

Supporting Information

Ordered mesoporous crystalline titania with high thermal stability from comb-like liquid crystal block copolymers

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Preparation of Amphiphilic PEO-*b*-PMA(Az) Diblock Copolymer.

The amphiphilic PEO-*b*-PMA(Az) diblock copolymers were prepared by atom transfer radical polymerization (ATRP) method reported elsewhere previously. The synthesis route involved three steps, the preparation of macroinitiator PEO-Br, the preparation of azobezene monomer and the subsequent polymerization of azobezene monomer initiated by PEO-Br. In the first step, monomethoxy PEO-5000 (10 g) was dissolved in THF (30 ml). Then 0.30 g triethylamine were added to the solution, after cooled to 0 °C by ice-water bath, a solution of 0.56 g 2-bromo-2-methylpropionylbromide in 10 ml of dry THF was added dropwise under stirring for 1 h. And then the mixture was stirred at room temperature for 24 h. After the mixture was filtered, half of the solvent was evaporated, and the PEO-Br was precipitated into cold ether. After dissolution in methanol, the solution was stored in refrigerator to recrystallize the product. In the second step, 20 g 4-butylaniline was added into the round flask (500 ml), and subsequently 48.7 g concentrated HCl (37 wt %) was added. After ultrasonic, the mixture was cooled to below 5 °C. 30 ml solution containing 9.25 g sodium nitrite (NaNO₂) was added dropwise under stirring for 30 min to obtain the diazonium salts. 7.9 g phenol was dissolved in 75 ml solution containing 12.96 g potassium hydroxide (KOH). Once completely dissolved, the obtained diazonium salts were added dropwise and the pH value was kept about 9. After reaction for 1 h, the pH value was adjusted to 6 ~ 7 by using HCl. Claybank precipitations (denoted as P1) were obtained. 8.6 g P1, 8.5 g 11-bromoundecanol, 14.22 g potassium carbonate (K₂CO₃), 0.39 g potassium iodide (KI) and 150 ml acetone were successively added

into the 250 ml round flask, and then the mixture was refluxed at 75 °C for 12 h. After rinsing and drying, the product (denoted as P2) was obtained. 10 g P2 and 2.97 g triethylamine were added into 150 ml THF in ice-water bath, and then 3.07 g methacryloyl chloride was added dropwise under stirring for 1 h. Finally, the mixture was stirred at room temperature for 12 h. After filtering, rinsing and dry, azobezene monomers (denoted as MA(Az))were obtained. In the third step, 0.5 g PEO-Br, 1.5 g MA(Az), 4 ml chlorobenzene, 26.36 µl HMTETA and 9.95 mg CuCl were added to an ampoules bottle. The bottle, containing reactants, was fully degassed with three freeze-pump-thaw cycles and sealed under vacuum. It was subsequently immersed in a thermostated oil bath at 80 °C under stirring to allow polymerization of MA(Az) for 20 h. The solution was passed through a neutral Al₂O₃ column with THF as eluent to remove the catalyst. The yellow filtrate was concentrated under reduced pressure and reprecipitated twice into acidic methanol. The yellow polymer (PEO-*b*-PMA(Az)) was collected by filtration and dried under vacuum.

