Supplementary material (ESI) for Journal of Materials Chemistry

Supporting Information

Systematic Extension of the Length of the Organic Conjugated π-System of Mesoporous Silica-based Organic-Inorganic Hybrid Materials

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Characterisation of the new organosilane precursors:

Characterisation of the organosilane precursor 4,4´-bis-((*E*)-2-(triethoxysilyl)vinyl)stilbene (BTEVS)

^{1}H NMR:

^{1}H NMR ($CDCl_3$, 200 MHz): δ 1.28 (*t*, 18 H, J = 7.0 Hz), 3.89 (*q*, 12 H, J = 7.0 Hz), 6.19 (*d*, 2 H, J = 19.3 Hz), 7.1 (*s*, 2 H), 7.22 (*d*, 2 H, J = 19.3 Hz), 7.48 (*s*, 8 H);

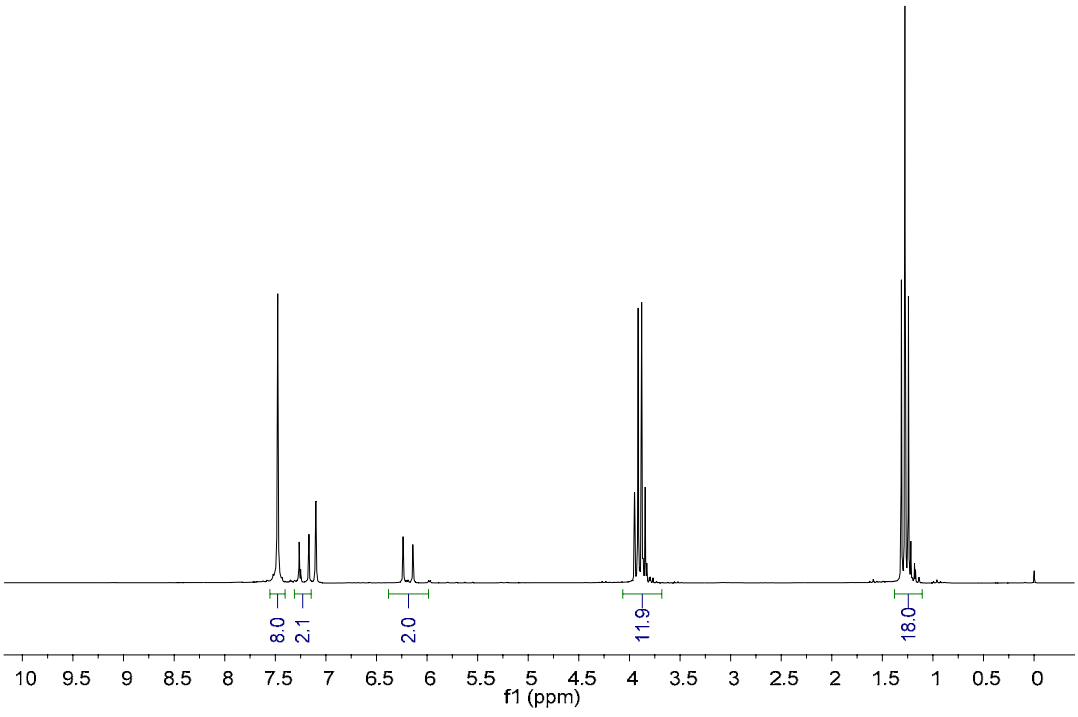

Figure S1. ^{1}H NMR spectrum of 4,4´-bis-((*E*)-2-(triethoxysilyl)vinyl)stilbene measured in $CDCl_3$.

^{13}C {^{1}H} NMR:

^{13}C {^{1}H} NMR ($CDCl_3$, 100 MHz): δ 18.4 (CH_3-CH_2), 58.7 (CH_3-CH_2), 117.7 (*C*H-Si), 126.8 ($C_{arom.}H$), 127.2 ($C_{arom.}H$), 128.6 (*C*H-$C_{arom.}$), 137.0 ($C_{arom.}$), 137.7 ($C_{arom.}$), 148.6 (*C*H-$C_{arom.}$);

