

A low dielectric constant material synergized by calix[4]arene and benzocyclobutene units

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Synthesis of (Benzocyclobutene-4-yl) dimethylsilane (BCB-SiH)

The **BCB-SiH** was synthesized according to the literature.¹ Into a three-necked flask (250 mL) equipped with a magnetic stirring bar, magnesium filings (1.28 g, 53 mmol) and two drops of 1,2-dibromoethane were first added at room temperature under nitrogen atmosphere. A mixture of BCB-Br (8.00 g, 44 mmol) and anhydrous THF (40.0 mL) was added into a pressure equalizing funnel, and a small part of the solution was added into the flask. Then, the temperature was increased to 70 °C and the reaction was triggered. The remaining BCB-Br solution was dropwise added into the flask. After the addition, keep the temperature at 70 °C and reacted for another 1 h. The color of mixture was changed to brown, and the magnesium filings was gradually dissolved. Subsequently, the reaction mixture was cooled to room temperature and a mixture of chlorodimethylsilane (4.17 g, 44 mmol) and anhydrous THF (20.0 mL) was slowly added. The mixture was further reacted at 70 °C for another 2 h and quenched with diluted hydrochloric acid (1.0 M). The organic phase was extracted using petroleum ether and concentrated under vacuum. The crude product was subjected to a flash column chromatography on silica gel with petroleum ether as eluent to afford 5.4 g product as a colorless liquid.

BCB-SiH, Yield: 76%. ¹H NMR (400 MHz, CDCl₃, ppm): δ = 7.39 (d, 1H, Ar-**H**), 7.24 (s, 1H, Ar-**H**), 7.07 (d, 1H, Ar-**H**), 4.39-4.41 (m, 1H, Si-**H**), 3.16 (s, 4H, -**CH**₂-), 0.31 (d, 6H, -**CH**₃).

