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Electronic Supplementary Information (ESI)

A Multifunctional Role of Trialkylbenzene for the Preparation of Aqueous Colloidal Mesostructured/Mesoporous Silica Nanoparticles with Controlled Pore Size, Particle Diameter, and Morphology

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Contents

Experimental details

1. Removal of surfactants and TAB of CMSS to obtain CMPS by a dialysis process.

The dialysis conditions used here (composition of the solution outside a dialysis tube) were different from those used in our previous studies.[1-7] That is, 2-PrOH was used in this study instead of EtOH in the previous ones. When EtOH was used for the dialysis solution in this study, an oil phase (derived from TAB) was observed on the colloidal solution even after the dialysis process was finished (Figure S1, AcOH/EtOH). Alternatively, when 2-PrOH was used, the oil phase was not observed. Therefore, we chose a more hydrophobic solution for dialysis in this case to remove hydrophobic molecules such as TAB.

The effectiveness of dialysis for the removal of surfactants was confirmed by IR spectra and thermogravimetric (TG) curves (Figure S2). P_TIPB2-as and P_TIPB2-dia were chosen as examples to show the differences of organics before and after the dialysis. The IR spectra (Figure S2a) show that the transmittance of the bands assigned to C-H stretching vibrations (from 3100 to 2800 cm^{-1}) and out-of-plane C-H vibrations (*ca.* 1500 cm^{-1}) decreased with the increase in the repeating number of dialysis process. In particular, those bands were not observed for the samples dialyzed over 4 times, which suggests that almost all of the organic compounds (CTAB and TIPB) were removed by the process. The TG curves (Figure S2b) show that the weight loss at *ca.* 300 ^{o}C due to the degradation and combustion of the organic compounds decreased with the increase of the repeating number of dialysis process. These results indicate that almost all of the organic compounds were removed by more than two times of dialysis. Accordingly, it is quite reasonable to consider that the organic compounds in CMSS are able to be removed by dialysis more than 3 times. In fact we repeated the process five times to make the process extra sure.

The bands assigned to TIPB (e.g. *ca.* 700 cm^{-1}: C-H out-of-plane vibrations in trisubstituted benzenes, 2000-1600 cm^{-1}: harmonic overtones of these bands) were not observed even for the sample before dialysis (P_TIPB2-as). This indicates that almost all of added TIPB were trapped in a filtering paper during filtration and volatilized during the drying process of CMSS for the preparation of powder samples. In addition, those bands assigned to TIPB were not observed for P_TIPB2-dia, meaning the absence of TIPB in and on particles after dialysis.

2. Measurement of swelling ratios of HDPE for TMB and TIPB.

Swelling ratios of HDPE for TMB and TIPB were calculated by using the following equations. Uptaken volume of TAB (ΔV) were calculated by multiplying with the density of the corresponding swelling liquid (TMB: 0.86 g/cm^3, TIPB: 0.845 g/cm^3) according to eq 1.

$$\text{Uptaken volume of TAB } (\Delta V) = \frac{(\text{Weight after swelling} - \text{Weight before swelling})}{\text{Density of TAB}} \quad (1)$$

Weight before swelling was also converted to a volume (V_0) by eq 2.

$$\text{Volume before swelling } (V_0) = \frac{\text{Weight before swelling}}{\text{Density of TAB}} \quad (2)$$

Then, the weight after swelling (V) was calculated by eq 3.

$$\text{Volume after swelling } (V) = V_0 + \Delta V \quad (3)$$

Swelling ratio was calculated by eq 4.

$$\text{Swelling ratio} = V/V_0 \quad (4)$$

Figures & Table

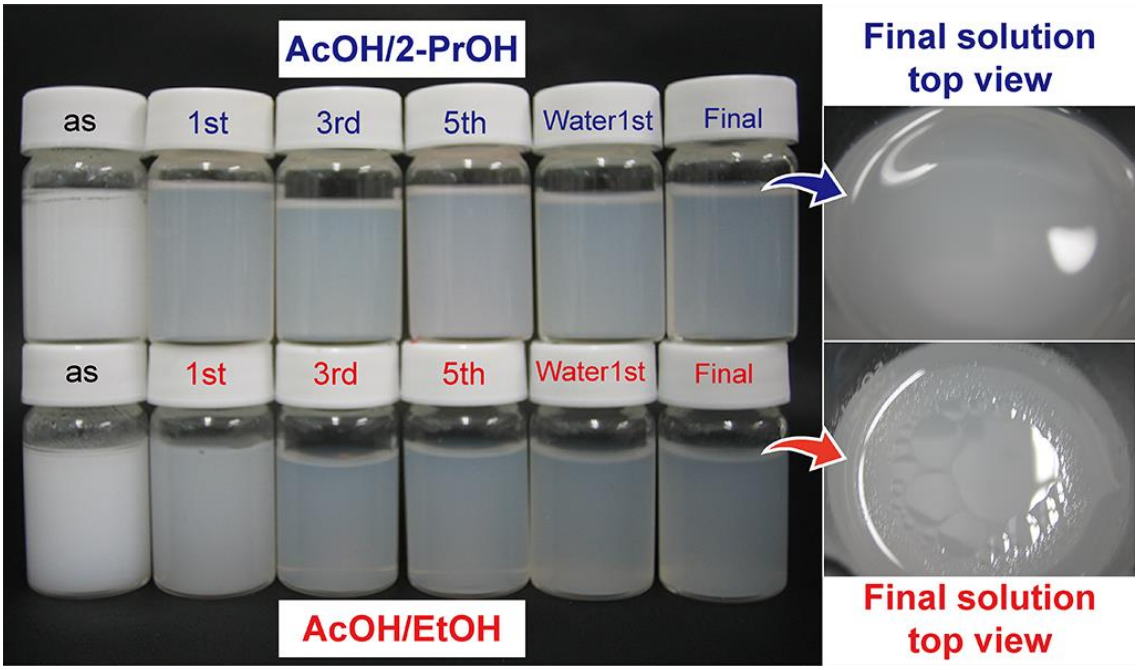

Figure S1 Variation in the appearance of P_TIPB8-as after the dialysis with AcOH/2-PrOH or AcOH/EtOH.

The notations of "as" and "final" were P_TIPB8-as and P_TIPB8-dia. 1st, 3rd, and 5th on the samples mean the repeated number of dialysis process. The samples denoted as "water 1st" means the nanoparticles after 5 times dialysis with AcOH/alcohol and once with water. When ethanol was used for the dialysis solution (AcOH/EtOH), an oil phase (derived from TIPB) remained even after the dialysis process. Alternatively, when 2-PrOH was used (AcOH/2-PrOH), an oil phase was not observed. On each dialysis condition, the colloidal solutions turned more transparent as the repeated number of dialysis increased. This indicates that surfactants and TIPB were removed gradually by the dialysis process.

