Electronic Supplementary Information for

Visible Light-Driven Suzuki-Miyaura Reactions by Self-Supported Pd Nanocatalysts in the Formation of Stille Coupling-Based Photoactive Microporous Organic Polymers

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Fig. S1 Magnified TEM images of St-MOP@Pd-3.

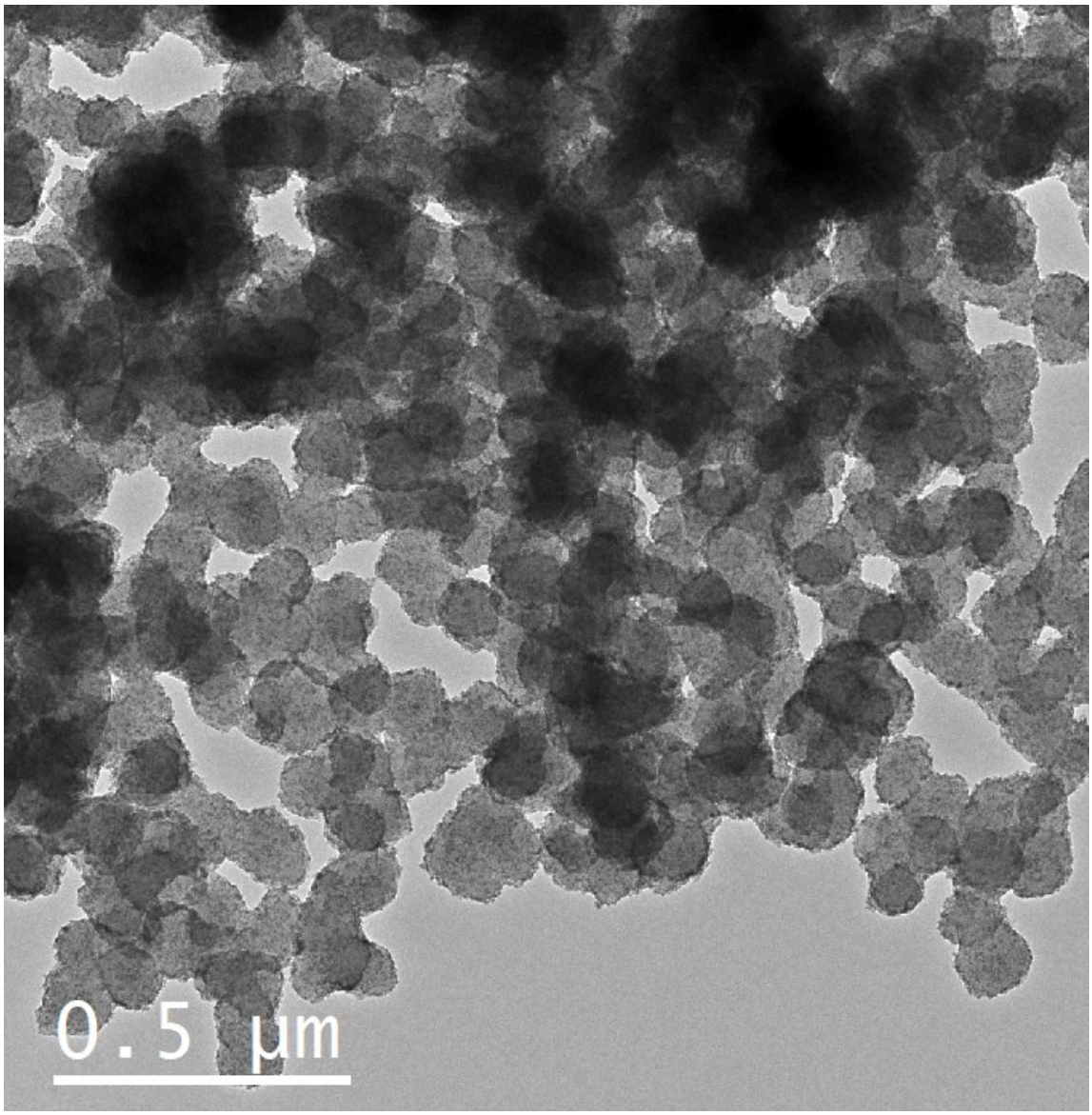
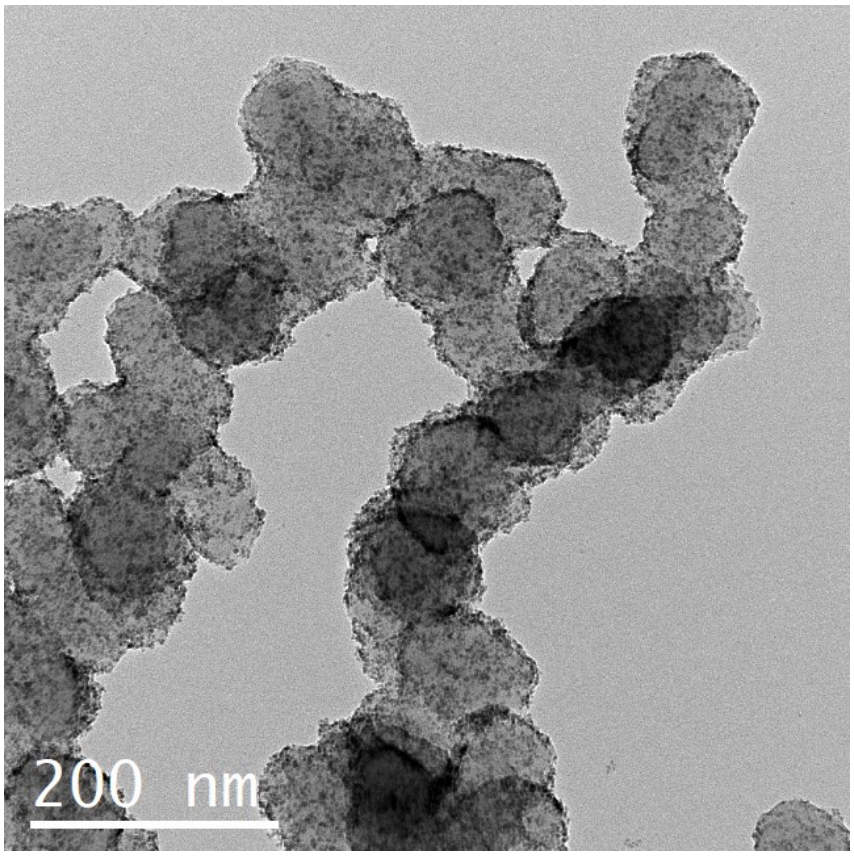