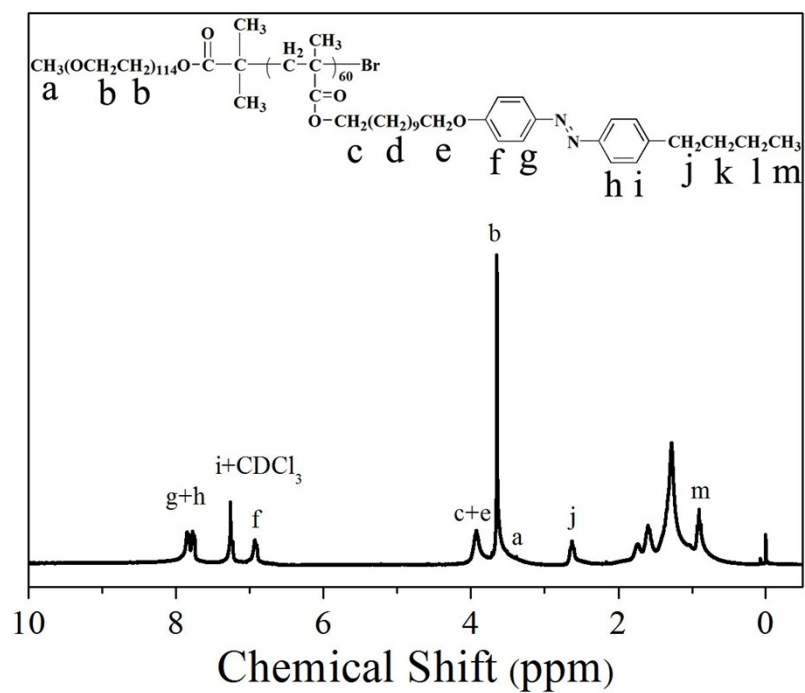


Fig. S1 Typical ^1H NMR spectrum of block copolymer PEO-*b*-PMA(Az) in CDCl_3 .

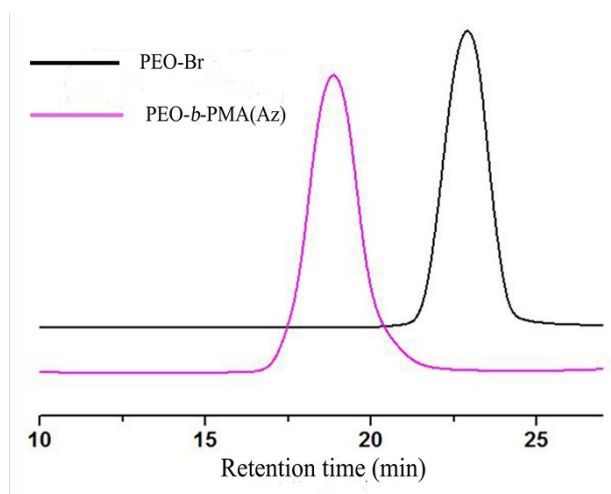


Fig. S2 GPC trace of PEO-Br and the lab-made diblock copolymer PEO-*b*-PMA(Az) using THF as an eluent.

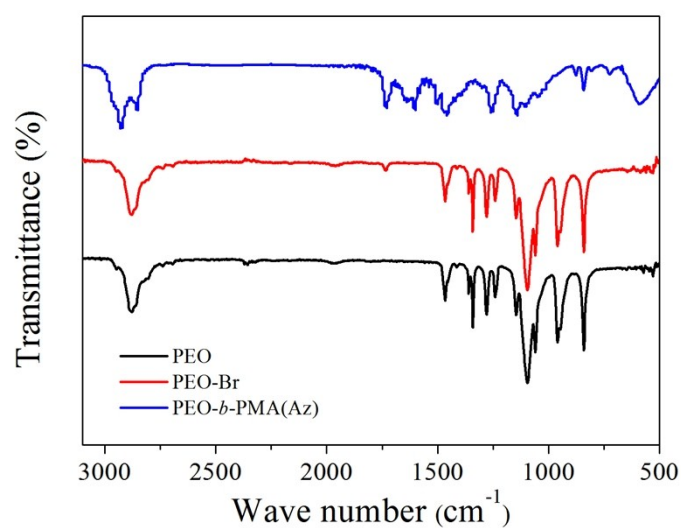


Fig. S3 FT-IR spectra of PEO, PEO-Br and PEO-*b*-PMA(Az).

Compared with PEO, a carbonyl stretch occurs at 1740 cm^{-1} in PEO-Br. After the polymerization of MA(Az), the adsorption peak of PEO-*b*-PMA(Az) at 1740 cm^{-1} increases, indicating the relative ratio of carbonyl obviously increases, due to the ester bond in PMA(Az). Due to the azobenzene in PMA(Az), the stretches of benzene skeleton at 1600 cm^{-1} and 1500 cm^{-1} occurs. Both indicate the presence of PMA(Az) block in the PEO-*b*-PMA(Az).

