}]$ in this system. TEM images were taken using a JEOL 2010 microscope operated at 200 kV. N₂ adsorption-desorption isotherms were measured at 77 K on a micromeritics ASAP 2010 analyzer. Thermal analysis was conducted on both a Thermogravimetric Analyzer (TGA) 2950 by TA instruments run at 15 °C/min from 25 to 1000°C with argon sweep gas and a differential scanning calorimeter (DSC) by TA instruments run at 15 °C/min from 25 to 700°C.

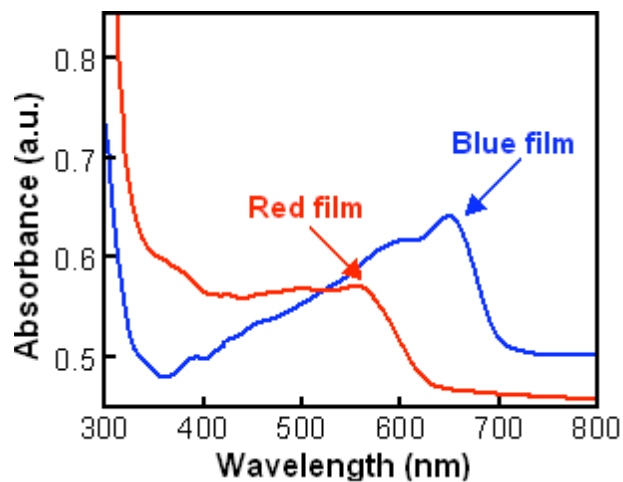
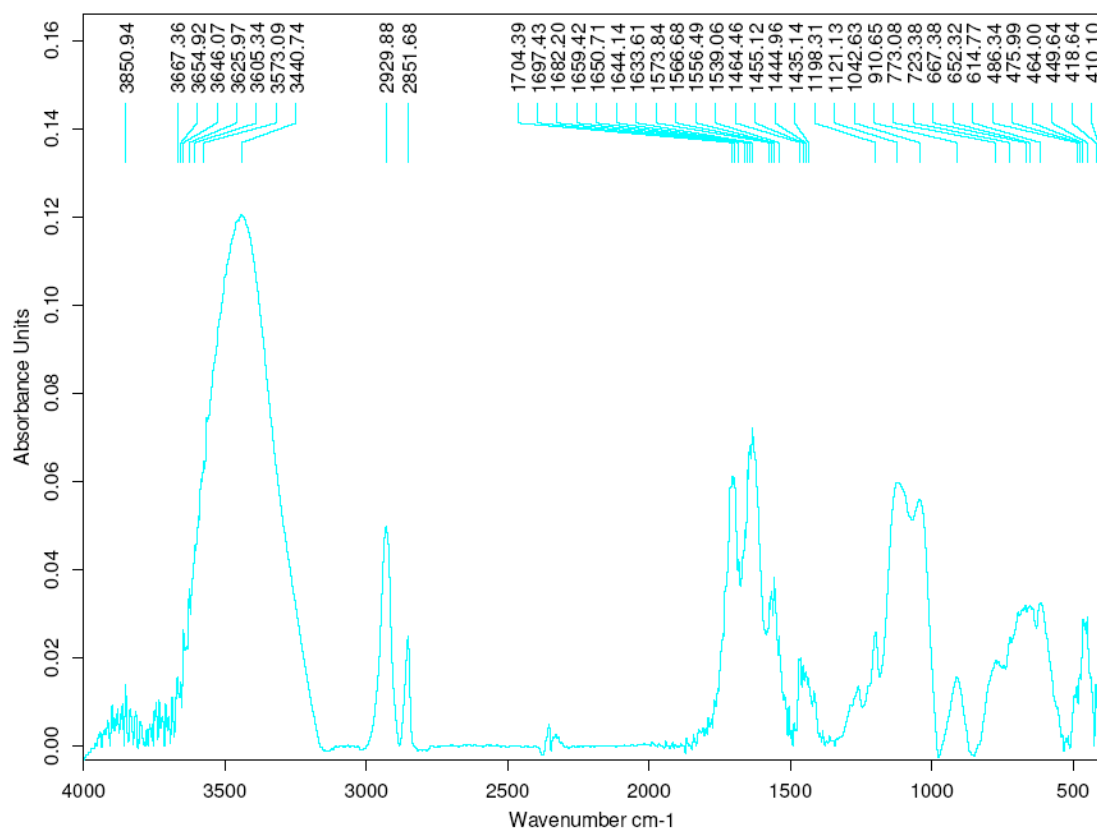


Figure 1. Typical UV-vis spectra of the blue and red PDA-PMO at 25°C and 103°C, respectively.

3. Stability of Si-C bonds

The existence of Si-C is confirmed by its characteristic FTIR peak at 773 nm,^{1,2} shown as the attached figure. (see Wrobel M.; Walkiewicz-Pietrzykowska, A. *Chem. Mater.* **2003**, **15**, 1749 –1756; as we as Socrates, G. *Infrared Characteristic Group Frequencies* (the second edition), Page 188-189.)



References

1. Kraus, A.; Schneider, M.; Gugel, A.; Mullen, K. *J. Mater. Chem.* **1997**, **7**, 763-765.

Reference 3a

Lu, Y. F.; Yang, Y.; Sellinger, A.; Lu, M.; Huang, J.; Fan, H.; Haddad, R.; Lopez, G.; Burns, A. R.; Sasaki, D. Y.; Shelnutt, J.; Brinker, C. J. *Nature* **2001**, 410, 913-917.