Supporting Information

Direct Synthesis of Core-shell MFI Zeolite with Spatially Tapered Trimodal Mesopores via Controlled Orthogonal Self-Assembly

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KEYWORDS: Core-shell zeolites, trimodal mesopores, MFI, organosilane, orthogonal self-assembly

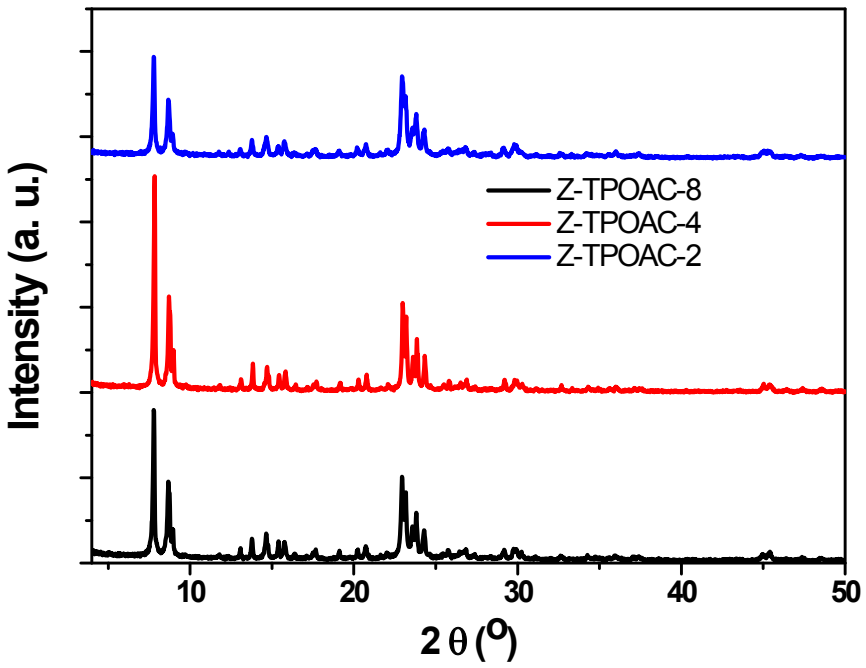


Figure S1. XRD patterns of different Z-TPOAC-n samples.

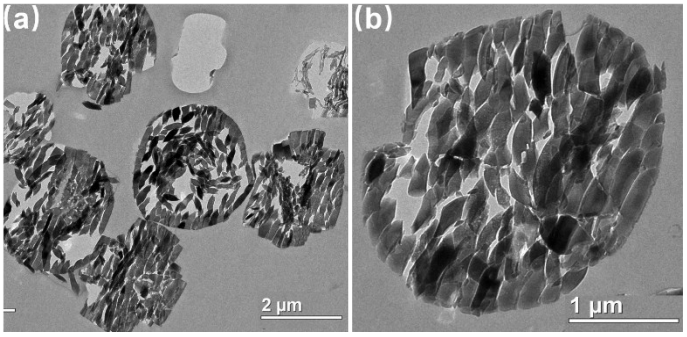
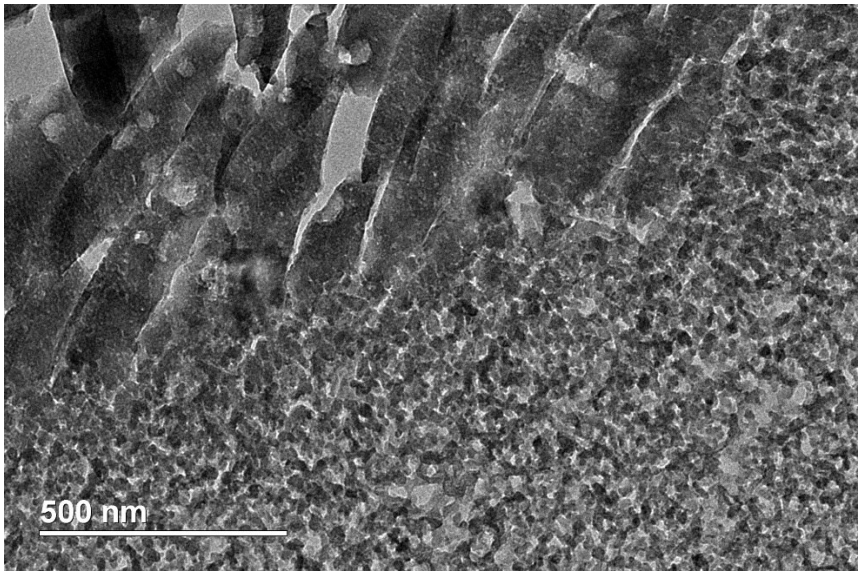
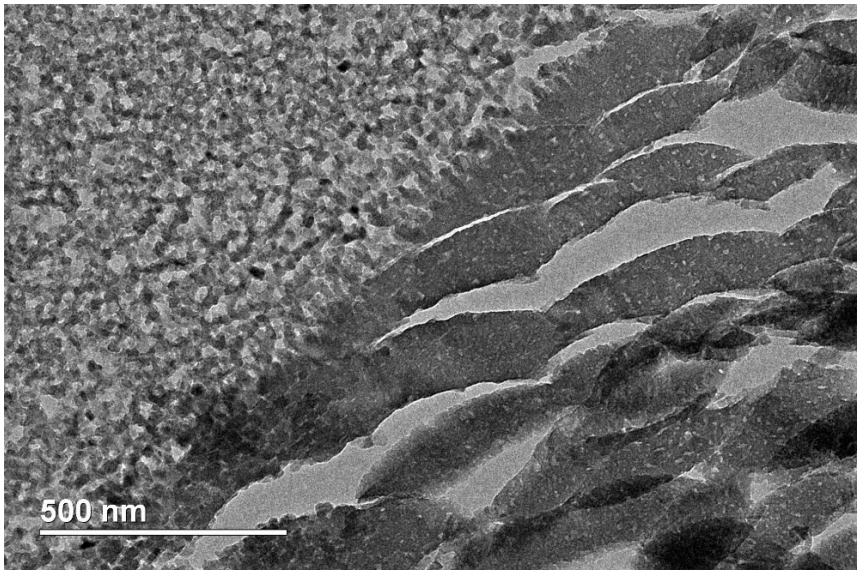