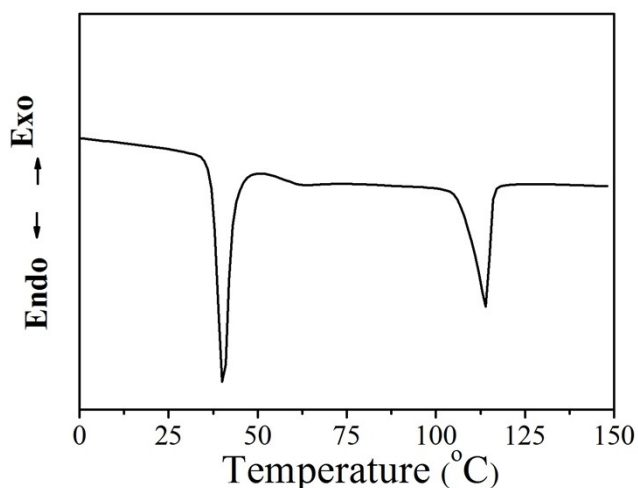


Fig. S4 DSC curve of PEO-*b*-PMA(Az) on the second heating process.

The sharp peak at 40 °C is the melting peak of PEO. Two endothermic transitions at 62 and 113 °C are observed, which are attributed to LC transitions.

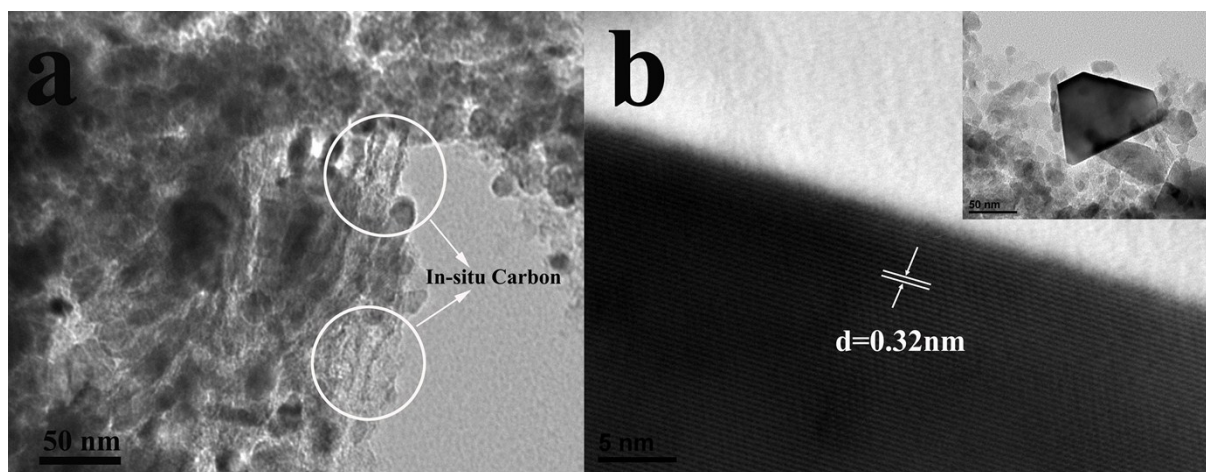


Fig. S5 TEM images of MT-800N.

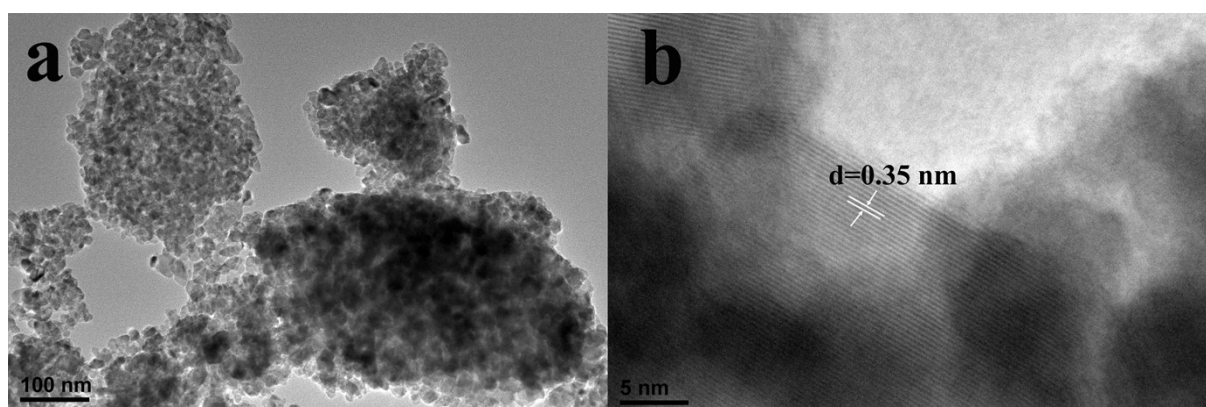


Fig. S6 TEM images of the as-made sample directly calcined at 600 °C in air (denoted as MT-600A).

