# Supporting Information

# Highly Ordered AIEgens Directed Silica Hybrid Mesostructures and Their Light-Emitting Behaviours

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## Experimental Section

### Synthetic route of $MTPE_4$-Br and $MTPE_{4-4}$.

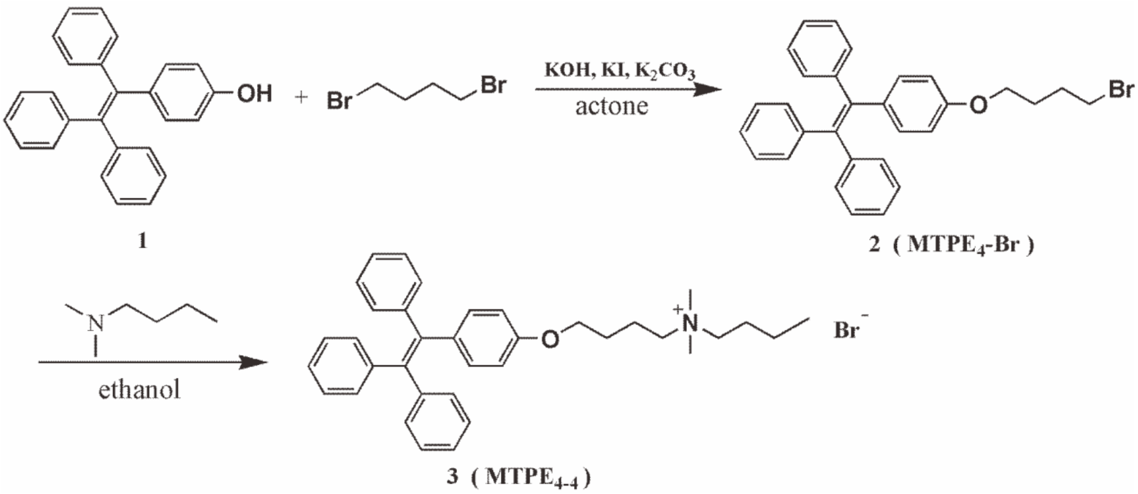

**Figure S1**. Synthetic route of $MTPE_4$-Br and $MTPE_{4-4}$.

$^1$H-NMR spectra of $MTPE_4$-Br after dissolution in $CDCl_3$.$^1$H NMR (500 MHz, Chloroform-*d*) δ 7.19 – 6.99 (m, 15H), 6.97 – 6.89 (m, 2H), 6.68 – 6.59 (m, 2H), 3.92 (t, *J* = 6.1 Hz, 2H), 3.48 (t, *J* = 6.7 Hz, 2H), 2.10 – 1.99 (m, 2H), 1.96 – 1.81 (m, 2H). $^{13}$C NMR (126 MHz, Chloroform-*d*): δ 157.41, 144.07, 144.00, 140.53, 140.13, 136.22, 132.59, 131.42, 131.39, 131.37, 127.76, 127.64, 126.39, 126.27, 113.57, 66.63, 33.55, 29.52, 27.94. HRMS (m/z): [M+H]$^+$ calcd. For $C_{30}H_{28}OBr$, 483.12453; found, 483.13402.

$^1$H-NMR spectra of MTPE$_5$-Br after dissolution in $CDCl_3$.$^1$H NMR (500 MHz, Chloroform-*d*) δ 7.17 – 6.98 (m, 15H), 6.97 – 6.88 (m, 2H), 6.66 – 6.57 (m, 2H), 3.90 (t, *J* = 6.4 Hz, 2H), 3.43 (t, *J* = 6.8 Hz, 2H), 1.98 – 1.88(m, 2H), 1.84 – 1.73 (m, 2H), 1.64 - 1.56 (m, 2H). $^{13}$C NMR (126 MHz, Chloroform-*d*): δ 157.58, 144.14, 144.07, 140.62, 140.13, 136.13, 132.63, 131.48, 131.45, 131.42, 127.81, 127.69, 126.44, 126.33, 113.64, 67.41, 33.69, 32.58, 28.54, 24.94. HRMS (m/z): [M+H]$^+$ calcd. For $C_{31}H_{30}OBr$, 497.14018; found, 497.14978.

$^1$H-NMR spectra of MTPE$_6$-Br after dissolution in $CDCl_3$. $^1$H NMR (500 MHz, Chloroform-*d*) δ 7.17 – 6.98 (m, 15H), 6.96 – 6.89 (m, 2H), 6.68 – 6.59 (m, 2H), 3.89 (t, *J* = 6.4 Hz, 2H), 3.43 (t, *J* = 6.8 Hz, 2H), 1.93 – 1.85 (m, 2H), 1.81 – 1.72 (m, 2H), 1.58 – 1.43 (m, 4H). $^{13}$C NMR (126 MHz, Chloroform-*d*): δ 157.65, 144.13, 144.07, 140.63, 140.08, 136.05, 132.60, 131.44, 131.41, 127.79, 127.66, 126.42, 126.29, 113.63, 67.55, 33.86, 32.74, 29.19, 28.01, 25.39. HRMS (m/z): [M+H]$^+$ calcd. For $C_{32}H_{32}OBr$, 511.15583; found, 511.16569.