Figure S2. TEM images of commercially available bulk ZSM-5 zeolite crystals with no discernable mesopores taken at different magnification.


500 nm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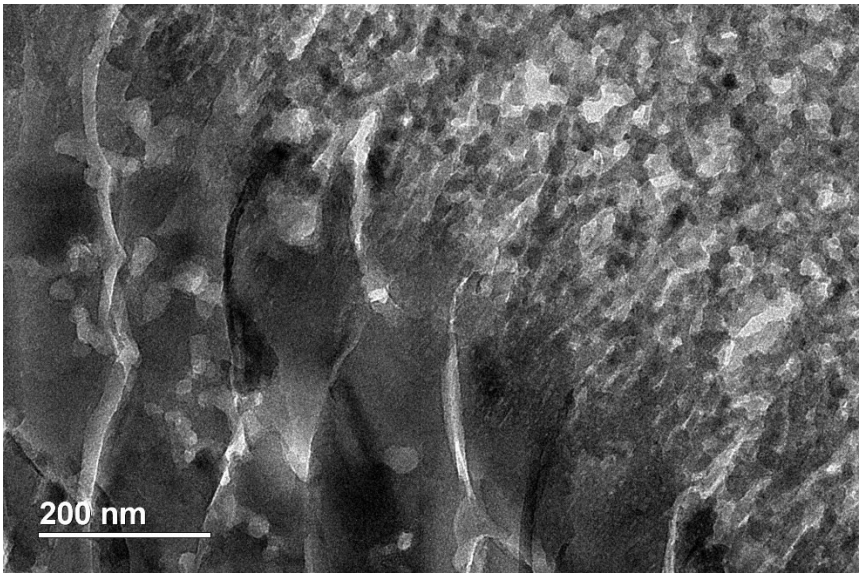
200 nm

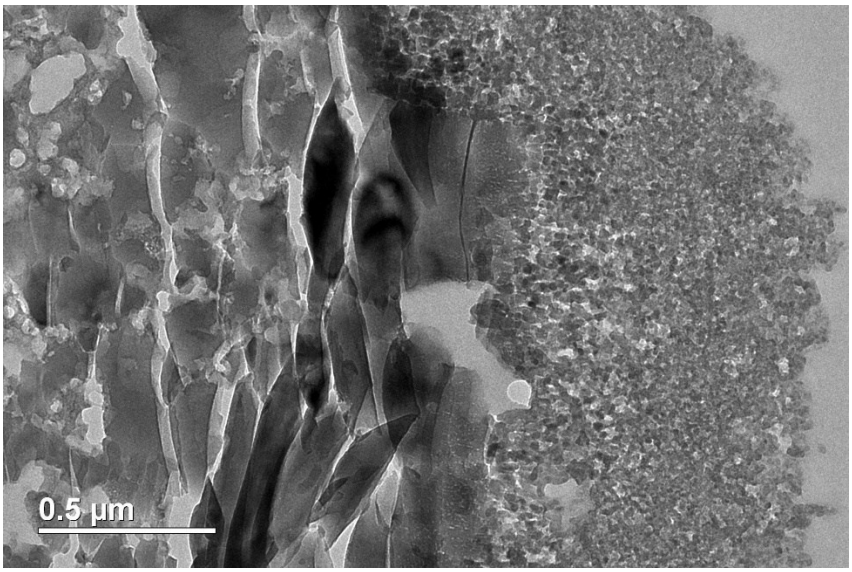

Figure S3. TEM images of Z-TPOAC-8 showing the mesopore distribution in the core-shell structure.

Table S1. Textural properties of as-made samples.