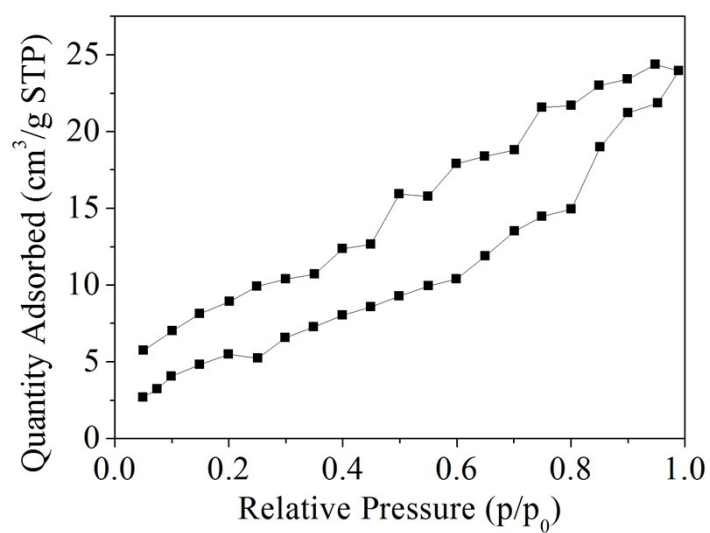


Fig. S7 Nitrogen adsorption-desorption isotherm of MT-350N.

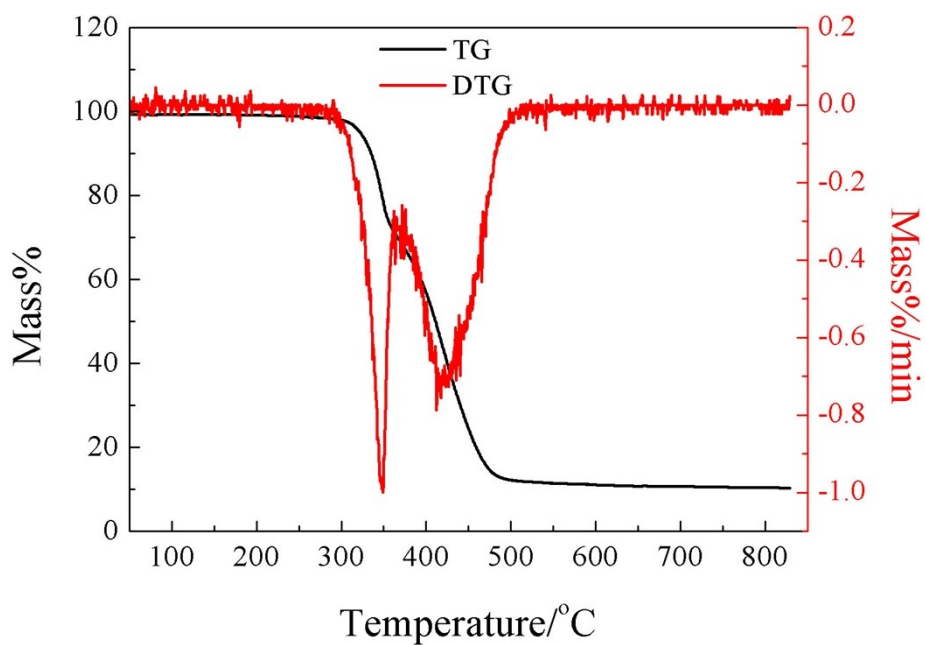


Fig. S8 TG curves of PEO-*b*-PMA(Az) in nitrogen atmosphere.