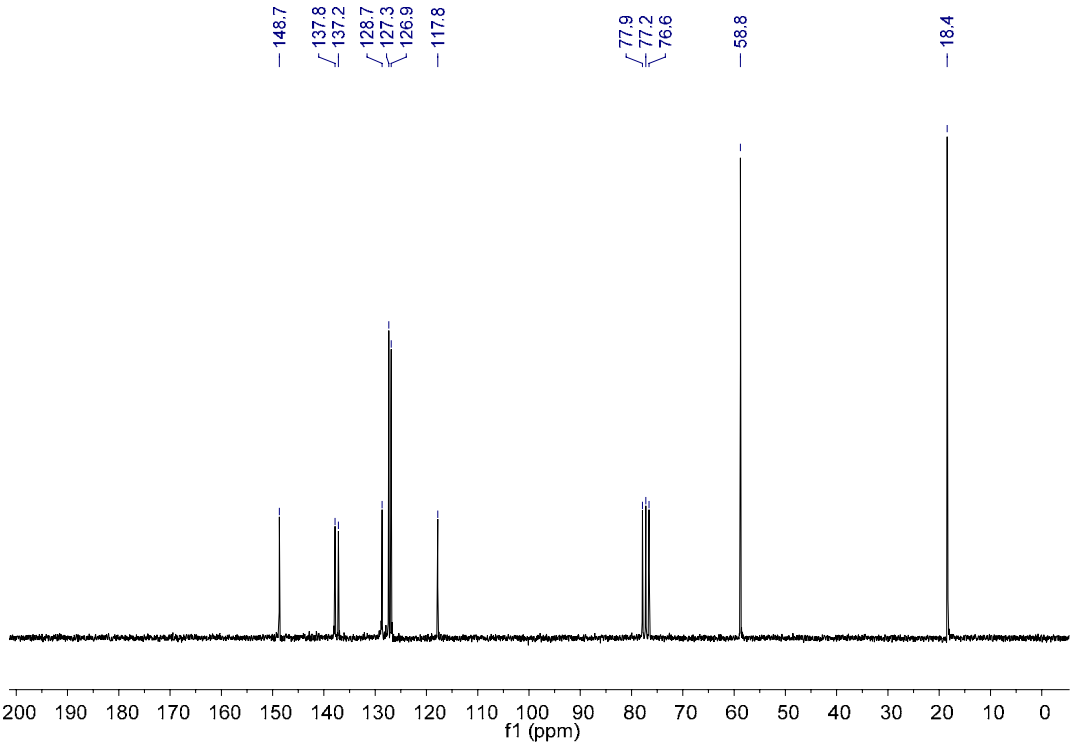

Figure S2. ^{13}C {^{1}H} NMR spectrum of 4,4′-bis-((*E*)-2-(triethoxysilyl)vinyl)stilbene measured in $CDCl_3$.

FT-IR:

FT-IR (film, cm^{-1}): 2975, 2926, 2887, 1602, 1513, 1390, 1166, 1102, 1079, 962, 827, 802

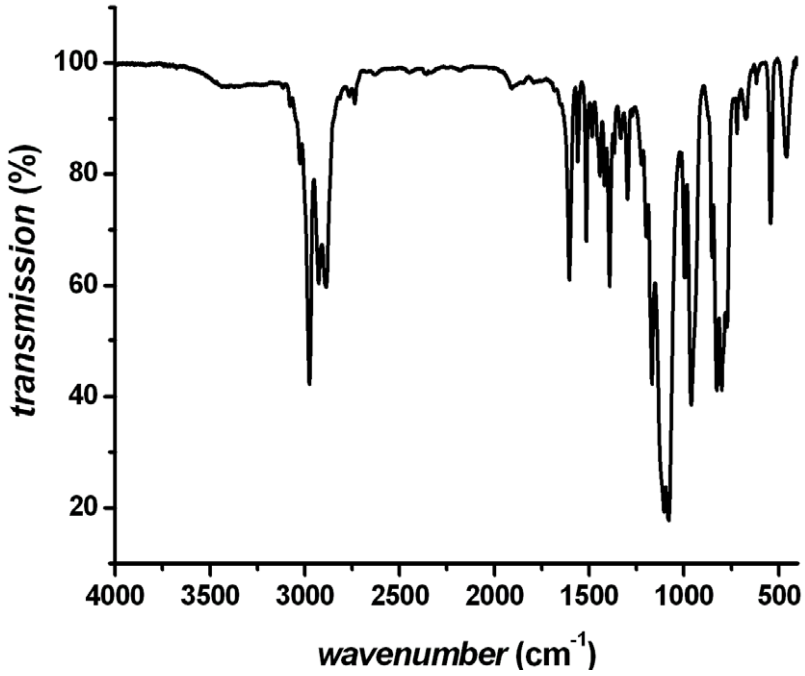

Figure S3. FT-IR spectrum of 4,4′-bis-((*E*)-2-(triethoxysilyl)vinyl)stilbene measured as film.