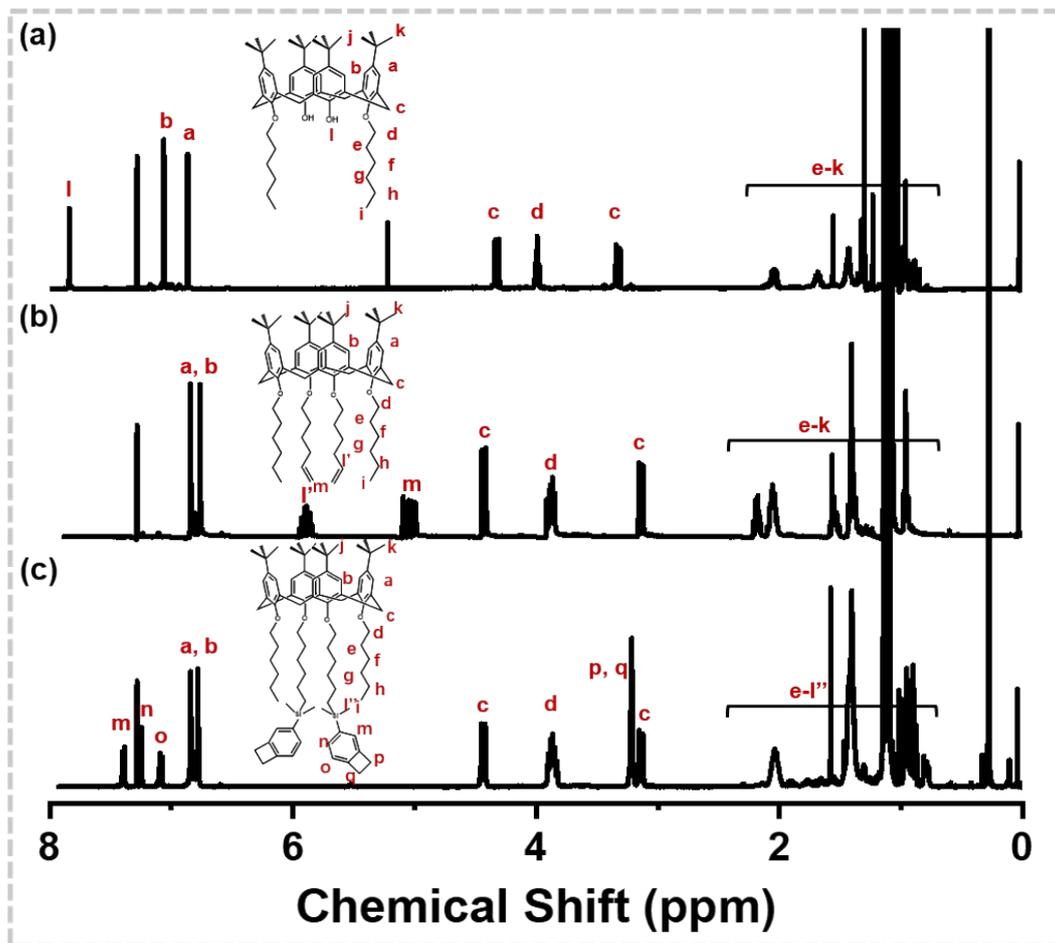


Fig. S1 ^1H NMR spectra for (a) CADH-OH, (b) CADH-ene, and (c) CADHBCB.