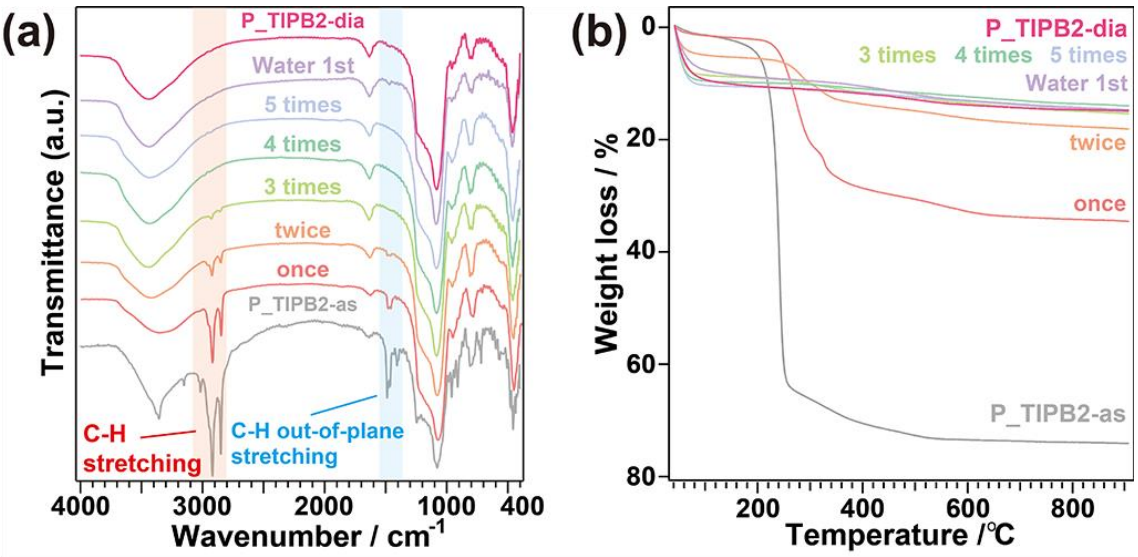

Figure S2 (a) IR spectra and (b) TG curves of P_TIPB2-as and P_TIPB2-dia, prepared by different repeating number of dialysis process, for the proof of successful dialysis for the removal of surfactants and TAB.

The notation on each graph (e.g. once, twice) means the repeating number of dialysis. The samples denoted as "water 1st" means the nanoparticles after 5 times dialysis with AcOH/alcohol and once with water.

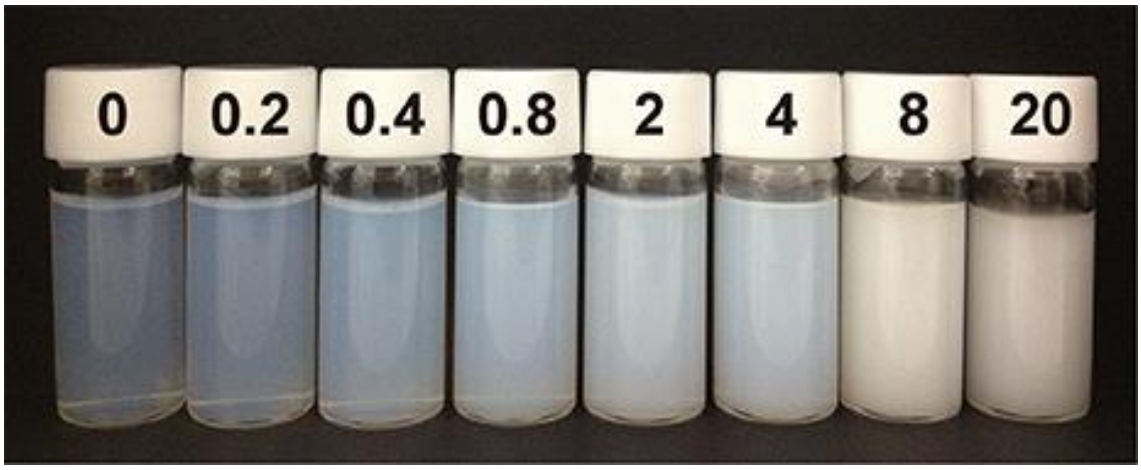

Figure S3 Appearances of P_TIPB*x*-as (x = 0, 0.2, 0.4, 0.8, 2, 4, 8, and 20).