Characterisation of the organosilane precursor 4,4´-bis-((*E*)-2-(triethoxysilyl)vinyl)diazene (BTEVAB)

^{1}H-NMR:

^{1}H-NMR ($CDCl_3$, 200 MHz) δ (ppm) = 1,16 (*t*, 18 H, *J* = 7,0 Hz, CH2-C**H**$_3$); 3,79 (*q*, 12 H, *J* = 7,0 Hz, O-C**H**$_2$); 6,18 (*d*, 2 H, *J* = 19,3 Hz, CH=C**H**-Si); 7,16 (*d*, 2 H, *J* = 19,3 Hz, C**H**=CH-Si); 7,48 (*m*, 4 H, CH=CH-$C_{arom.}$-$C_{arom.}$-**H)**; 7,79 (*m*, 4 H, N=N-$C_{arom.}$-$C_{arom.}$-**H)**

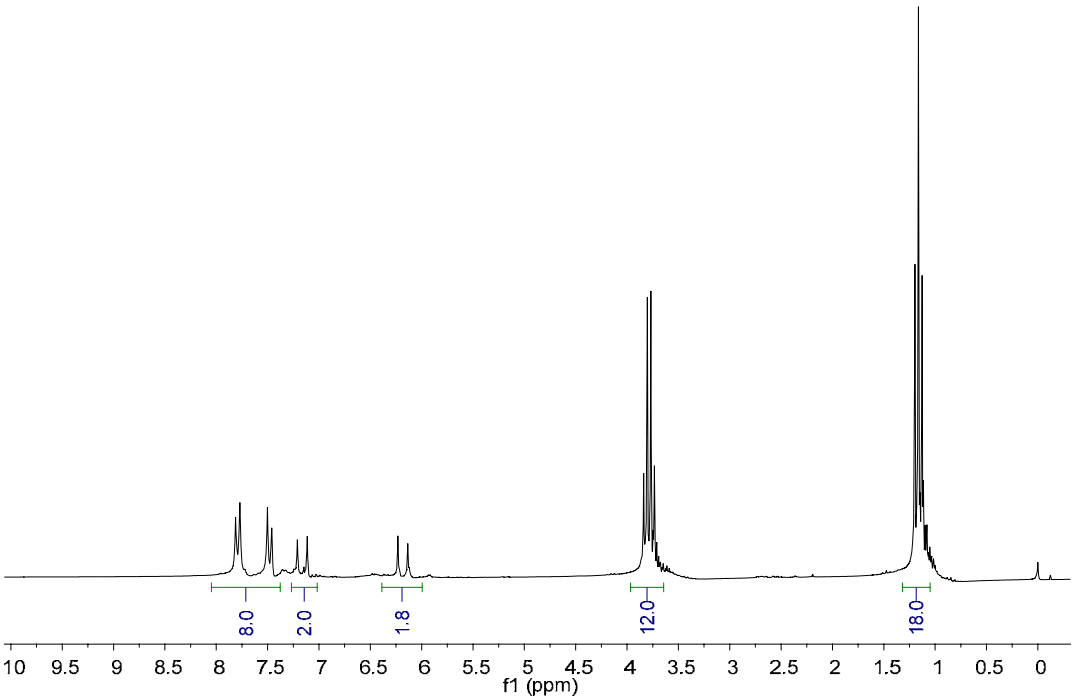

Figure S4. ^{1}H NMR spectrum of 4,4´-bis-((*E*)-2-(triethoxysilyl)vinyl)diazene measured in $CDCl_3$.