$^1$H-NMR spectra of MTPE$_7$-Br after dissolution in $CDCl_{3.}$$^1$H NMR (400 MHz, Chloroform-*d*) δ 7.18 – 6.98 (m, 15H), 6.96 – 6.89 (m, 2H), 6.68 – 6.59 (m, 2H), 3.88 (t, *J* = 6.4 Hz, 2H), 3.41 (t, *J* = 6.8 Hz, 2H), 1.93 – 1.83 (m, 2H), 1.81 – 1.70 (m, 2H), 1.52 – 1.33 (m, 6H). $^{13}$C NMR (126 MHz, Chloroform-*d*): δ 157.68, 144.13, 144.07, 140.63, 140.05, 135.99, 132.58, 131.46, 131.42, 131.40, 127.77, 127.65, 126.39, 126.27, 113.61, 67.67, 33.97, 32.76, 29.25, 28.60, 28.13, 25.98. HRMS (m/z): [M+H]$^+$ calcd. For $C_{33}H_{34}OBr$, 525.17148; found, 525.18167.

$^1$H-NMR spectra of MTPE$_8$-Br after dissolution in $CDCl_3$.$^1$H NMR (400 MHz, Chloroform-*d*) δ 7.17 – 7.00 (m, 15H), 6.97 – 6.92 (m, 2H), 6.68 – 6.61 (m, 2H), 3.89 (t, *J* = 6.5 Hz, 2H), 3.43 (t, *J* = 6.9 Hz, 2H), 1.92 – 1.85 (m, 2H), 1.80 – 1.73 (m, 2H), 1.50 – 1.35 (m, 8H). $^{13}$C NMR (126 MHz, Chloroform-*d*): δ 157.87, 144.29, 144.22, 140.82, 140.19, 136.08, 132.75, 131.61, 131.57, 127.95, 127.83, 126.58, 126.45, 113.80, 67.83, 34.14, 32.98, 29.48, 29.43, 28.90, 28.30, 26.21. HRMS (m/z): [M+H]$^+$ calcd. For $C_{34}H_{36}OBr$, 539.18713; found, 539.19486.

$^1$H-NMR spectra of MTPE$_{10}$-Br after dissolution in $CDCl_3$.$^1$H NMR (400 MHz, Chloroform-*d*) δ 7.23 – 7.08 (m, 15H), 7.05 – 6.98 (m, 2H), 6.75 – 6.65 (m, 2H), 3.94 (t, *J* = 6.5 Hz, 2H), 3.47 (t, *J* = 6.8 Hz, 2H), 2.00 – 1.87 (m, 2H), 1.87 – 1.75 (m, 2H), 1.59 – 1.47 (m, 4H), 1.45 – 1.33 (m, 8H). $^{13}$C NMR (126 MHz, Chloroform-*d*): δ 157.72, 144.13, 144.08, 144.07, 140.64, 140.02, 135.93, 132.56, 131.45, 131.42, 131.39, 127.76, 127.64, 126.38, 126.25, 113.61, 67.81, 34.08, 32.87, 29.49, 29.41, 29.35, 28.80, 28.22, 26.10. HRMS (m/z): [M+H]$^+$ calcd. For $C_{36}H_{40}OBr$, 567.21843; found, 567.22913.

$^1$H-NMR spectra of MTPE$_{4\text{-}4}$ after dissolution in DMSO.$^1$H NMR (500 MHz, DMSO-$d_6$) δ 7.20 – 7.05 (m, 9H), 7.01 – 6.92 (m, 6H), 6.89 – 6.84 (m, 2H), 6.74 – 6.66 (m, 2H), 3.94 (t, *J* = 6.0 Hz, 2H), 3.33 – 3.21 (m, 4H), 3.01 (s, 6H), 1.84 – 1.75 (m, 2H), 1.74 – 1.66 (m, 2H), 1.65 – 1.57 (m, 2H), 1.34 – 1.24 (m, 2H), 0.92(t, *J* = 7.3 Hz, 3H). $^{13}$C NMR (126 MHz, DMSO-$d_6$): δ 157.46, 143.99, 143.92, 143.89, 140.64, 140.15, 135.90, 132.40, 131.17, 131.13, 128.36, 128.24, 126.95, 126.88, 126.83, 114.20, 66.95, 63.19, 62.87, 50.49, 26.04, 24.18, 19.68, 19.31, 14.00. HRMS (m/z): [M-Br]$^+$ calcd. For $C_{36}H_{48}ON$, 504.3266; found, 504.3271.

$^1$H-NMR spectra of MTPE$_{5\text{-}4}$ after dissolution in DMSO.$^1$H NMR (500 MHz, DMSO-$d_6$) δ 7.20 – 7.03 (m, 9H), 7.01 – 6.90 (m, 6H), 6.89 – 6.82 (m, 2H), 6.72 – 6.64 (m, 2H), 3.90 (t, *J* = 6.3 Hz, 2H), 3.29 – 3.20 (m, 4H), 2.99 (s, 6H), 1.78 – 1.67 (m, 4H), 1.66 – 1.58 (m, 2H), 1.44 – 1.35 (m, 2H), 1.33 – 1.23 (m, 2H), 0.93 (t, *J* = 7.4 Hz, 3H). $^{13}$C NMR (126 MHz, DMSO-$d_6$): δ 157.60, 143.99, 143.93, 143.90, 140.66, 140.12, 135.77, 132.39, 131.17, 131.13, 128.36, 128.24, 126.94, 126.87, 126.82, 114.15, 67.39, 63.27, 50.42, 28.61, 24.19, 22.98, 21.95, 19.69, 14.00. HRMS (m/z): [M-Br]$^+$ calcd. For $C_{37}H_{44}ON$, 518.3423; found, 518.3432.