Sample	Surface Area (m^2/ g)			Pore Volume (cm^3/ g)		
	S_{total}[a]	S_{micro}[b]	S_{ext}[c]	V_{total}[d]	V_{micro}[e]	V_{meso}[f]
Z-Bulk	329	218	111	0.19	0.12	0.07
Z-TPOAC-8	407	206	201	0.62	0.11	0.51
Z-TPOAC-4	370	227	143	0.34	0.12	0.22
Z-TPOAC-2	361	233	128	0.32	0.12	0.20

[a]BET surface area.

[b]*t*-Plot micropore surface area.

[c]*t*-Plot external surface area.

[d]Total pore volume of pores calculated at P/P_o = 0.98

[e]*t*-Plot micropore volume.

[f]$V_{meso} = V_{total}-V_{micro}$

Table S2. Local minimums in the trimodal mesopore distribution of the core-shell Z-TPOAC-n zeolites.

Sample	Local Minimums		
	First (nm)	Second (nm)	Third (nm)
Z-TPOAC-8	3.2	5.1	11.3
Z-TPOAC-4	2.6	5.1	13.7
Z-TPOAC-2	2.6	5.1	15

Table S3. Trimodal mesopore size and volume distribution of the core-shell Z-TPOAC-n zeolites.

Sample	**First mesopores (2.6-5.0 nm)**			**Second mesopores (5.0-14.5 nm)**			**Third mesopores (>14.5 nm)**		
	Peak (nm)	**Volume (cm^3/g)**	**Volume percentage (%)**	**Peak (nm)**	**Volume (cm^3/g)**	**Volume percentage (%)**	**Peak (nm)**	**Volume (cm^3/g)**	**Volume percentage (%)**
Z-TPOAC-8	4.0	0.0395	7.80	6.7	0.1564	30.89	32	0.3104	61.31
Z-TPOAC-4	4.0	0.0443	20.28	9.0	0.08	36.61	25	0.0942	43.11
Z-TPOAC-2	4.0	0.0635	33.63	12	0.0448	23.73	23	0.0805	42.64

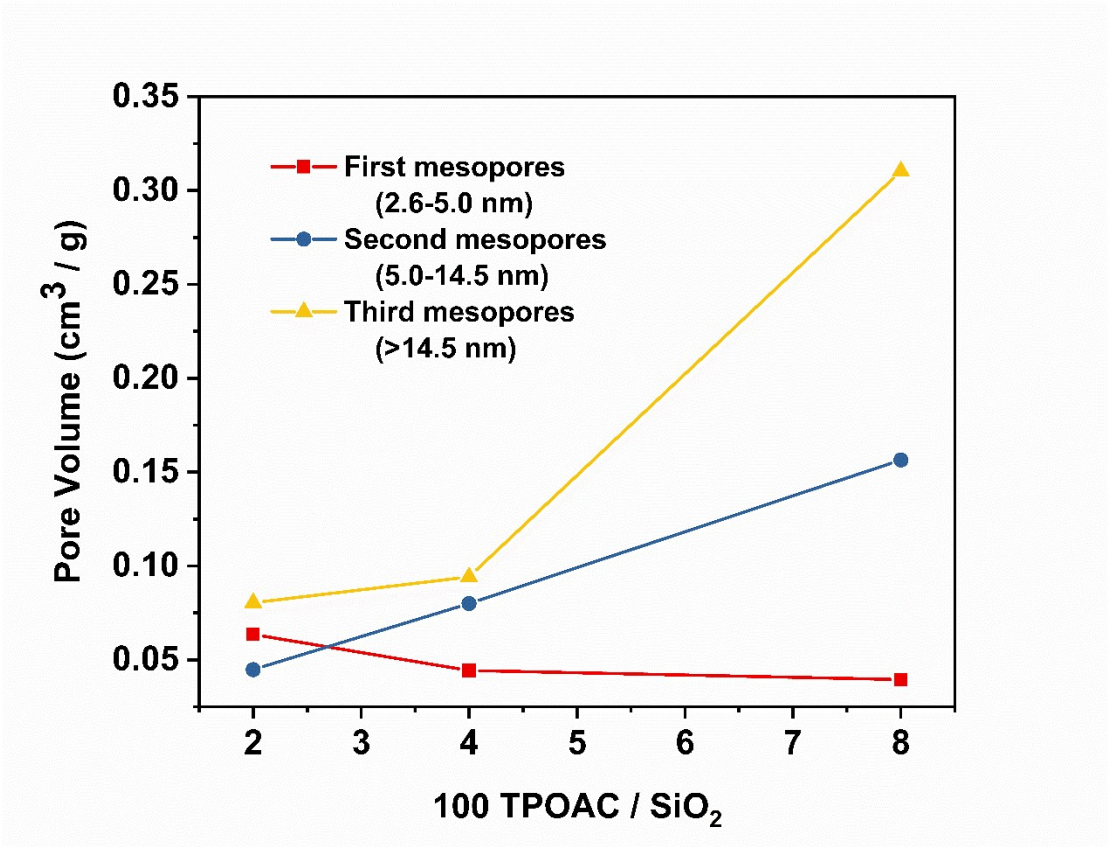

Figure S4. Variation of the mesopore pore volume in the trimodal mesopore pore range of 2.6-5.0 nm, 5.0-14.5 nm and >14.5 nm as a function of the amount of TPOAC added in the zeolite synthesis system.

