Supplementary Information

POSS-based Meso-/macro-porous Covalent Networks: Supporting and Stabilizing Pd for Suzuki-Miyaura Reaction at Room Temperature

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Table S1. CHN elemental analysis and BET surface areas of samples POSS-TPA_x.

Sample	N (%)	C (%)	H (%)	S_{BET} (m^2/g)	Pore volume (m^3/g)	Pore size (nm)	Molar ratio POSS/PDA
POSS-TPA_a	8.88	43.08	8.16	206	1.11	21.5	1/2.7
POSS-TPA_b	8.85	47.25	8.42	151	0.89	23.5	1/2.8
POSS-TPA_c	8.80	48.83	8.30	144	1.12	31.3	1/2.9
POSS-TPA_d	8.40	50.75	8.24	120	0.61	20.2	1/3.3

Table S2. Suzuki coupling of bromobenzene with phenylboronic acid over catalyst Pd/POSS-TPA_a.

Entry	Catalyst amount (g)	Yield[a] (%)		TOF[b]
		10 min	30 min	
1	0.005	17	49	1133
2	0.01	90	92	3033
3	0.015	91	93	2000
4	0.02	92	99	1533

Reaction conditions: phenylboronic acid (1.5 mmol), bromobenzene (1 mmol), Na_2CO_3 (0.15 g), deionized water (3 mL) and ethanol (3 mL), room temperature. [a] The yield of product. [b] TOF = [mol product]/([mol Pd][reaction time 1/6 h]).

Table S3. The catalytic performance of Pd/POSS-TPA_a for the Suzuki coupling reaction with different phenylboronic acid/bromobenzene molar ratio.

Entry	Phenylboronic acid/bromobenzene molar ratio	Yield[a] (%)		TOF[b]
		10 min	30 min	
1	1.1:1	80	87	1333
2	1.3:1	81	92	1349
3	1.5:1	92	98	1533

Reaction conditions: bromobenzene (1 mmol), Na_2CO_3 (0.15 g), deionized water (3 mL) and ethanol (3 mL), catalyst (0.02 g, 0.0036 mmol), room temperature. [a] The yield of product. [b] TOF = [mol product]/([mol Pd][reaction time 1/6 h]).

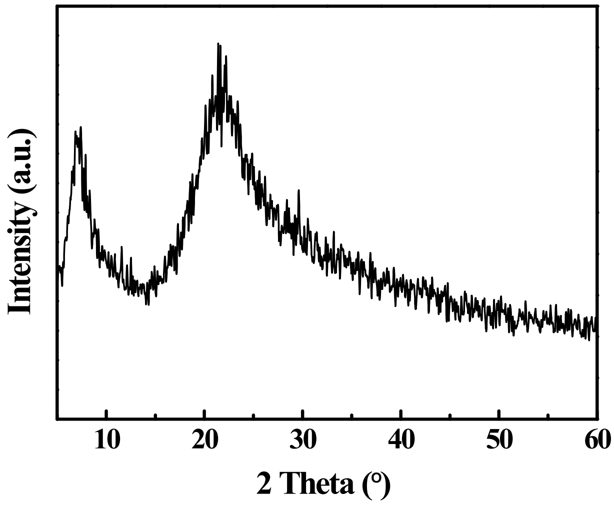

Figure S1. XRD pattern of POSS.

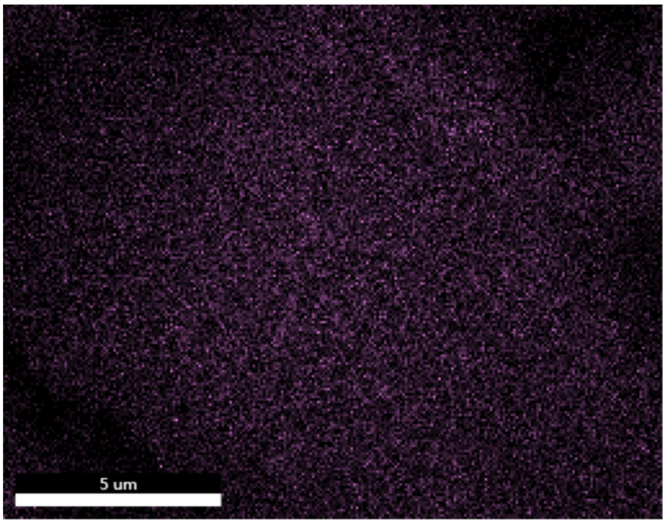

Figure S2. EDS elemental mapping of Si element for POSS-TPA_a.