$^1$H-NMR spectra of MTPE$_{6\text{-}4}$ after dissolution in DMSO.$^1$H NMR (500 MHz, DMSO-*d*$_6$) δ 7.20 – 7.04 (m, 9H), 7.01 – 6.91 (m, 6H), 6.89 – 6.80 (m, 2H), 6.71 – 6.63 (m, 2H), 3.88 (t, *J* = 6.3 Hz, 2H), 3.28 – 3.17 (m, 4H), 2.98 (s, 6H), 1.77 – 1.58 (m, 6H), 1.50 – 1.39 (m, 2H), 1.37 – 1.23 (m, 4H), 0.93 (t, *J* = 7.3 Hz, 3H). $^{13}$C NMR (126 MHz, DMSO-*d$_6$*): δ 157.65, 144.00, 143.94, 143.91, 140.68, 140.09, 135.71, 132.39, 131.18, 131.14, 128.35, 128.23, 126.93, 126.86, 126.81, 114.13, 67.57, 65.40, 63.31, 63.21, 50.40, 28.93, 26.00, 25.55, 24.21, 22.14, 19.69, 15.66, 14.01. HRMS (m/z): [M-Br]$^+$ calcd. For $C_{38}H_{46}ON$, 532.3579; found, 518.3589.

$^1$H-NMR spectra of MTPE$_{7\text{-}4}$ after dissolution in DMSO.$^1$H NMR (500 MHz, DMSO-*d*$_6$) δ 7.20 – 7.05 (m, 9H), 7.02 – 6.91 (m, 6H), 6.88 – 6.82 (m, 2H), 6.70 – 6.65 (m, 2H), 3.88 (t, *J* = 6.4 Hz, 2H), 3.25 – 3.19 (m, 4H), 2.98 (s, 6H), 1.71 – 1.59 (m, 6H), 1.45 – 1.34 (m, 4H), 1.32 – 1.24 (m, 4H), 0.93 (t, *J* = 7.4 Hz, 3H). $^{13}$C NMR (126 MHz, DMSO-*d$_6$)*: δ 157.66, 144.00, 143.94, 143.91, 140.68, 140.09, 135.69, 132.38, 131.17, 131.14, 128.35, 128.23, 126.93, 126.86, 126.82, 114.13, 67.65, 63.36, 63.20, 50.41, 29.04, 28.67, 26.20, 25.81, 24.19, 22.11, 19.69, 14.00. HRMS (m/z): [M-Br]$^+$ calcd. For $C_{39}H_{48}ON$, 546.3736; found, 546.3748.

$^1$H-NMR spectra of MTPE$_{8\text{-}4}$ after dissolution in DMSO.$^1$H NMR (500 MHz, DMSO-*d*$_6$) δ 7.19 – 7.04 (m, 9H), 7.01 – 6.91 (m, 6H), 6.88 – 6.81 (m, 2H), 6.70 – 6.64 (m, 2H), 3.86 (t, *J* = 6.4 Hz, 2H), 3.26 – 3.18 (m, 4H), 2.98 (s, 6H), 1.71 – 1.55 (m, 6H), 1.44 – 1.21 (m, 10H), 0.93 (t, *J* = 7.3 Hz, 3H). $^{13}$C NMR (126 MHz, DMSO-*d$_6$*): δ 157.68, 144.00, 143.94, 143.92, 140.69, 140.07, 135.66, 132.39, 131.18, 131.15, 128.33, 128.22, 126.92, 126.85, 126.80, 114.13, 67.71, 63.35, 63.16, 50.40, 29.14, 29.03, 28.91, 26.22, 25.91, 24.22, 22.19, 19.69, 14.01. HRMS (m/z): [M-Br]$^+$ calcd. For $C_{40}H_{50}ON$, 560.3892; found, 560.3893.

$^1$H-NMR spectra of MTPE$_{10\text{-}4}$ after dissolution in DMSO.$^1$H NMR (500 MHz, DMSO-*d*$_6$) δ 7.18 – 7.05 (m, 9H), 7.01 – 6.91 (m, 6H), 6.88 – 6.81 (m, 2H), 6.70 – 6.63 (m, 2H), 3.85 (t, *J* = 6.4 Hz, 2H), 3.29 – 3.19 (m, 4H), 3.00 (s, 6H), 1.70 – 1.56 (m, 6H), 1.43 – 1.19 (m, 14H), 0.93 (t, *J* = 7.4 Hz, 3H). $^{13}$C NMR (126 MHz, DMSO-*d$_6$*): δ 157.69, 143.98, 143.92, 140.69, 140.04, 135.63, 132.39, 131.19, 131.15, 128.29, 128.18, 126.91, 126.82, 126.78, 114.10, 67.73, 63.35, 63.15, 50.40, 29.39, 29.28, 29.21, 28.99, 26.28, 26.02, 24.24, 22.24, 19.69, 14.01. HRMS (m/z): [M-Br]$^+$ calcd. For $C_{42}H_{54}ON$, 588.4205; found, 588.4205.