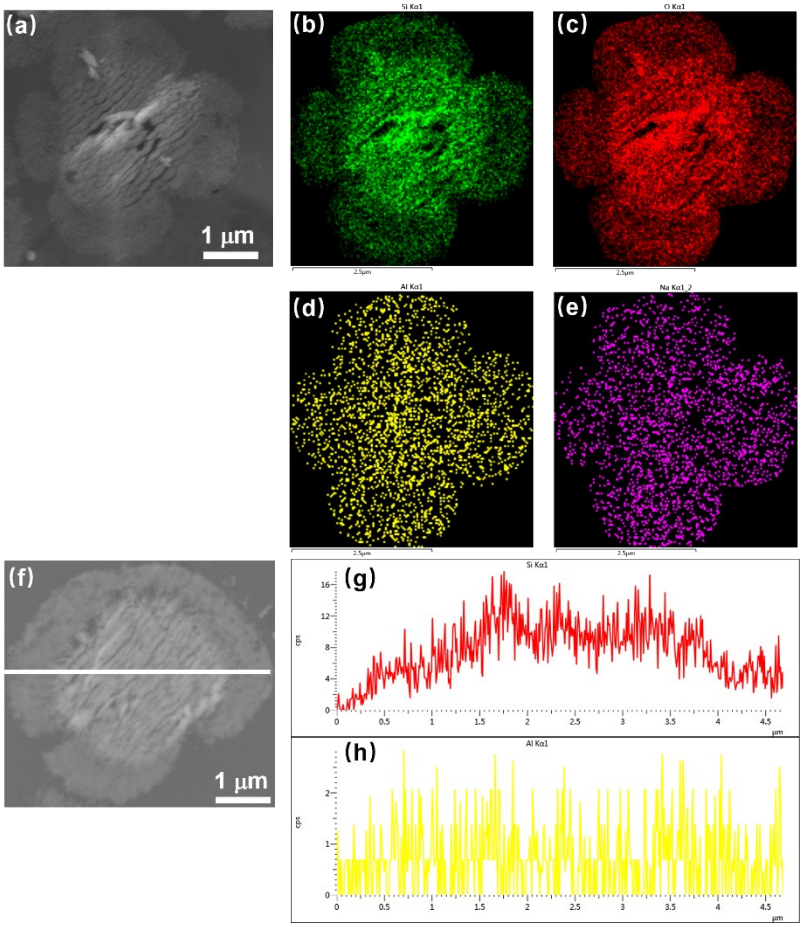

Figure S5. SEM-EDX elemental analysis of core-shell dual-structure Z-TPOAC-8 zeolite, (a) SEM image used for EDX-mapping, (b-e) element distribution of (b) Si, (c) O, (d) Al, (e) Na. (f) SEM-EDX line-scanning of (g) Si and (h) Al.

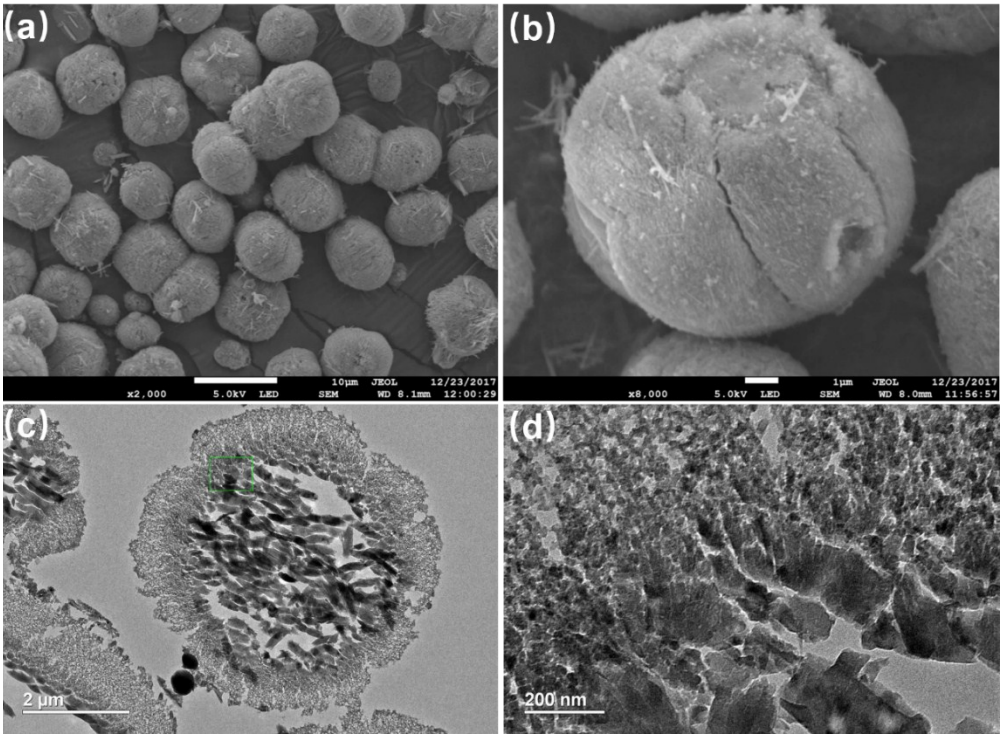

Figure S6. (a,b) SEM images, (c) low-resolution TEM images of core-shell dual-structure Z-TPOAC-4 sample, (d) magnified TEM image of marked area in (c) showing the core-shell boundary.