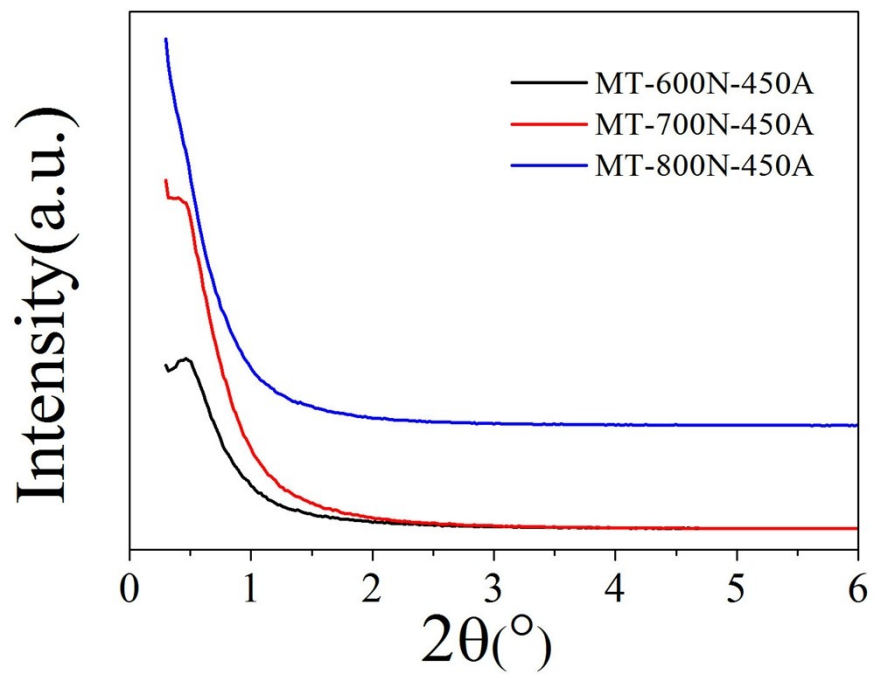


Fig. S9 SAXRD patterns of mesoporous titanias calcined at 450 °C in air.

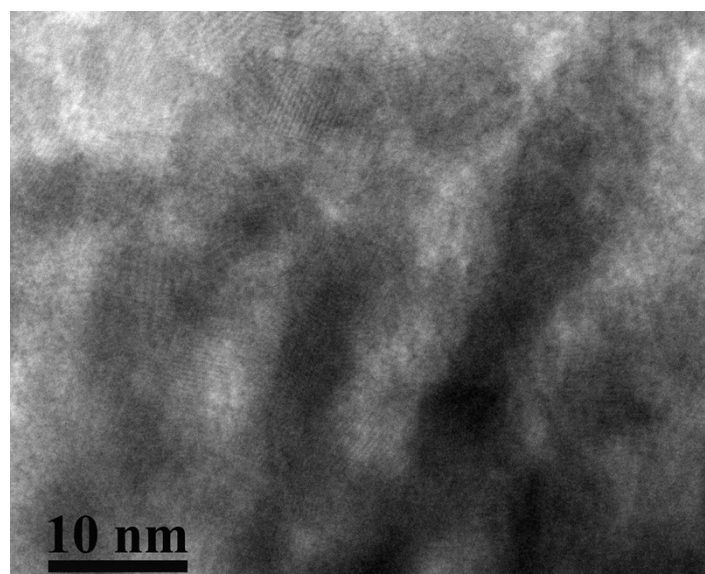


Fig. S10 HRTEM images of MT-600N-450A

Table S1. Physicochemical properties of mesoporous titania materials.

	BET surface area (m ² /g)	Pore volume (cm ³ /g)	Pore size (nm)	Crystallite size ^{a)} (nm)	d ₁₀₀ ^{b)} (nm)	a ^{c)} (nm)
MT-350N	21	-	-	7.0	19.6	17.0
MT-600N	165	0.13	2.55,4.73	9.0	16.8	14.5
MT-700N	193	0.17	4.87	9.7	16.2	14.0
MT-800N	239	0.23	2.37	14.7(A) ^{d)} , 25.0(R) ^{e)}	-	-
MT-600N-450A	126	0.28	3.27	11.5	19.0	16.4
MT-700N-450A	137	0.32	4.78	12.4	18.4	15.9
MT-800N-450A	108	0.37	4.81	15.9(A), 29.6(R)	-	-
T-700N-450A	33	0.01	5.82	20.5	-	-

^{a)} The sizes were calculated from the 101 reflection for anatase and 110 reflection for rutile in the WAXRD patterns; ^{b)} d values were calculated using the Bragg equation; ^{c)} the unit-cell parameters were calculated using the formula $a = \sqrt{3} d_{100}/2$; ^{d)} A refers to anatase phase; ^{e)} R refers to rutile phase.