^{13}C $\{^{1}H\}$-NMR:

^{13}C $\{^{1}H\}$-NMR ($CDCl_3$, 50 MHz) δ(ppm) = 17,9 (CH_2-**C**H_3); 58,2 (O-**C**H_2); 119,8 (Si-**C**H); 123,2 (**C**H=CH-Si); 127,2 (N=N-$C_{arom.}$-**C**$_{arom.}$-H); 139,7 (CH=CH-$C_{arom.}$-**C**$_{arom.}$-H); 147,8 (**C**$_{arom.}$-CH=CH); 152,2 (**C**$_{arom.}$-N=N)

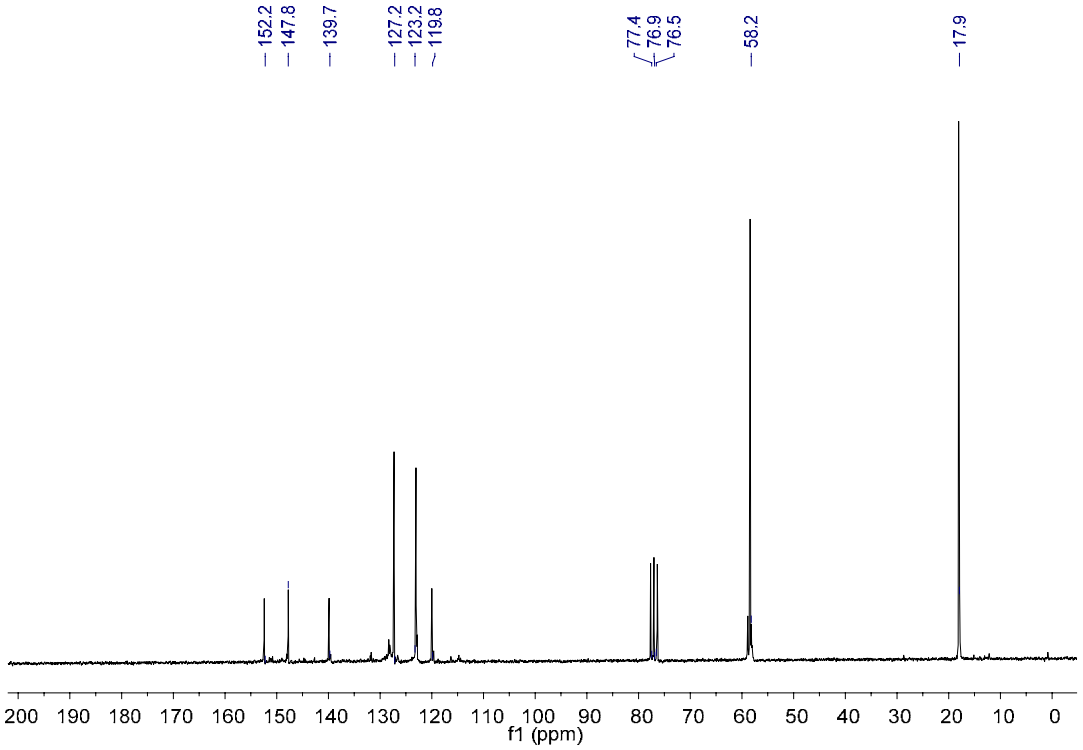

Figure S5. ^{13}C $\{^{1}H\}$ NMR spectrum of 4,4´-bis-((*E*)-2-(triethoxysilyl)vinyl)diazene measured in $CDCl_3$.

FT-IR:

FT-IR (Film, cm^{-1}): 2973, 2925, 2886, 1600, 1390, 1166, 1101, 1078, 959, 805

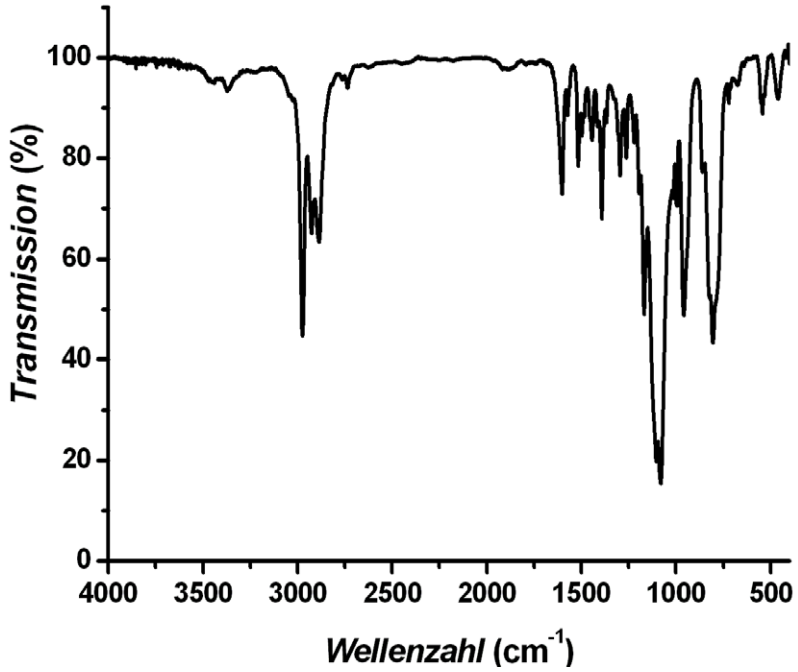

Figure S6. FT-IR spectrum of 4,4′-bis-((*E*)-2-(triethoxysilyl)vinyl)diazene measured as film.

Characterisation of the mesoporous hybrid materials

Ethene-bridged hybrid material (1):

The powder X-ray diffraction pattern of the mesoporous ethene-bridged hybrid material reveals only one reflection at 2.05 ° 2θ (d = 4.31 nm), indicating a periodic arrangement of the mesopores. The lack of further reflections in the wide-angle region indicates no crystal-like arrangement of the organic spacers within the pore walls.

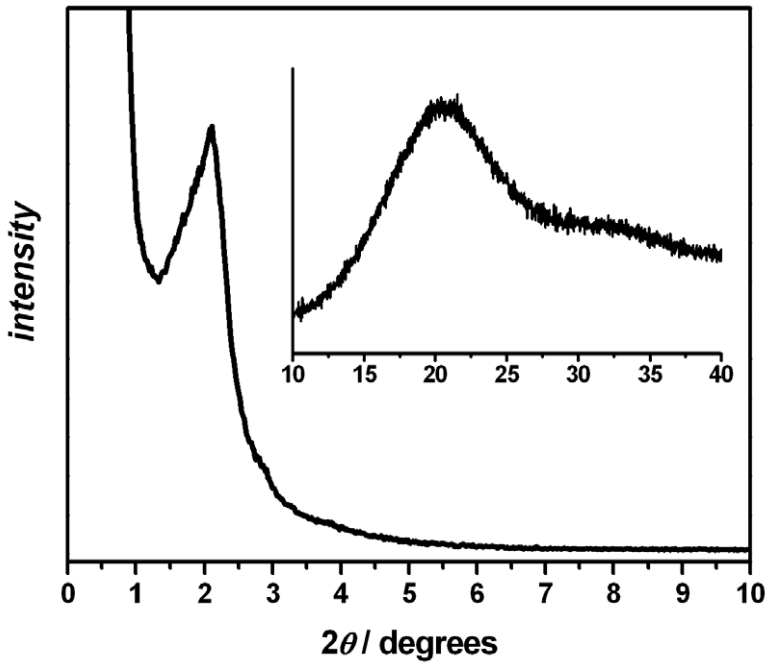

Figure S7. Powder X-ray diffraction pattern of the mesoporous ethene-bridged hybrid material.

Benzene-bridged hybrid material (2):

The powder X-ray diffraction pattern of the mesoporous benzene-bridged hybrid material reveals at least one sharp reflection at 2.02 ° 2θ (d = 4.37 nm), indicating a periodic arrangement of the mesopores. In addition three peaks at 2θ = 11.59 ° (d = 0.76 nm), 23.26 ° (0.38 nm), 35.39 ° (0.25 nm), which can be attributed to a crystal-like arrangement of the organic spacers within the pore walls.