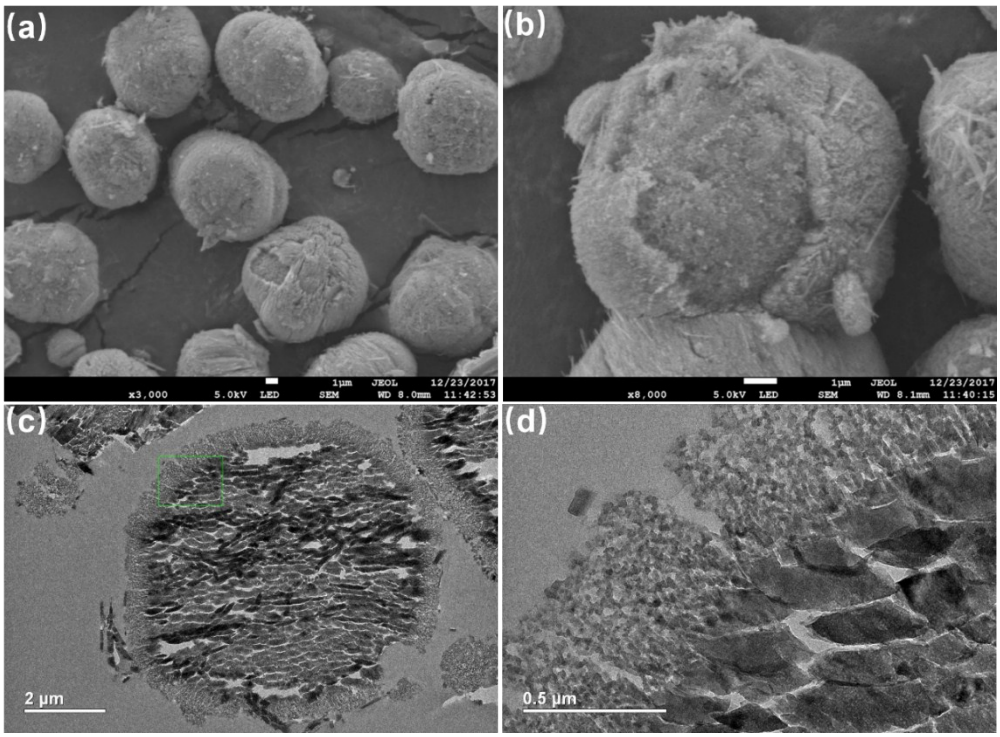

Figure S7. (a,b) SEM images, (c) low-resolution TEM images of core-shell dual-structure Z-TPOAC-2 sample, (d) magnified TEM image of marked area in (c) showing the core-shell boundary.

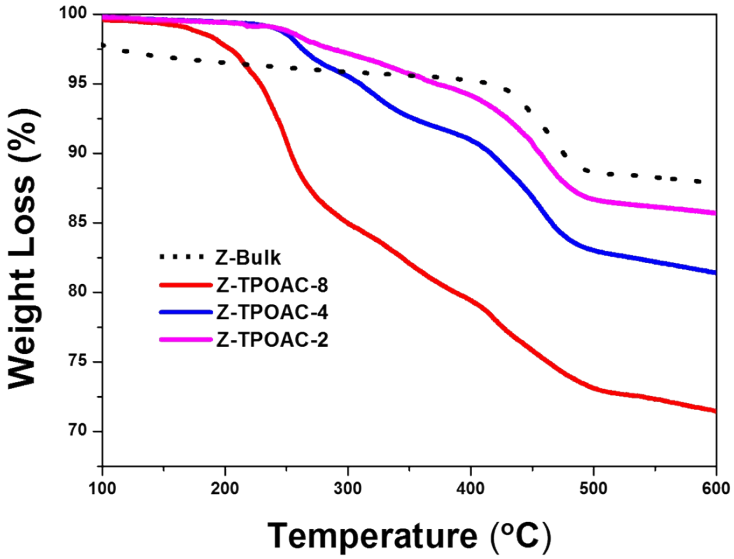

Figure S8. TGA curves of different Z-TPOAC-n samples (shown as solid lines) in comparison with the TGA curve of as synthesized Z-Bulk sample synthesized only with structure-directing agent TPABr (shown as dashed line). All the samples were dried at 60 °C for more than 12 h before measurement.