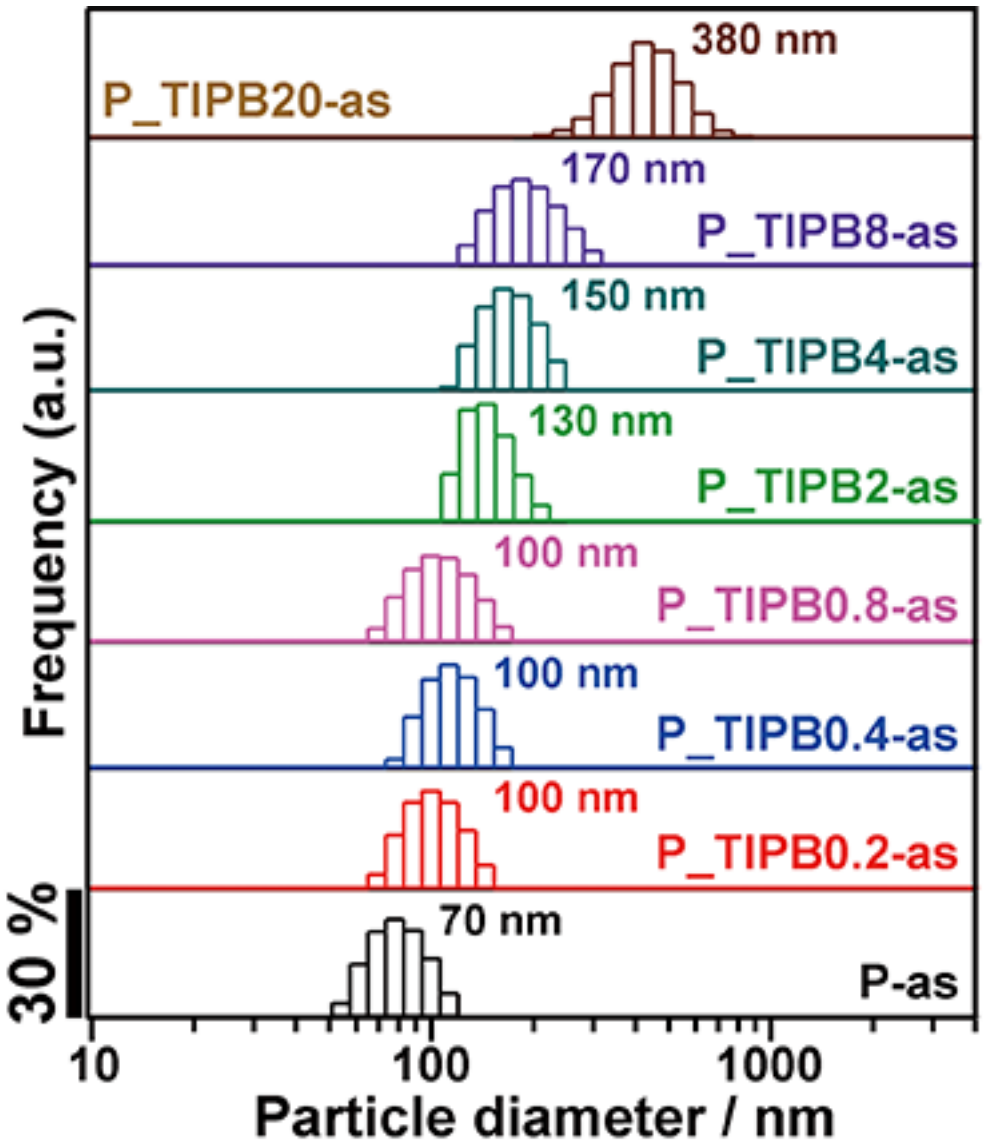

Figure S4 Particle size distribution (DLS) of P_TIPB*x*-as (*x* = 0, 0.2, 0.4, 0.8, 2, 4, 8, and 20).

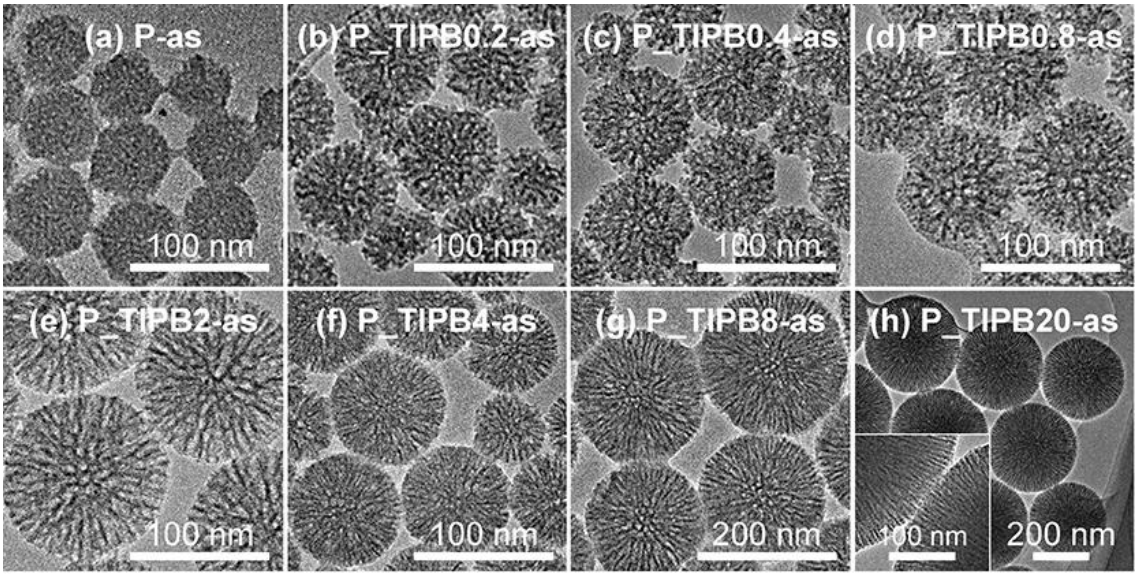

Figure S5 TEM images of P_TIPB*x*-as: *x* = (a) 0, (b) 0.2, (c) 0.4, (d) 0.8, (e) 2, (f) 4, (g) 8, and (h) 20.

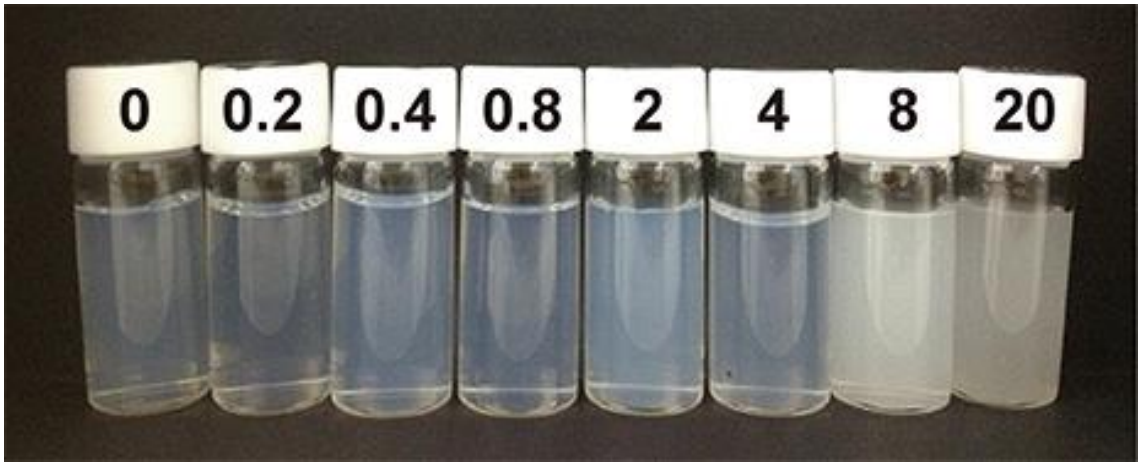

Figure S6 Appearances of P_TIPB*x*-dia (*x* = 0, 0.2, 0.4, 0.8, 2, 4, 8, and 20).