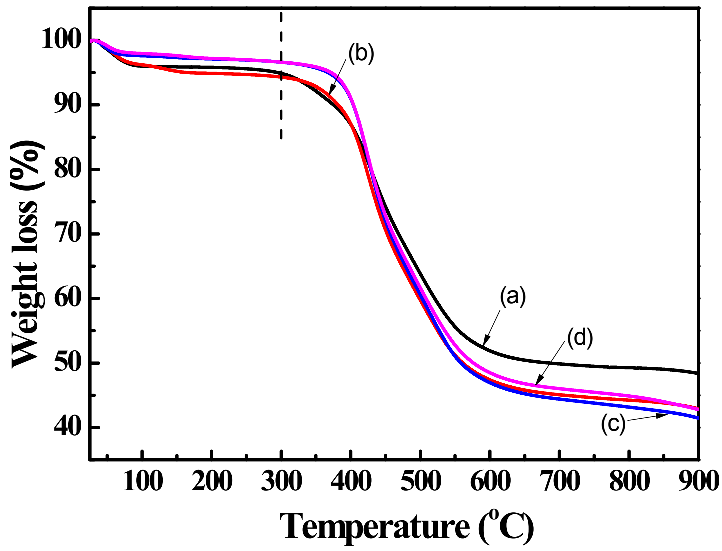

Figure S3. TG curves of (a) POSS-TPA$_a$, (b) POSS-TPA$_b$, (c) POSS-TPA$_c$, and (d) POSS-TPA$_d$.

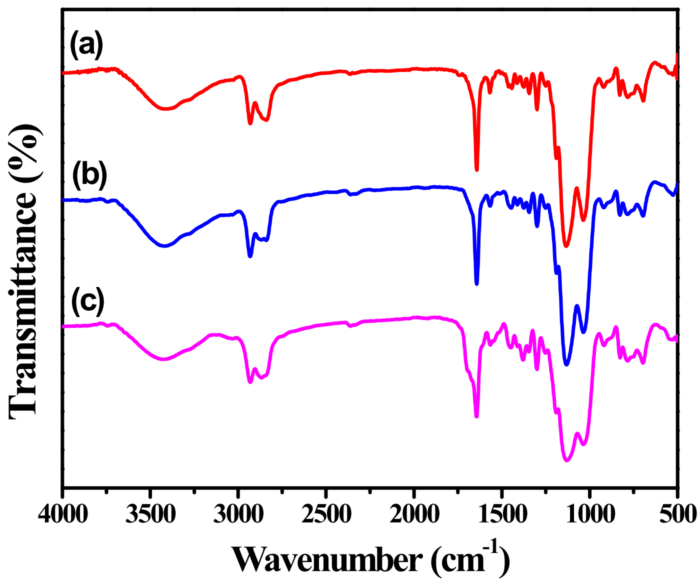

Figure S4. FT-IR spectra of (a) POSS-TPA$_b$, (b) POSS-TPA$_c$, and (c) POSS-TPA$_d$.