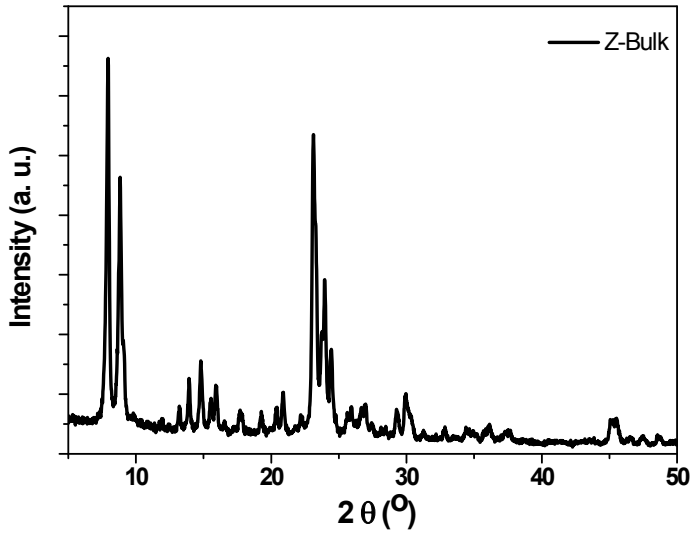

Figure S9. Powder XRD patterns of as-synthesized Z-Bulk.

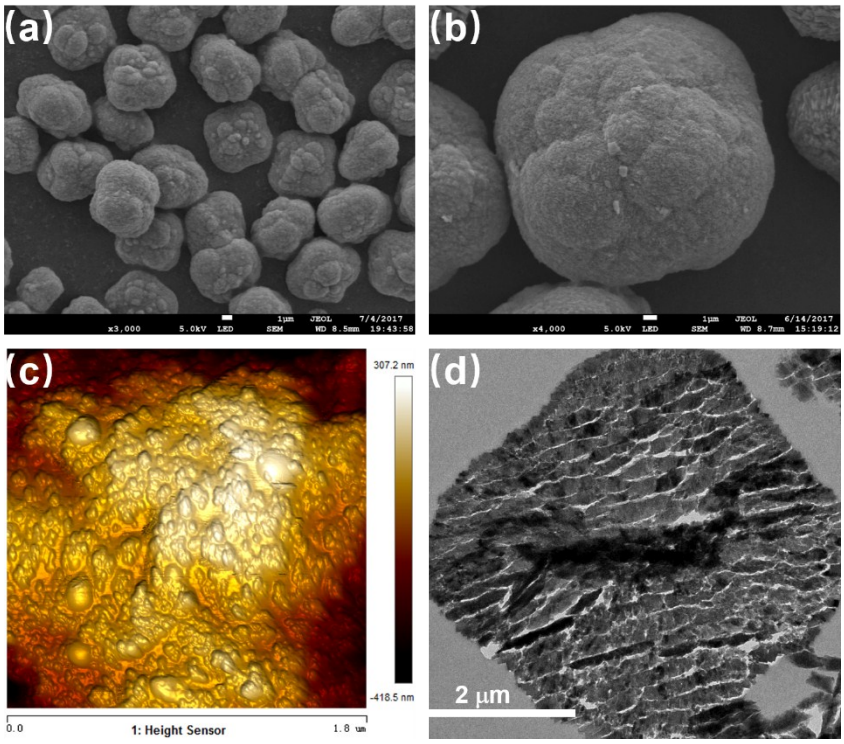

Figure S10. (a, b) SEM images, (c) AFM amplitude mode image, (d) Low-resolution cross-sectional TEM image of Z-Bulk sample.

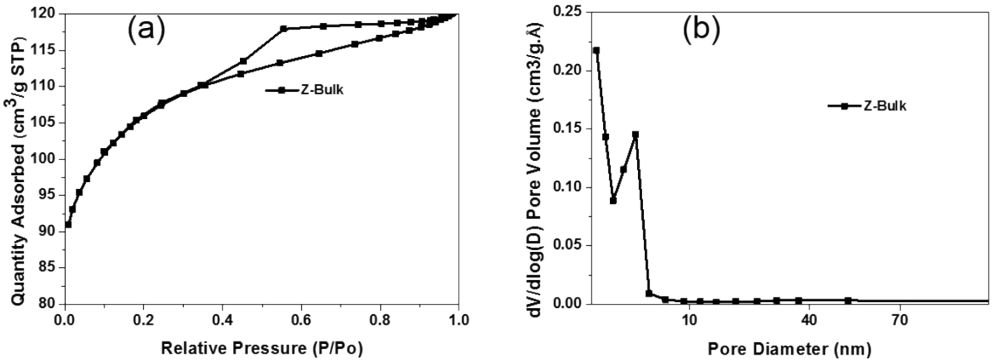

Figure S11. (a) N_2 adsorption–desorption isotherms, and (b) BJH mesopore size distribution of as-made Z-Bulk.