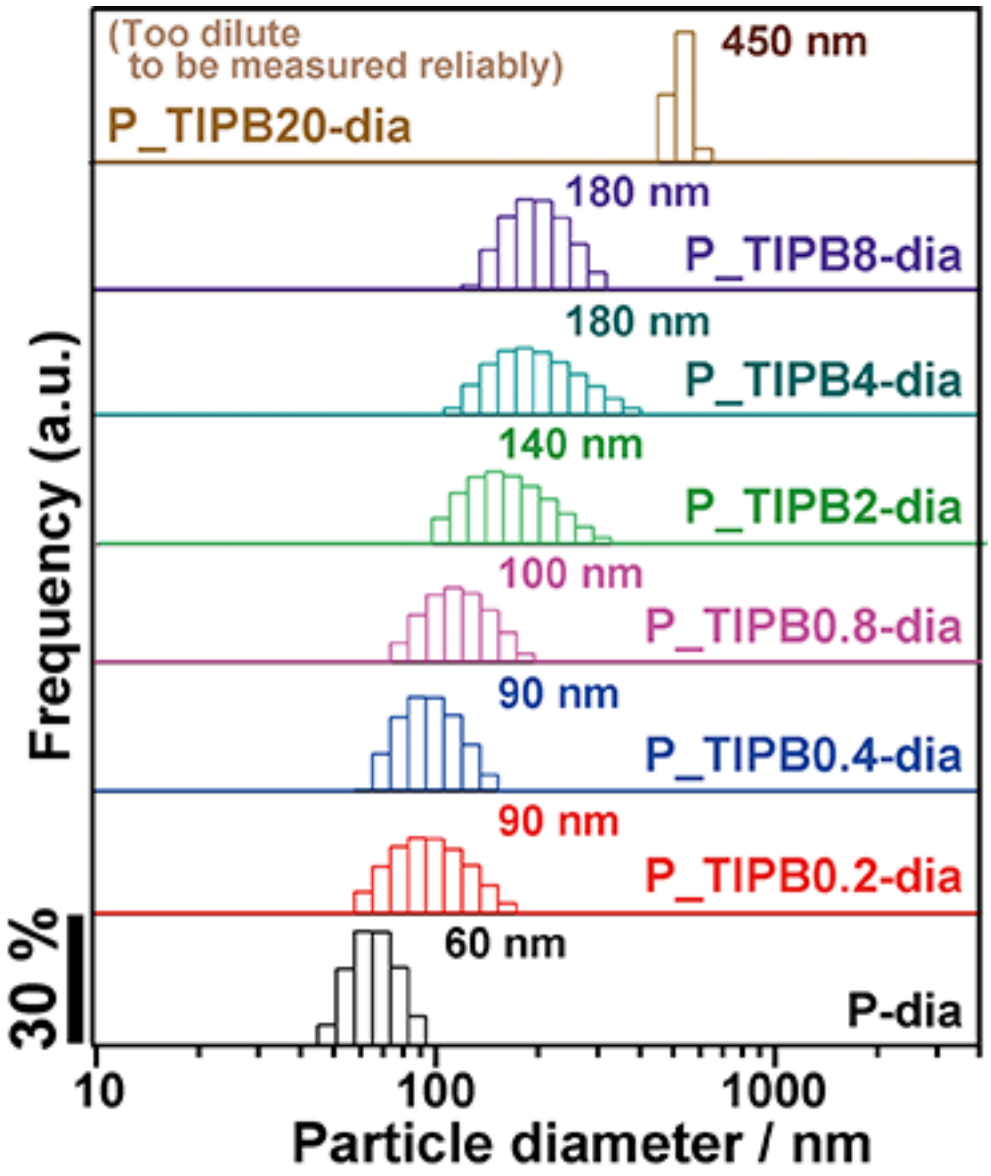

Figure S7 Particle size distribution (DLS) of P_TIPB*x*-dia (*x* = 0, 0.2, 0.4, 0.8, 2, 4, 8, and 20).

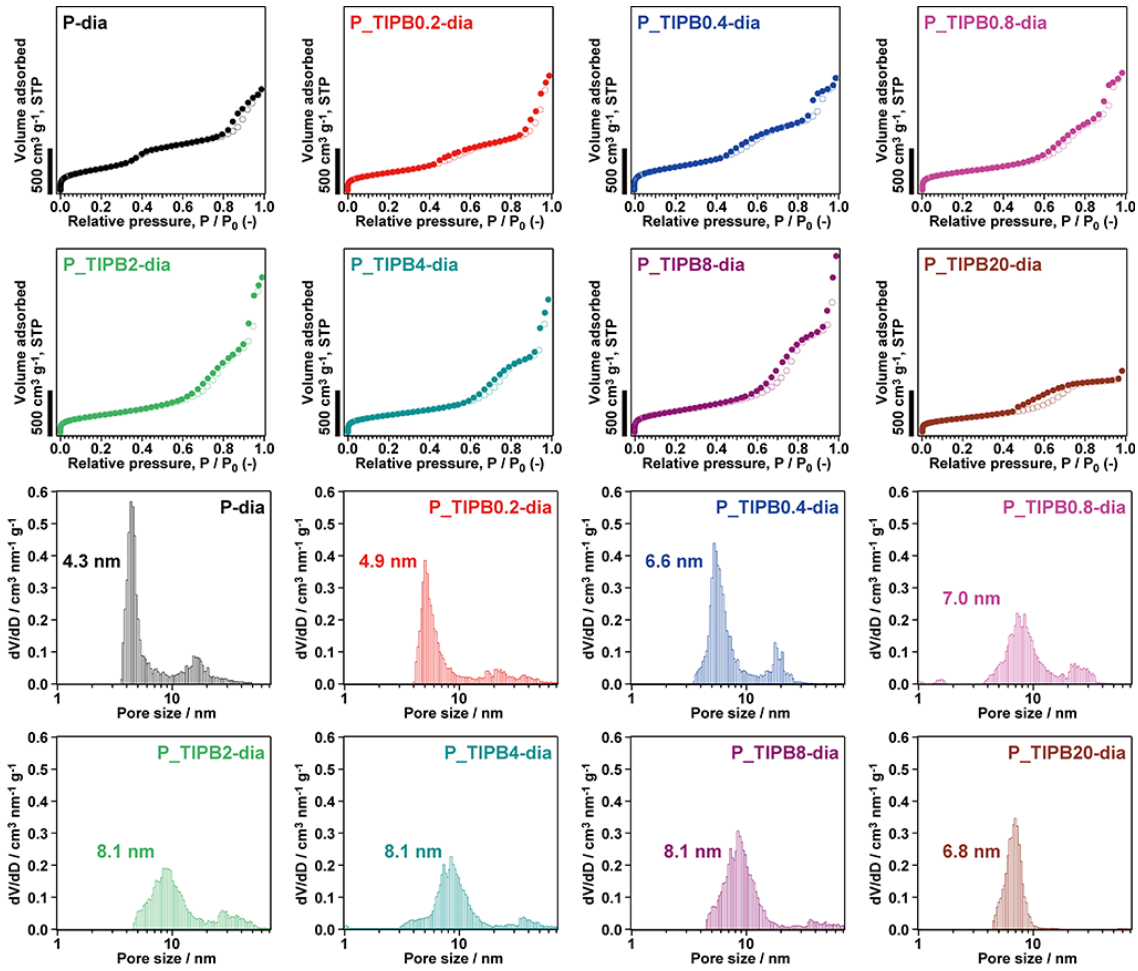

Figure S8 N_2 adsorption-desorption isotherms and pore size distributions (NLDFT) of dried samples of P_TIPB*x*-dia (*x* = 0, 0.2, 0.4, 0.8, 2, 4, 8, and 20).