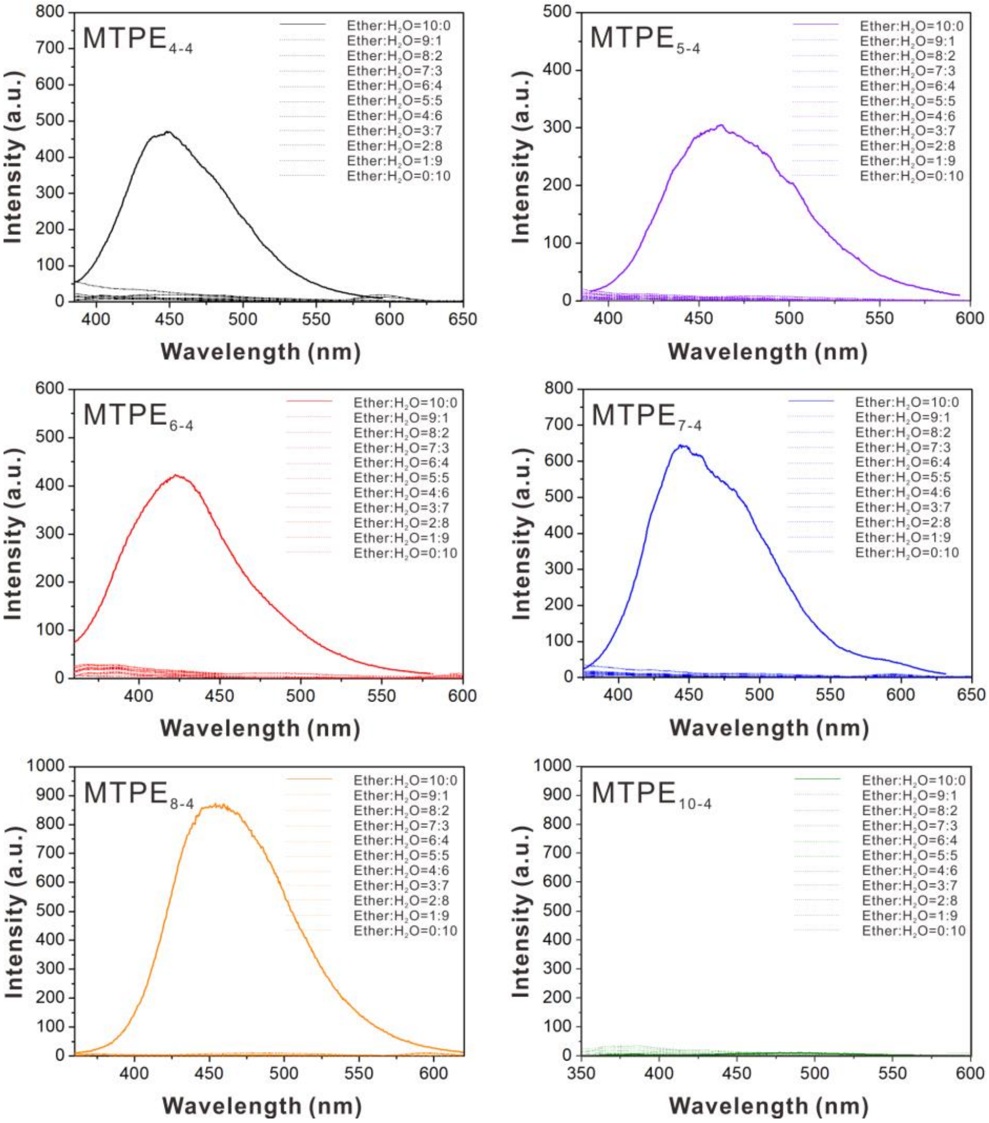

**Figure S2**. Emission spectra of solution of MTPE$_{n-4}$ (10 μM) in water-ether mixtures. MTPE$_{10-4}$ remains non-emissive in pure ether due to the sample adsorb water rapidly in air. Before mixed with pure ether, the MTPE$_{10-4}$ easily absorbed water and turned into a sticky substance. The sample adhered to inner wall of cuvette and cannot be dispersed even by sonication.