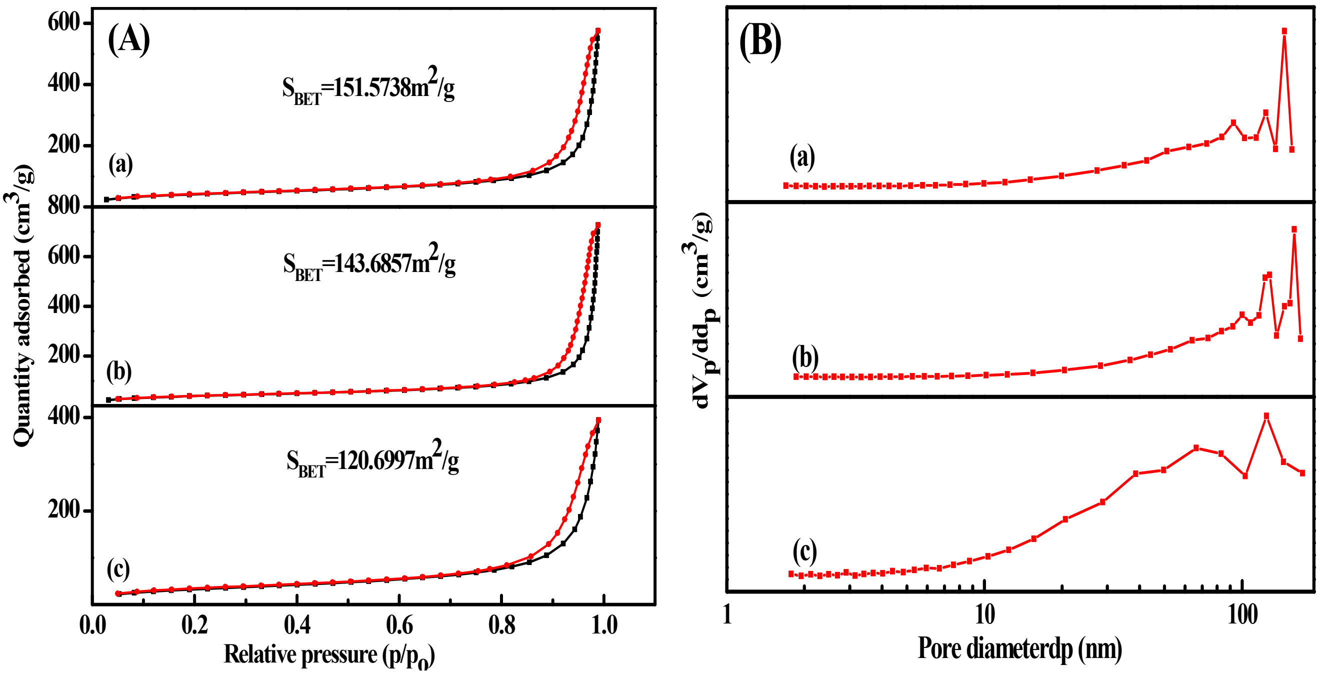

Figure S5. (A) Nitrogen adsorption–desorption isotherms and (B) BJH pore size distributions of (a) POSS-TPA$_b$, (b) POSS-TPA$_c$, and (c) POSS-TPA$_d$.

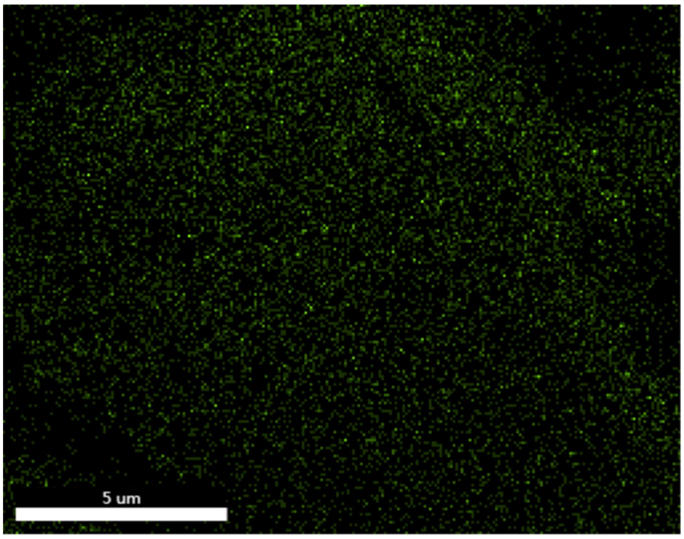

Figure S6. EDS elemental mapping of Pd element for Pd/POSS-TPA$_a$.

Table S4 Comparison of the catalytic efficiency of Pd/POSS-TPA$_a$ with previously reported catalysts.