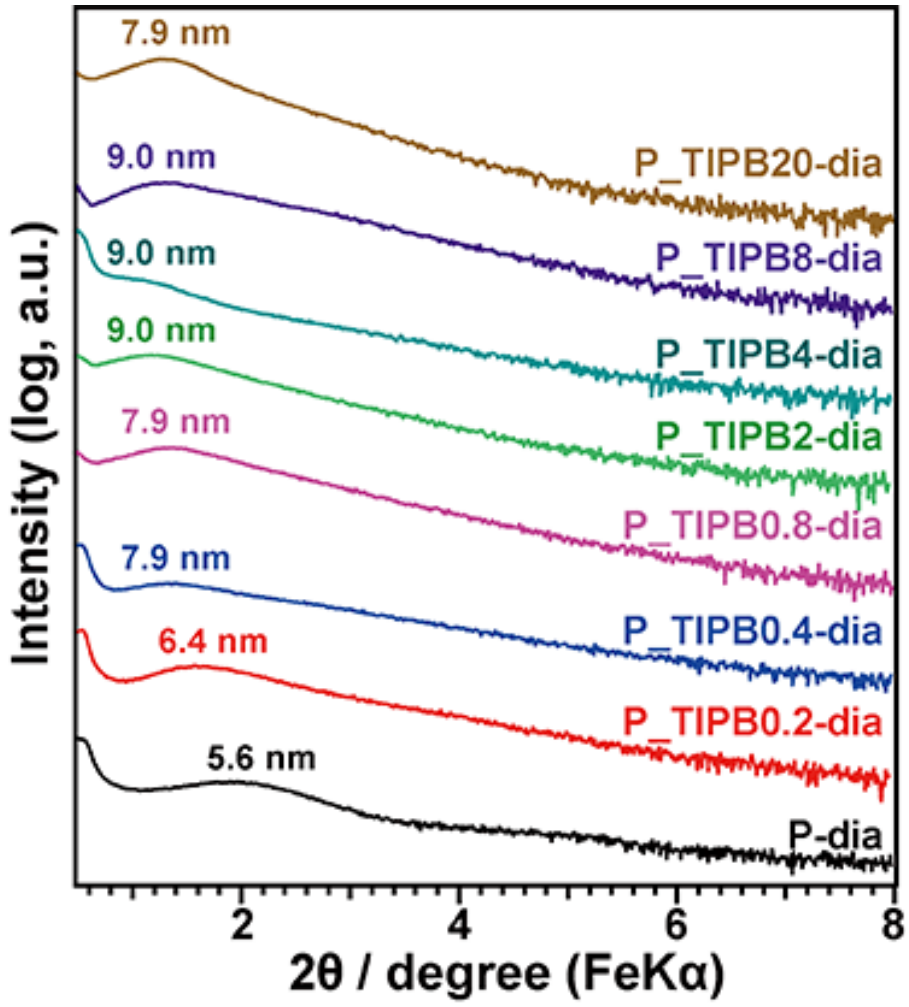

Figure S9 Powder XRD patterns of dried samples of P_TIPB*x*-dia (*x* = 0, 0.2, 0.4, 0.8, 2, 4, 8, and 20).

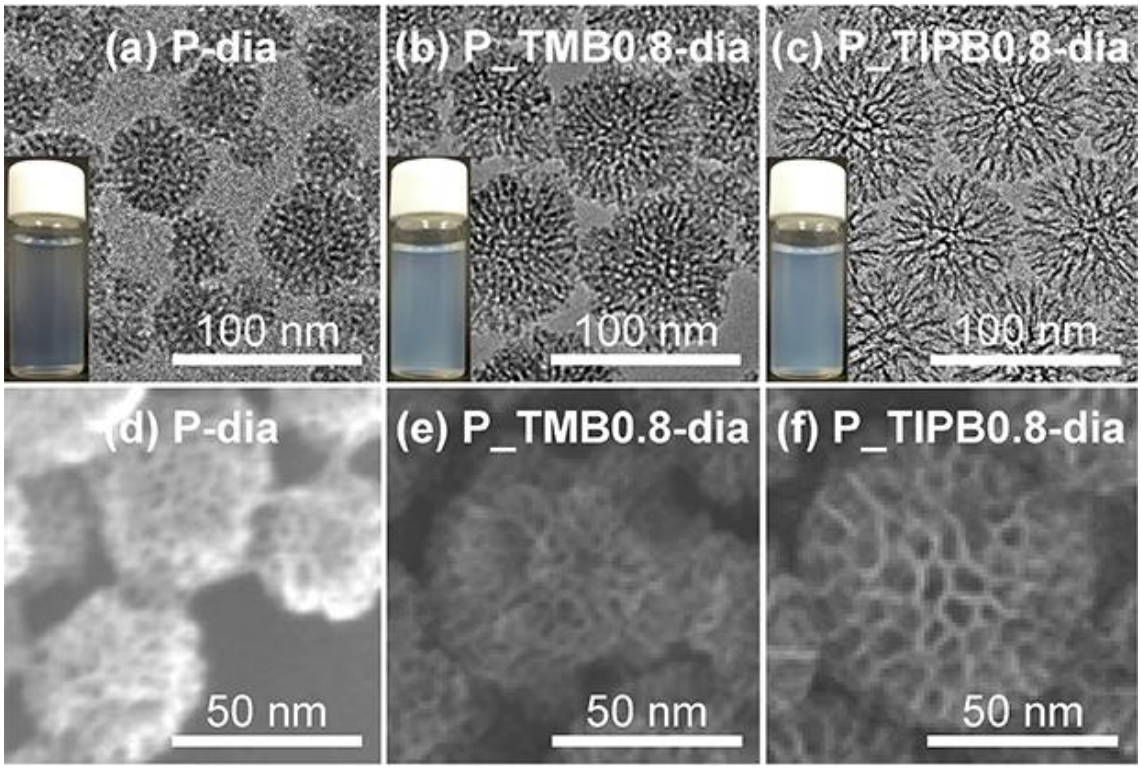

Figure S10 TEM images of CMPS: (a) P-dia, (b) P_TMB0.8-dia, (c) P_TIPB0.8-dia; and SEM images of CMPS: (d) P-dia, (e) P_TMB0.8-dia, and (f) P_TIPB0.8-dia (inset: appearance of each sample).