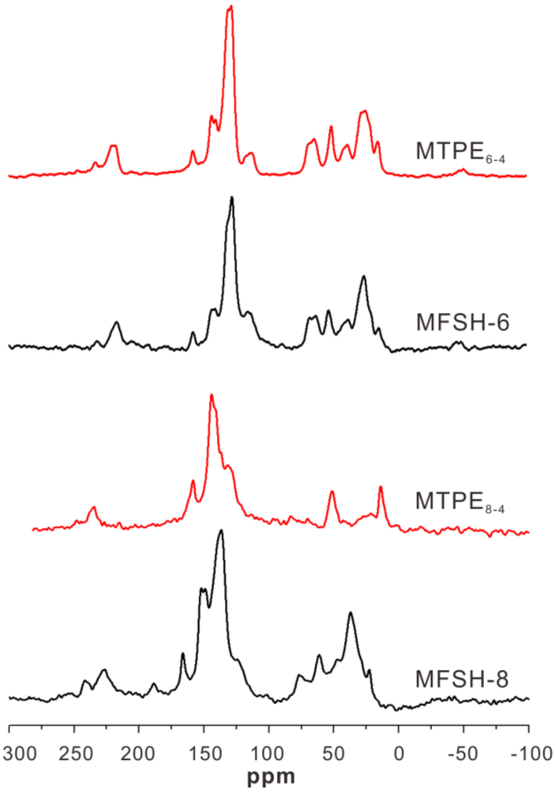

**Figure S3.** The solid $^{13}$C NMR spectra of MTPE$_{n-4}$ and MFSHs.

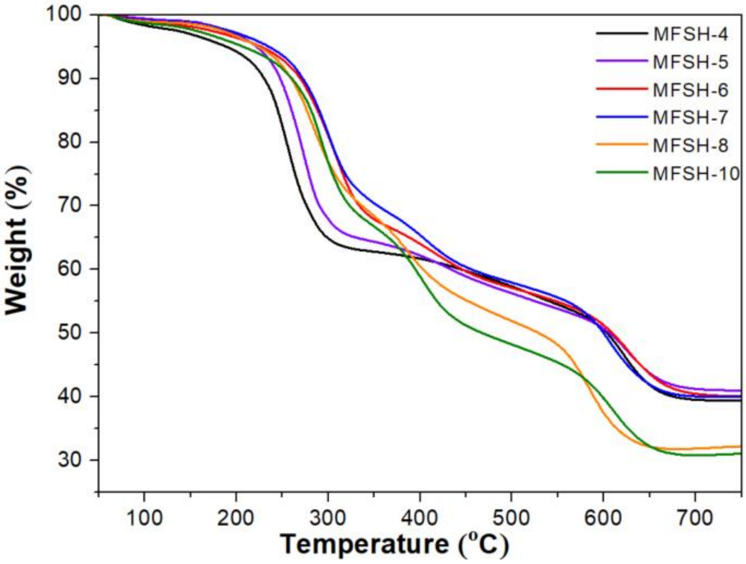

**Figure S4.** TGA curves of MFSHs.

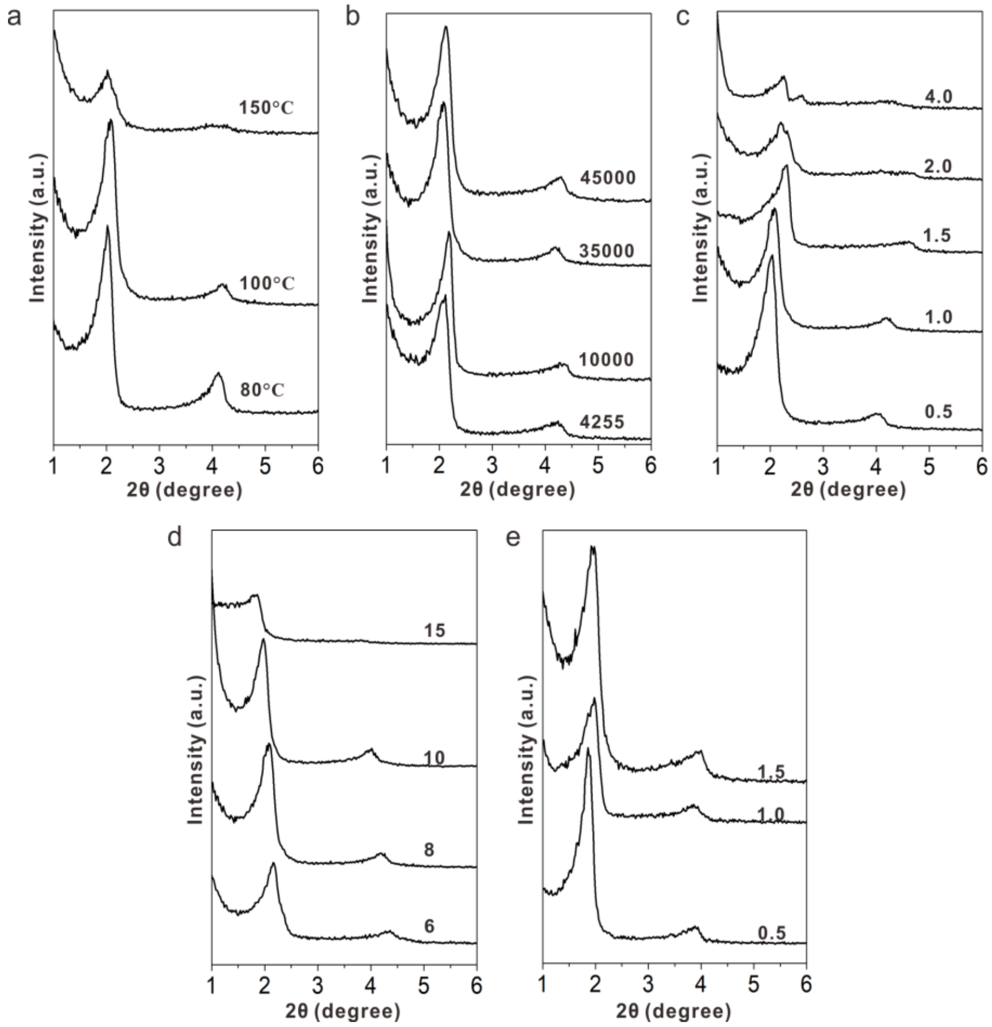

**Figure S5.** XRD patterns of MFSH-7 synthesized with different conditions. XRD patterns of MFSH-7 (a) synthesized with different temperature : 80°C, 100°C and 150°C. The synthesis composition was 1 MTPE$_{7\text{-}4}$ : 1 CES : 8 TEOS : 35000 $H_2O$. (b) synthesized by changing the concentration of reaction system at 100°C. The synthesis composition was 1 MTPE$_{7\text{-}4}$ : 1 CES : 8 TEOS : x $H_2O$, where x = 4255, 10000, 35000 and 45000. (c) synthesized by changing CES addition amount at 100°C. The synthesis composition was 1 MTPE$_{7\text{-}4}$ : x CES : 8 TEOS : 35000 $H_2O$, where x = 0.5, 1.0, 1.5, 2.0 and 4.0. (d) synthesized by changing TEOS addition amount at 100°C. The synthesis composition was 1 MTPE$_{7\text{-}4}$ : 1 CES : x TEOS : 35000 $H_2O$, where x = 6, 8, 10 and 15. (e) synthesized by changing HCl addition amount at 100°C. 1 MTPE$_{7\text{-}4}$ : 1 CES : x HCl : 8 TEOS : 35000 $H_2O$, where x = 0.5, 1.0 and 1.5.

It can be observed that 80-100°C is favourable for the formation of lamellar structured MFSH-7. The reaction concentration (amount of water) has no obvious influence on the structure of hybrids, but if the concentration of surfactant is lower than 0.5 mg/ml, only a small amount of products can be obtained. The amount of CES and TEOS can be adjusted in a broad range. The pH of solution of 7-10 is favourable for the structural formation. MFSH$_{4\text{-}6}$ with lamellar mesostructure were all synthesized with the molar compositions of Template : CES : TEOS = 1 : 1 : 8, the temperature was 100°C.