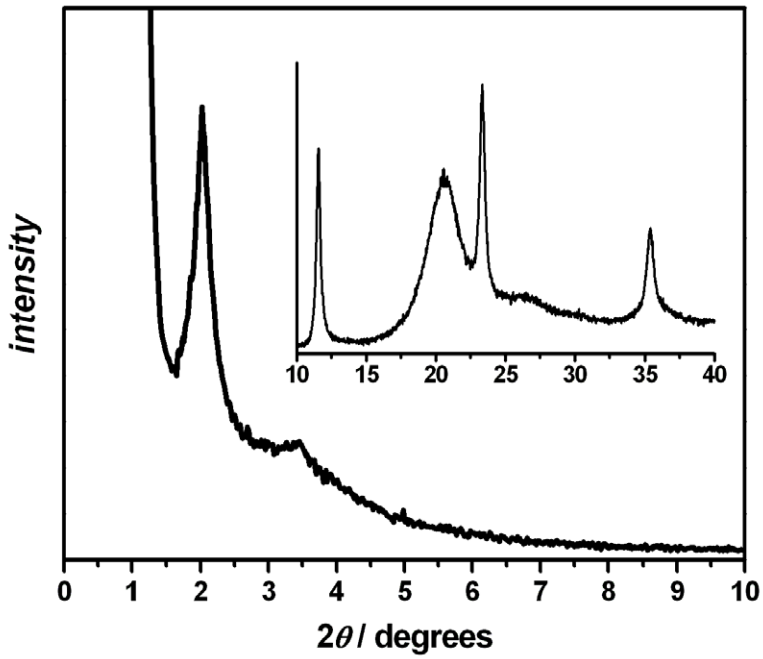

Figure S8. Powder X-ray diffraction pattern of the mesoporous benzene-bridged hybrid material.

The nitrogen physisorption measurement shows a type IV isotherm with a capillary condensation step at p/p^0 = 0.3. The mean pore diameter and the pore volume, as determined from the desorption branch by the BJH method, are 2.7 nm and 0.56 x 10^{-6} m^3/g, respectively. The specific surface area determined by the BET method is 760 m^2/g.

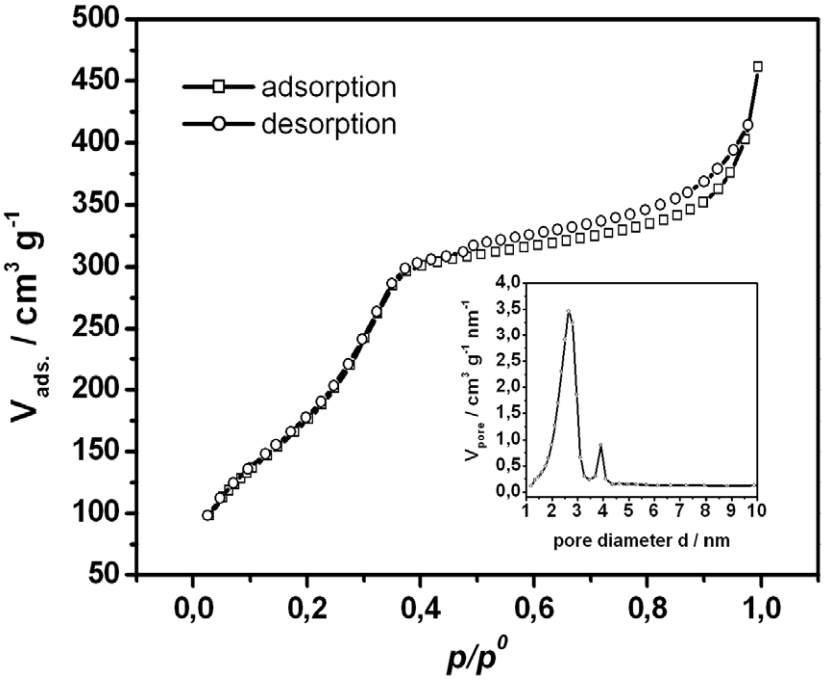

Figure S9. N_2-physisorption measurement of the mesoporous benzene-bridged PMO material measured at 77 K.

1,4-divinylbenzene-bridged hybrid material (3):

The powder X-ray diffraction pattern of the mesoporous 1,4-divinylbenzene-bridged hybrid material reveals one sharp reflection at 1.87 ° 2θ (d = 4.72 nm), indicating a periodic arrangement of the mesopores. In addition five peaks at 2θ = 7.42 ° (d = 1.19 nm), 14.78 ° (0.60 nm), 22.17 ° (0.40 nm), 29.82 ° (0.30 nm), 37.42 ° (0.24 nm) which can be attributed to a crystal-like arrangement of the organic spacers within the pore walls.