Fig. S1 Magnified TEM images of St-MOP@Pd-3 (continued).



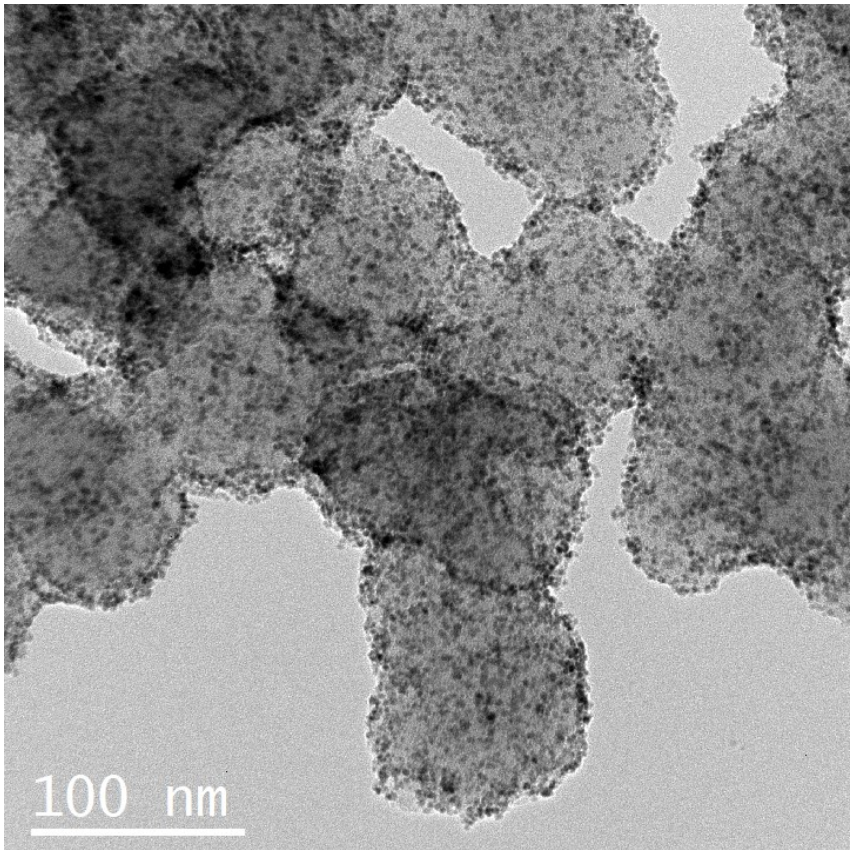


Fig. S2 XRD patterns of St-MOP@Pd materials.