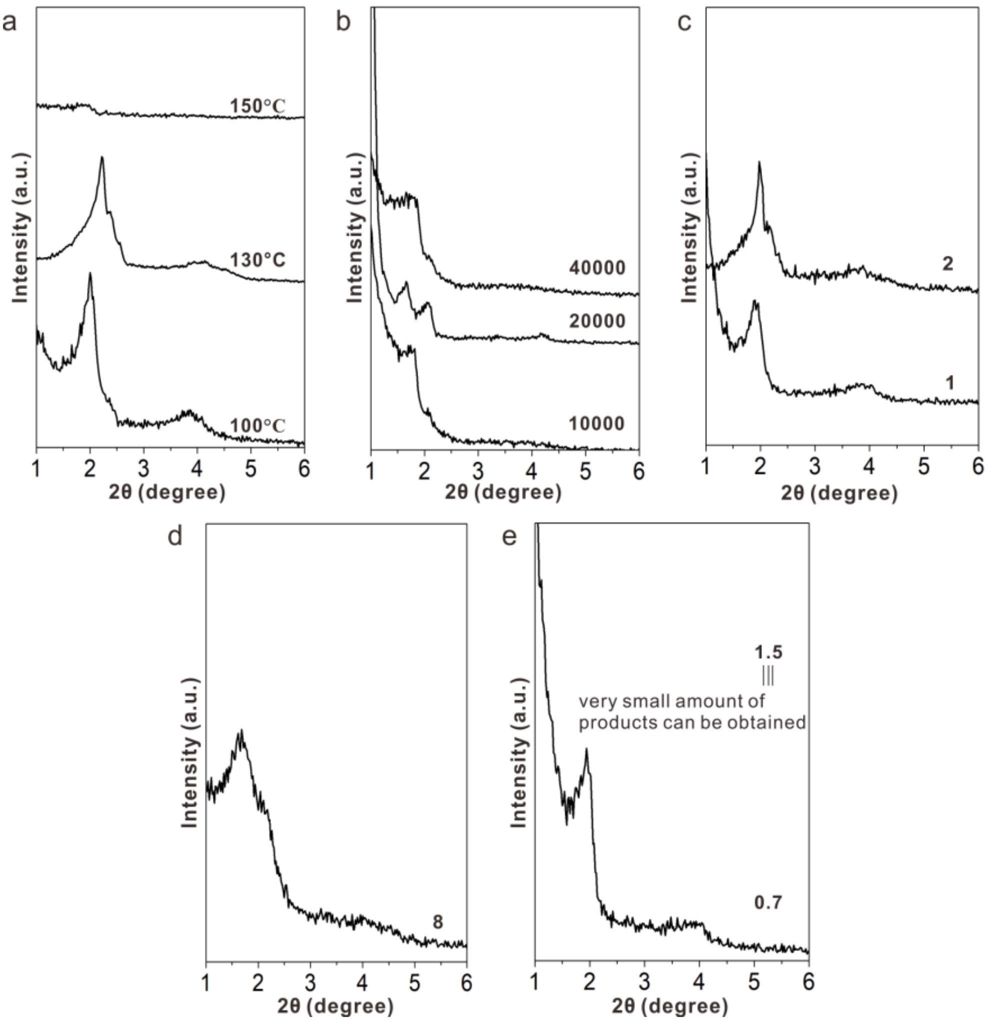

**Figure S6.** XRD patterns of MFSH-8 synthesized with different conditions. XRD patterns of MFSH-8 (a) synthesized with different temperature: 100°C, 130°C and 150°C. The synthesis composition was 1 $MTPE_{8-4}$ : 1.5 CES : 6 TEOS : 35000 $H_2O$. (b) synthesized by changing the concentration of reaction system at 130°C. The synthesis composition was 1 $MTPE_{8-4}$ : 1.5 CES : 6 TEOS : x $H_2O$, where x = 10000, 20000 and 40000. (c) synthesized by changing CES addition amount at 130°C. The synthesis composition was 1 $MTPE_{8-4}$: x CES : 6 TEOS : 35000 $H_2O$, where x = 1 and 2. (d) synthesized by adding more TEOS. The synthesis composition was 1 $MTPE_{8-4}$ : 1.5 CES : 8 TEOS : 35000 $H_2O$ at 130°C. (e) synthesized by changing HCl amount. The synthesis composition was 1 $MTPE_{8-4}$ : 1.5 CES : x HCl : 6 TEOS : 35000 $H_2O$ at 130°C, where x = 0.7 and 1.5. When x = 1.5, very small amount of products can be obtained.

It can be observed that bicontinuous cubic gyroid structure can be synthesized within a very narrow range. (i) The synthesis temperature of 100-130°C is favorable for the structural formation, when the temperature reaches 150°C, no highly ordered mesostructure can be formed. (ii) The concentration of reaction system plays an important role and the bicontinuous cubic gyroid structure can be formed in very dilute concentration (1 mg/ml). (iii) A suitable amount of the co-structure directing agent (CES) and TEOS is necessary. The moral ratio of CES/Template can be adjusted in the range of 1.5-2 and the moral ratio of TEOS/Template can be adjusted in the range of 6-8. The moral ratio of TEOS/CES can be adjusted in the range of 3-4. The bicontinuous cubic gyroid structure can’t be formed with more CES or TEOS. (iv) The pH of the solution affects the organic/inorganic interaction and the condensation rate of the TEOS, which influence the mesostructure of the hybrids. If the pH of the system is higher than 10 or lower than 8, only very small amount of products are obtained. Finally, we choose the best synthetic conditions for MFSH-8 and MFSH-10 and the molar compositions was Template : CES : TEOS :

$H_2O$ = 1: 1.5: 6: 35000, the synthesis temperature was 130°C.