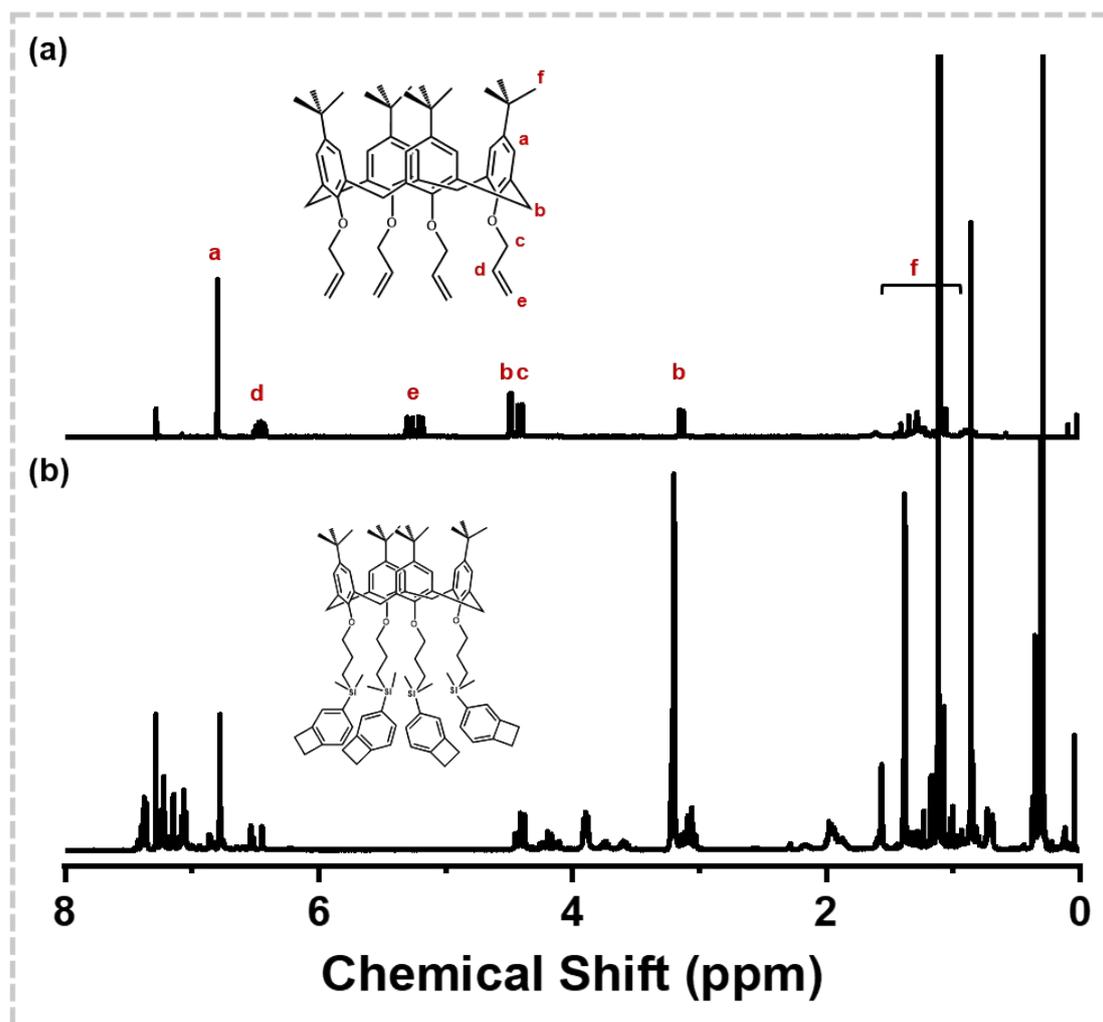


Fig. S2 ¹H NMR spectra for (a) CADH-ene and (b) CATPBCB.

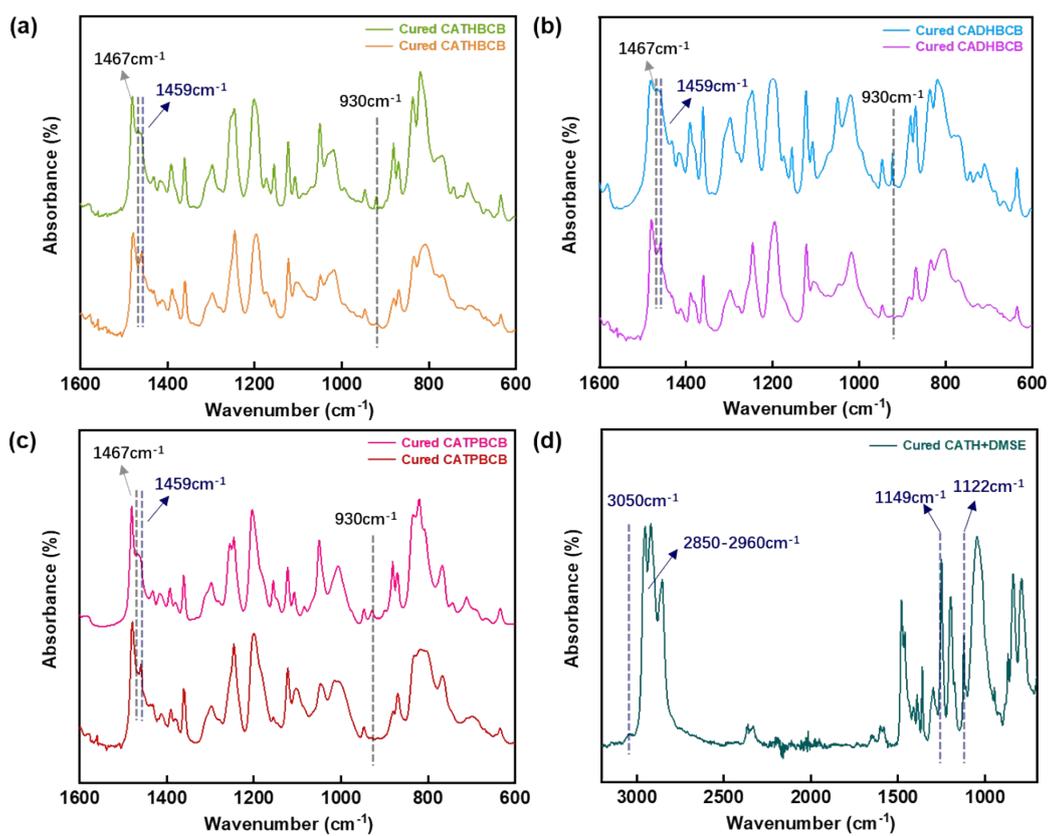


Fig. S3 FT-IR spectra for (a) CATHBCB and cured CATHBCB, (b) CADHBCB and cured CADHBCB, (c) CATPBCB and cured CATPBCB, (d) cured CATH+DMSE.

References

- (1) D. L. Zhou, J. H. Li, Q. Y. Guo, X. Lin, Q. Zhang, F. Chen, D. Han and Q. Fu, *Adv. Funct. Mater.*, 2021, **31**, 2102074.