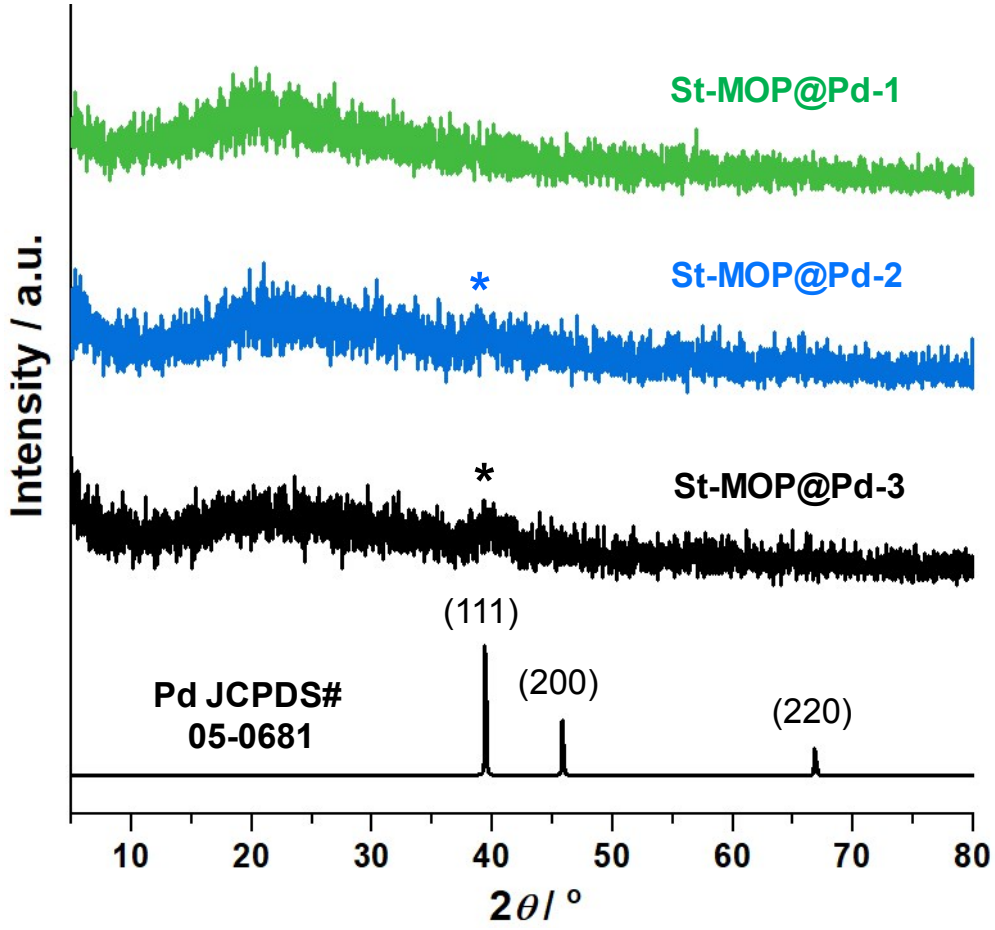


Fig. S3. Control photocatalytic reactions of St-MOP which was obtained through acid-etching of Pd Nps of St-MOP@Pd-2 and St-MOP/$(PPh_3)_4Pd$. Reaction conditions: St-MOP (8.3 mg), $(PPh_3)_4Pd$ (0.81 mg), 1-acetyl-4-bromobenzene (0.500 mmol), phenylboronic acid (0.625 mmol), K_2CO_3 (0.750 mmol), MeOH, 25°C, 5 h, white LED irradiation (0.9 mW/cm^2).