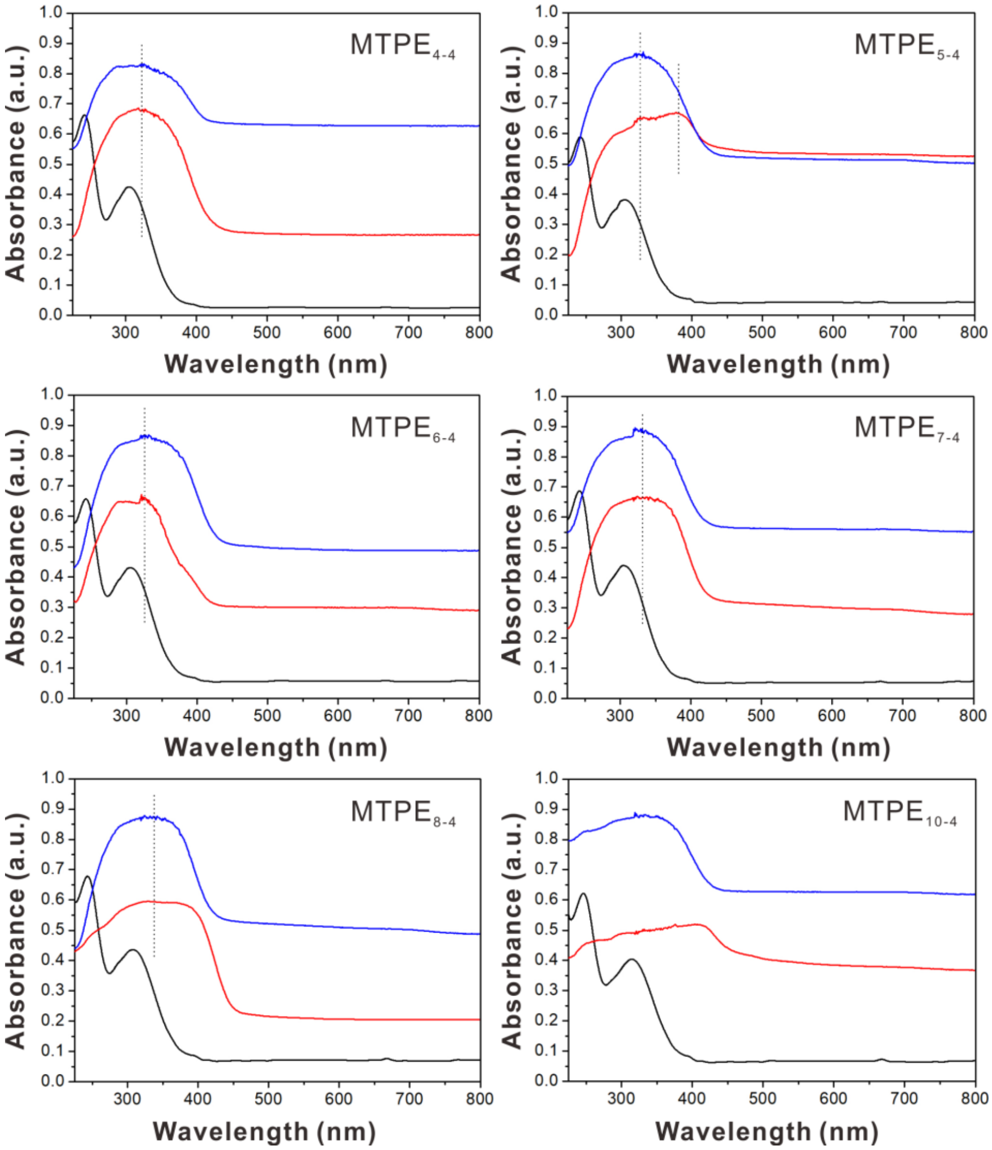

**Figure S7.** The Ultraviolet-visible absorption spectra of MTPE$_{n-4}$ in a dilute water solution (the black line), in pure MTPE $_{n-4}$ solid (red line) and in MFSHs (blue line).

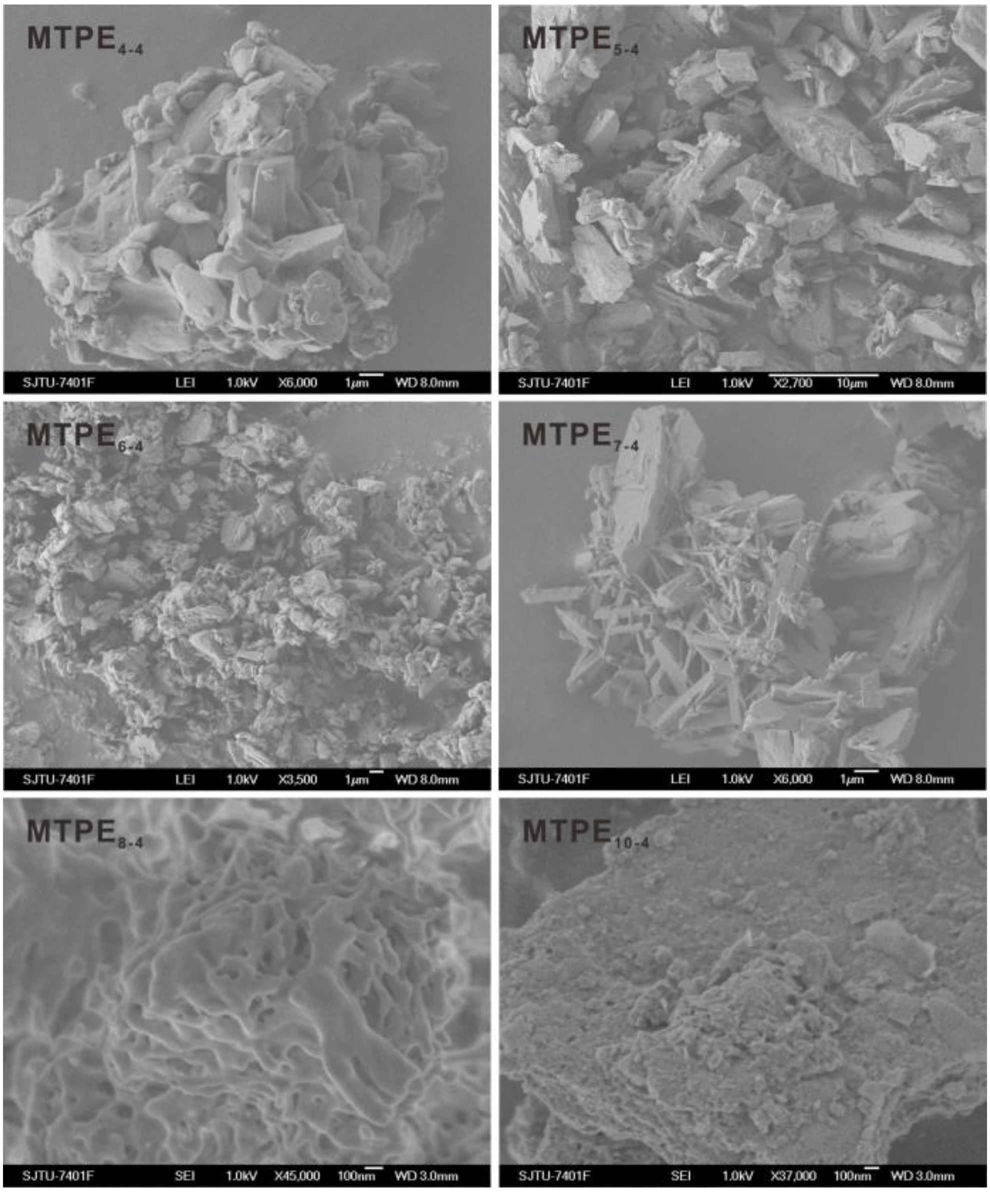

**Figure S8**. SEM images of pure MTPE$_{n-4}$ solid.