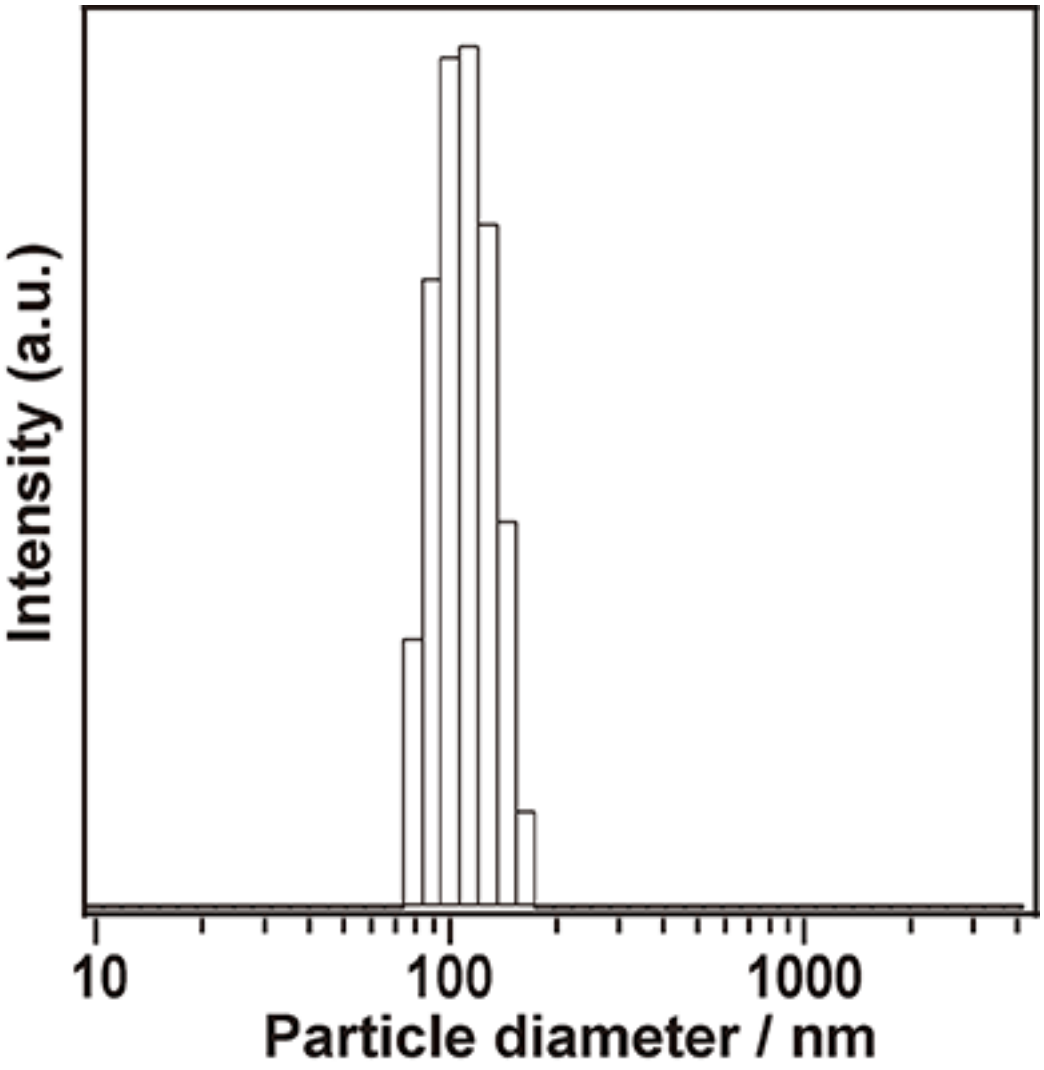

Figure S11 Particle size distribution (DLS) of P_TMB0.8-dia.

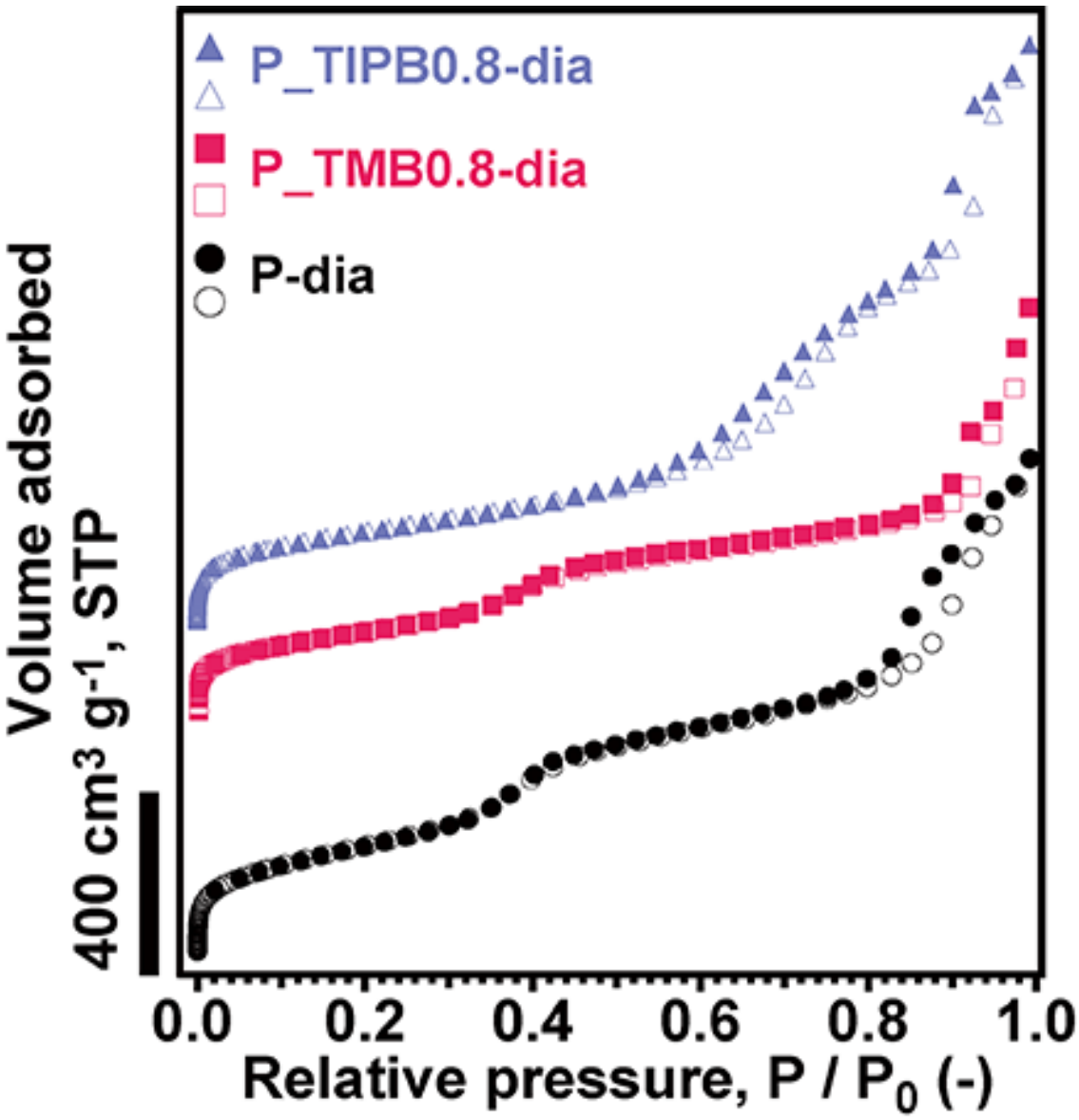

Figure S12 N_2 adsorption-desorption isotherms of dried samples (P-dia, P_TMB0.8-dia, and P_TIPB0.8-dia).