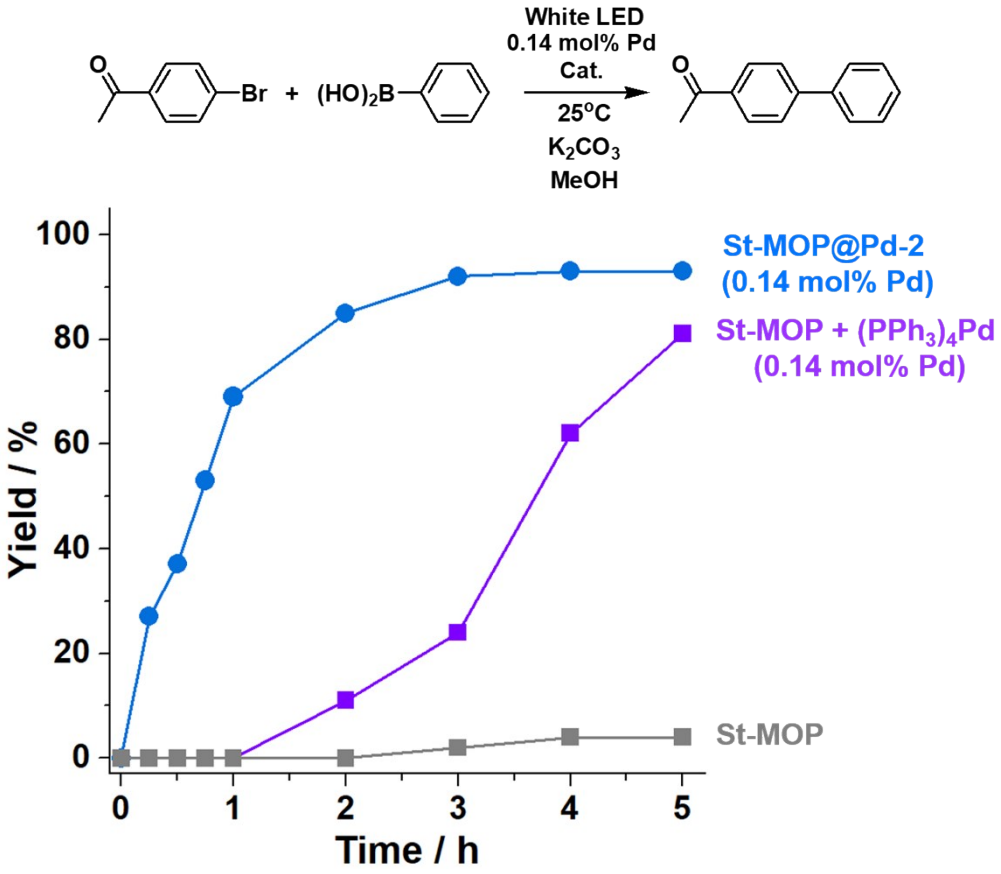


Fig. S4. A control photocatalytic reaction after removal of St-MOP@Pd-2 from the reaction mixture. Reaction conditions: St-MOP@Pd (9.0 mg, 0.14 mol% Pd), 1-acetyl-4-bromobenzene (0.500 mmol), phenylboronic acid (0.625 mmol), K_2CO_3 (0.750 mmol), MeOH, 25°C, 5 h, white LED irradiation (0.9 mW/cm^2).

