## SUPPORTING INFORMATION

## Hierarchically Structured Biphenylene-Bridged

## Periodic Mesoporous Organosilica

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**Figure S1.** Plan-view TEM micrograph of the CTAB-columnar-lamellar Bp-PMO sample, demonstrating the significant shrinkage of the structure due to the existence of a lamellar phase.



**Figure S2.** A) 2D-SAXS pattern of an as-prepared F127-circular Bp-PMO sample and B) planview TEM micrograph showing the preservation of highly-ordered circular structure and minor shrinkage of the structure of a calcined sample F127-circular-250 Bp-PMO.



**Figure S3.** DFT pore-size distribution from the adsorption branch (•) and the desorption branch (•) of the sample F127-circular-250 Bp-PMO



**Figure S4.** TEM micrographs of a F127-cubic-200 Bp-PMO. A) Plan-view along the [111] direction and B) Plan-view along the [110] direction.



**Figure S5.** A) 13C-MAS NMR and B) 29Si NMR spectra of the calcined F127-cubic-250 Bp-PMO.