Entry	Catalyst	Reaction conditions	Yield(%)	TOF(h^{-1})	Ref. (year)
1	Fe_3O_4@C–Pd@mCeO_2 (Pd 3.05 wt%)	Bromobenzene (1.0 mmol), Phenylboronicacid (1.2 mmol), K_2CO_3 (2.0 mmol), 5.0 mL ETOH/H_2O (1:1) ,80°C, 3h	95	116.3	1(2015)
2	Pd@Im–Phos–SiO_2@Fe_3O_4 (Pd 0.3 mol%)	Bromobenzene (1.0 mmol), Phenylboronicacid (1.5 mmol), K_2CO_3 (1.5 mmol), 2.0 mL ETOH/H_2O (1:1), 60 °C, 18h	90	16.67	2(2016)
3	Ionic liquid-tagged palladium complex (Pd 0.1 mol%)	Bromobenzene (1.0 mmol), Phenylboronicacid (1.2 mmol), K_2CO_3 (2.0 mmol), 5.0 mL H_2O, r.t. 50min	76	912	3(2014)
4	Bisoxazoline/Pd composite microsphere (Pd 0.1 mol%)	Bromobenzene (1.0 mmol), Phenylboronicacid (1.0 mmol), K_2CO_3 (2.0 mmol), 5.0 mL H_2O/PEG400 (10:1), 70°C, 4h	98	245	4(2015)
5	Pd/C (Pd 0.7 mol%)	Bromobenzene (2.0 mmol), Phenylboronicacid (2.5 mmol), KOH (8.0 mmol), NaCl (6.0 g), 6.0 mL Di-n-butyl ether, 100°C, 1h	24.7	35.2	5(2014)
6	Pd/bentonite (Pd 0.06 mol%)	Bromobenzene (0.5 mmol), Phenylboronicacid (0.6 mmol), K_2CO_3 (1.0 mmol), 5.0 mL MeOH, r.t. 5h	95	316	6(2013)
7	Pd/UiO-66 (Pd 0.59 mol%)	Bromobenzene (0.5 mmol), Phenylboronicacid (0.6 mmol), Na_2CO_3 (1.0 mmol), 6.0 mL ETOH/H_2O (1:2), 80°C, 2h	100	86	7(2016)
8	Pd/COF-LZU1 (Pd 0.5 mol %)	Bromobenzene (1.0 mmol), Phenylboronicacid (1.5 mmol), K_2CO_3 (2.0 mmol), 4.0 mL p-xylene, 150°C, 3h	97	64.67	8(2011)
9	HMMS–salpr–Pd (Pd 1mol%)	Bromobenzene (0.5 mmol), Phenylboronicacid (0.6 mmol), K_2CO_3 (1.0 mmol), 6.0 mL ETOH/H_2O (1:1), 70 °C, 6h	92	16.25	9(2015)
10	Fe_3O_4/PPy–Pd (Pd 1 mol%)	Bromobenzene (0.5 mmol), Phenylboronicacid (0.75 mmol), K_2CO_3 (1.0 mmol), 5.0 mL H_2O, 70°C, 8h	96.5	12.06	10(2015)
11	PdNP-2 (Pd 0.001 mol%)	Bromobenzene (1.0 mmol), Phenylboronicacid (1.5 mmol), K_3PO_4 (2.0 mmol), 10.0 mL ETOH/H_2O (1:1), 80°C, 24h	89	3708	11(2016)
12	Wool–Pd (Pd 0.45 mol %)	Bromobenzene (0.2 mmol), Phenylboronicacid (0.22 mmol), K_2CO_3 (0.3 mmol), 5.0 mL H_2O, 75°C, 3h	85	62.9	12(2012)
13	Pd/bentonite (Pd 0.06 mol %)	Bromobenzene (0.5 mmol), Phenylboronicacid (0.6 mmol), K_2CO_3 (1.0 mmol), 5.0 mL MeOH, r.t. 5h	95	316.6	13(2013)
14	Pd@imine–SiO2 (Pd 0.463 mol%)	Bromobenzene (0.5 mmol), Phenylboronicacid (0.6 mmol), Na_2CO_3 (1.5 mmol), 4 ml iPrOH/H_2O (1:1), r.t. 1h	100	215.9	14(2015)
15	Pd/POSS-TPA$_a$ (Pd 0.36 mol %)	Bromobenzene (1 mmol), Phenylboronicacid (1.5 mmol), Na_2CO_3 (1.0 mmol), 6.0 mL ETOH/H_2O (1:1), r.t, 10 min	92	1533	Our work

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