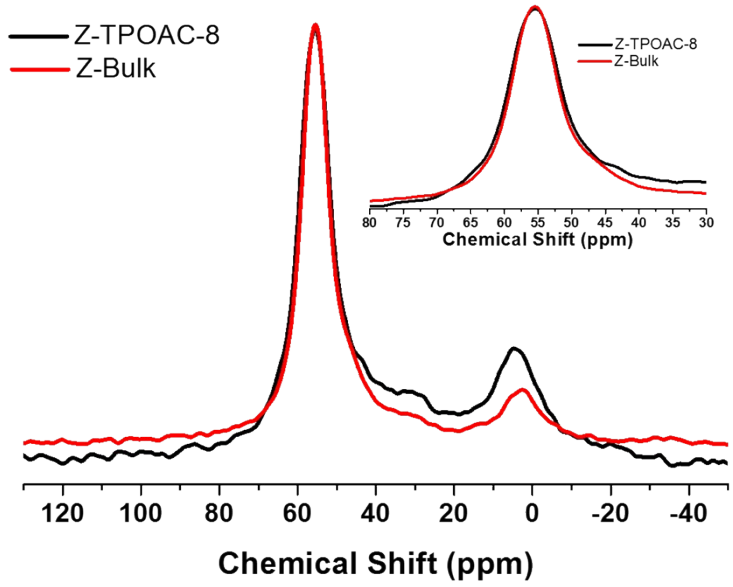

Figure S12. ^{27}Al MAS NMR spectra of mesoporous Z-TPOAC-8 and conventional Z-Bulk samples.

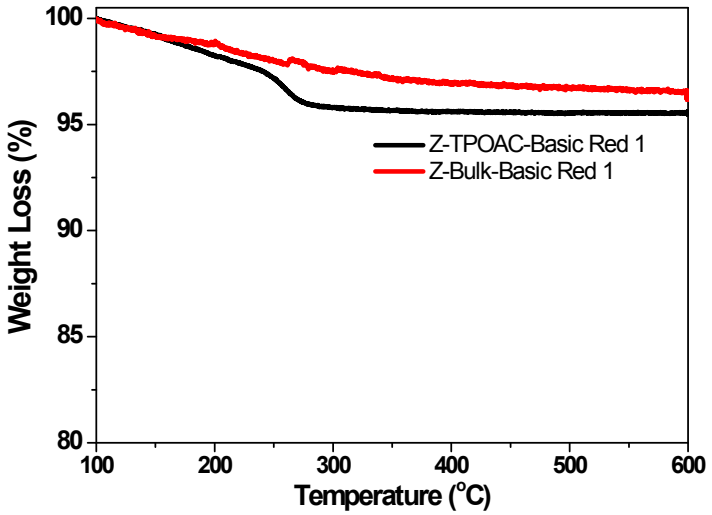

Figure S13. Relative weight loss by TGA of as-synthesized Z-Bulk and Z-TPOAC-8 samples after rhodamine 6G Dye adsorption.

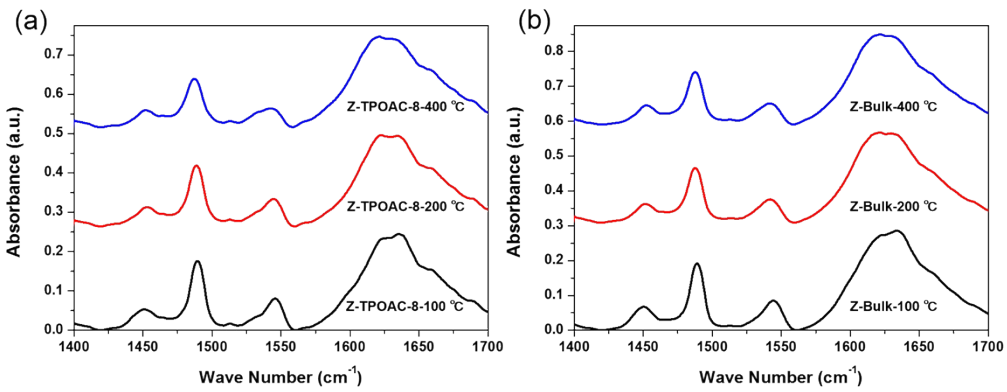

Figure S14. Py-FTIR spectra of H^+-form (a) Z-TPOAC-8 and (b) Z-Bulk samples at different desorption temperature.

Table S4. Numbers of Brønsted and Lewis acid sites of H^+-form Z-TPOAC-8 and Z-Bulk samples calculated from FTIR spectra of pyridine desorption at different temperatures.

Unit	200 °C desorption		
mmol/g	B	L	B/L Ratio
Z-TPOAC-8	0.09412	0.01926	4.89
Z-Bulk	0.08825	0.02508	3.52

Table S5. TOF values in the Suzuki–Miyaura cross coupling reactions

TOF (h^{-1})	**Cycle 1**	**Cycle 2**	**Cycle 3**	**Cycle 4**
Pd/C	49.3	49	47.8	47.8
Z-Bulk	48.7	48.6	48.0	45.7
Z-TPOAC-8	49.1	49.0	49.3	49.3