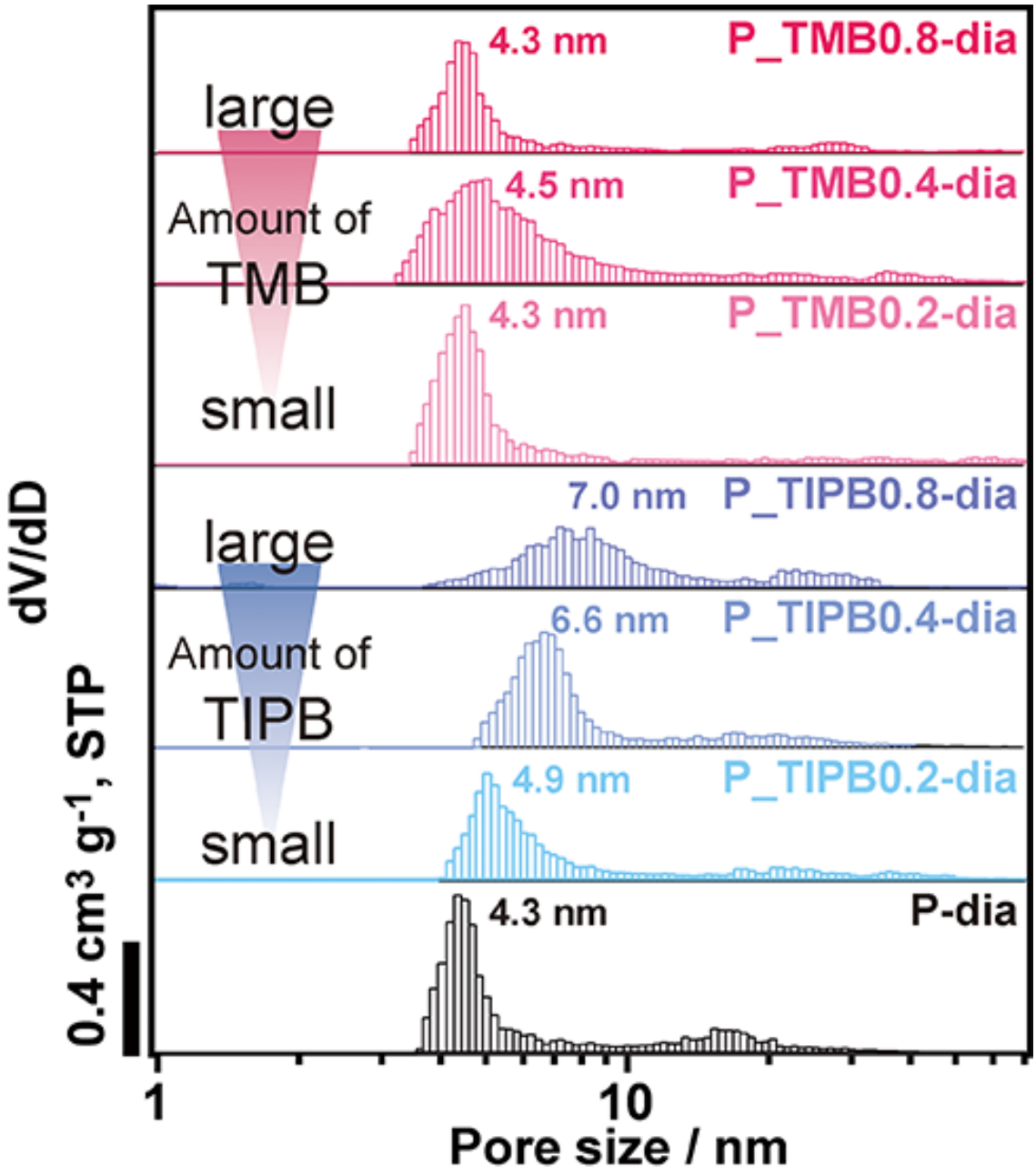

Figure S13 Pore size distributions (NLDFT) of P_TMB*x*-dia and P_TIPB*x*-dia (*x* = 0, 0.2, 0.4, and 0.8).