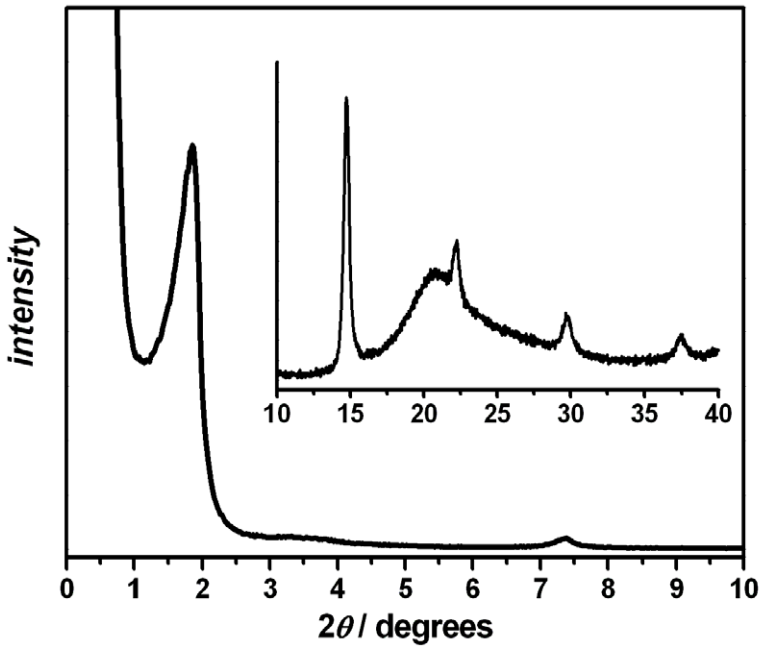

Figure S10. Powder X-ray diffraction pattern of the mesoporous 1,4-divinylbenzene-bridged hybrid material.

The nitrogen physisorption measurement shows a type IV isotherm with a capillary condensation step at p/p^0 = 0.35. The mean pore diameter and the pore volume, as determined from the desorption branch by the BJH method, are 2.8 nm and 0.62 x 10^{-6} m^3/g, respectively. The specific surface area determined by the BET method is 794 m^2/g.

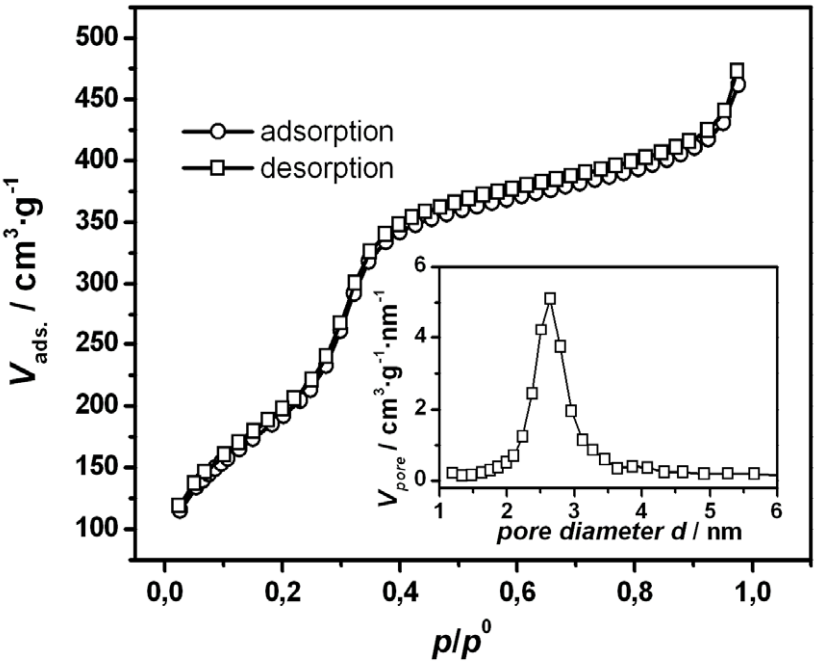

Figure S11. N_2-physisorption measurement of the mesoporous 1,4-divinylbenzene-bridged PMO material measured at 77 K.