TOF=mol(yield)/mol(M)/t, M=Pd

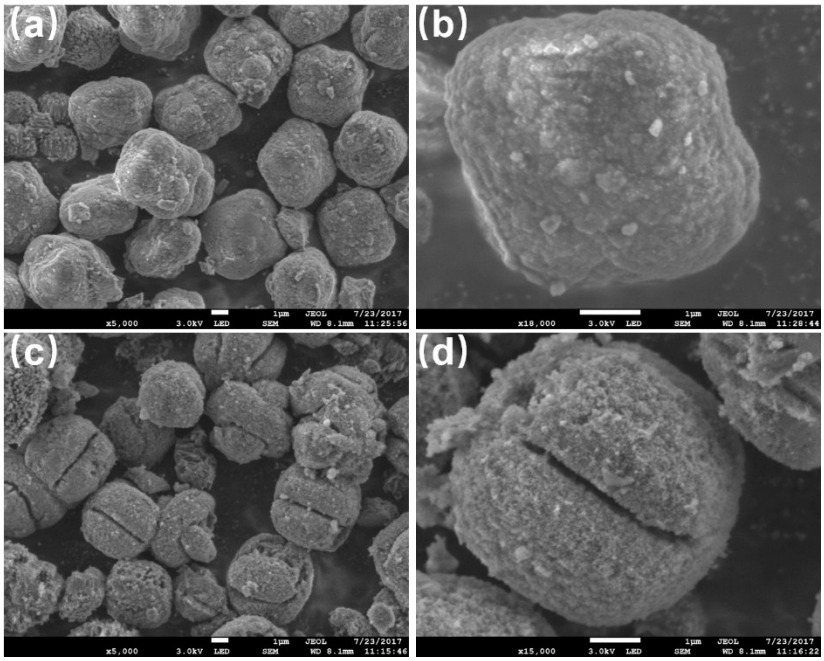

Figure S15. SEM images of zeolite samples after four catalytic cycles, (a, b) sample Z-Bulk, (c, d) sample of core-shell dual-structured Z-TPOAC-8 sample.

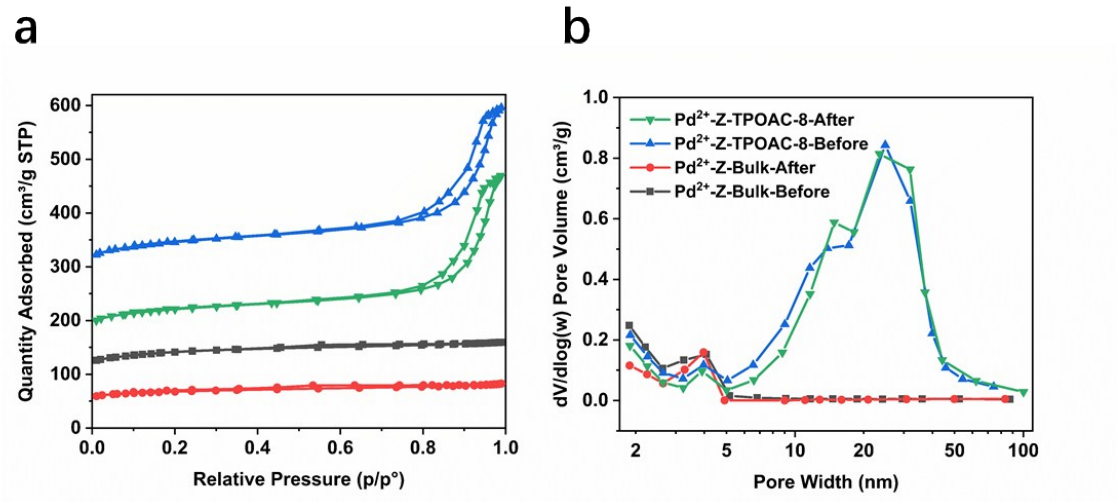

Figure S16. (a) N_2 adsorption-desorption isotherms of Pd^{2+}-exchanged ZSM-5 zeolites before and after the Suzuki–Miyaura cross coupling reactions. The isotherms for Pd^{2+}-Z-TPOAC-8-before, Pd^{2+}-Z-TPOAC-8-After, and Pd^{2+}-Z-Bulk-before were vertically offset by 240, 120, and 40 cm^3/g respectively. (b) BJH mesopore size distribution corresponding to the desorption branch. All samples were degassed at 100 °C for 4 h.

Table S6. Textural properties of Pd^{2+}-exchanged ZSM-5 zeolites before and after the Suzuki–Miyaura cross coupling reactions.

Sample	Surface Area (m^2 / g)			Pore Volume (cm^3 / g)		
	S_{total}[a]	S_{micro}[b]	S_{ext}[c]	V_{total}[d]	V_{micro}[e]	V_{meso}[f]
Pd^{2+}-Z-Bulk-Before	303	177	127	0.18	0.10	0.08
Pd^{2+}-Z-Bulk-After	213	140	61	0.13	0.08	0.05
Pd^{2+}-Z-TPOAC-8-Before	328	143	186	0.55	0.08	0.47
Pd^{2+}-Z-TPOAC-8-After	310	151	159	0.53	0.08	0.45

[a]BET surface area.

[b]*t*-Plot micropore surface area.

[c]*t*-Plot external surface area.

[d]Total pore volume of pores calculated at P/P_o = 0.98

[e]*t*-Plot micropore volume.

[f]$V_{meso} = V_{total} - V_{micro}$