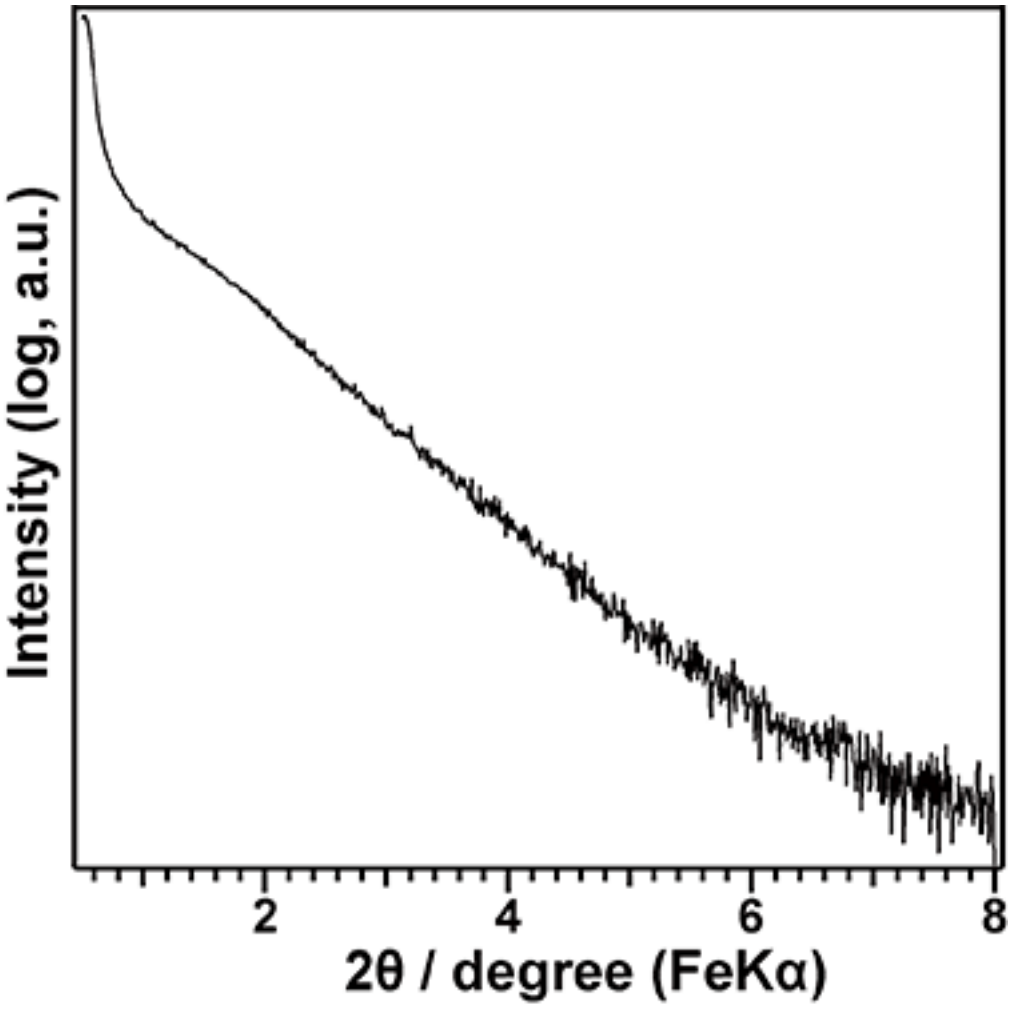

Figure S14 Powder XRD pattern of dried sample (P_TMB20-dia).

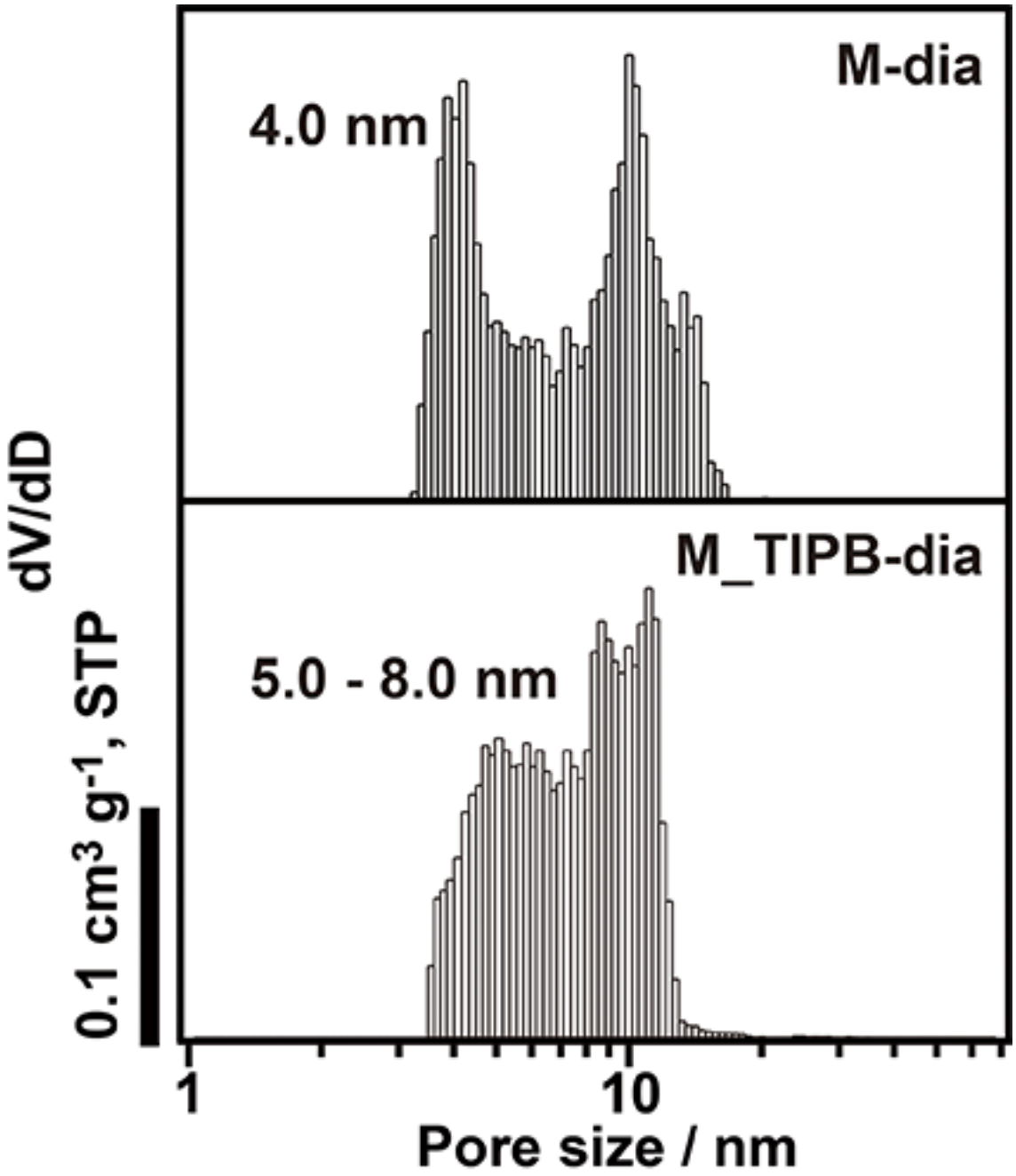

Figure S15 Pore size distributions (NLDFT) of dried samples (M-dia and M_TIPB-dia).

Table S1 Swelling ratios of TMB and TIPB: SD means standard deviation of swelling ratios (n = 3).

	Trialkylbenzene (TAB)					
	TMB			TIPB		
	1	2	3	1	2	3
Weight before swelling (g)	0.103	0.102	0.105	0.114	0.083	0.107
Weight after swelling (g)	0.110	0.111	0.111	0.116	0.086	0.107
Density of TAB ($g\,cm^{-3}$)	0.86	0.86	0.86	0.845	0.845	0.845
Uptaken volume of TAB (cm^3), ΔV	0.00814	0.0105	0.00698	0.00237	0.00355	0.000
Volume before swelling (cm^3), V_0	0.100	0.099	0.102	0.111	0.081	0.104
Volume after swelling (cm^3), $V = V_0 + \Delta V$	0.108	0.110	0.109	0.113	0.084	0.104
Swelling ratio (-), V/V_0	1.08	1.11	1.07	1.02	1.04	1.00
Average of swelling ratio		1.09 (SD 0.0129)			1.02 (SD 0.0148)	

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