^{29}Si MAS NMR

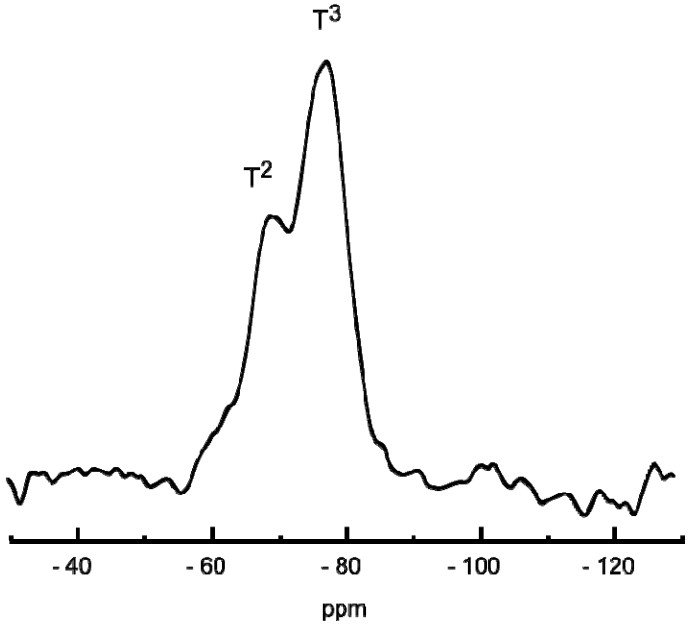

Figure S12. ^{29}Si MAS NMR spectrum of the mesoporous 4,4´-divinylstilbene-bridged hybrid material.

Transmisson electron microscopy:

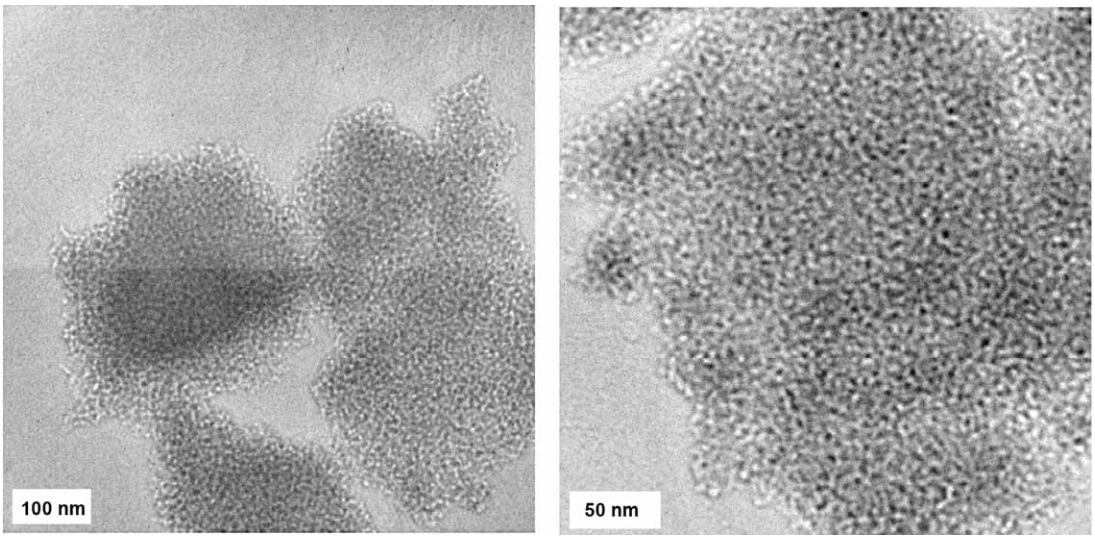

Figure S13. TEM images of the mesoporous 4,4´-divinylstilbene-bridged hybrid material.

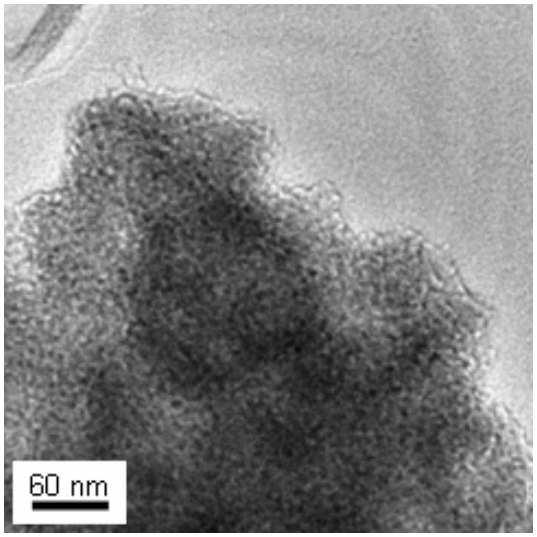

Figure S14. TEM image of the mesoporous 4,4´-divinylazobenzene-bridged hybrid material