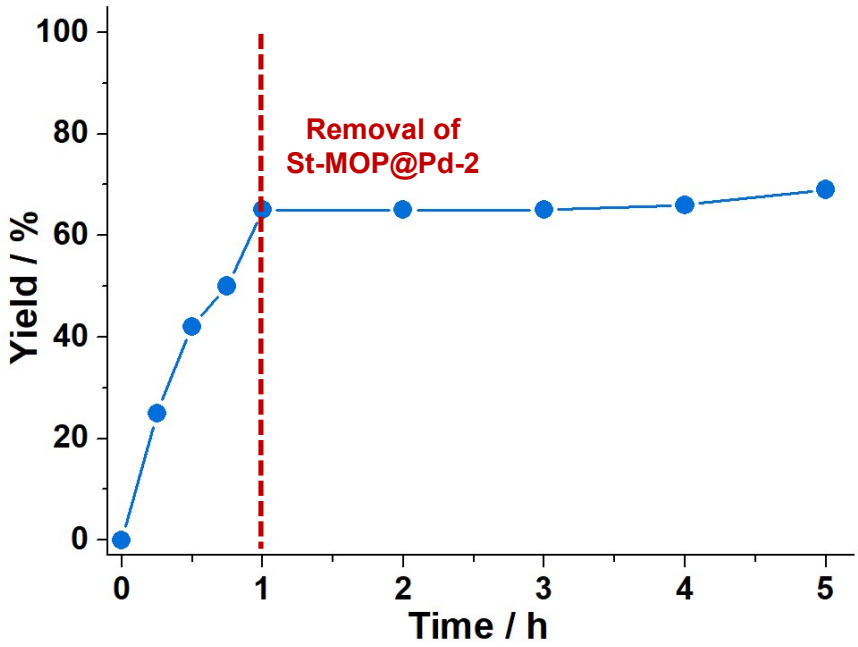


Fig. S5. The model systems of St-MOP and their optimized structures.

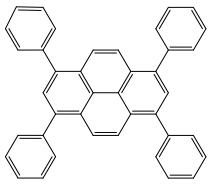
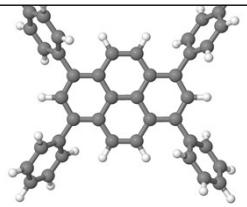
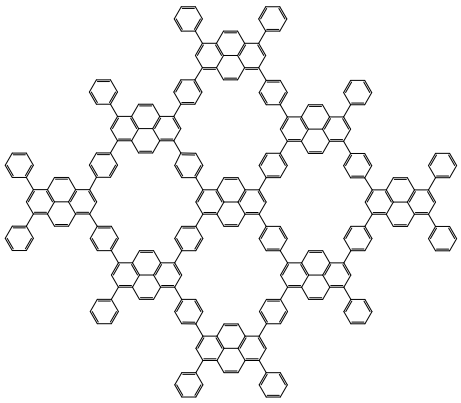
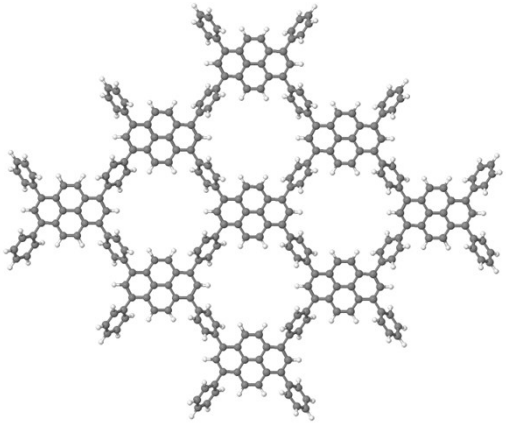
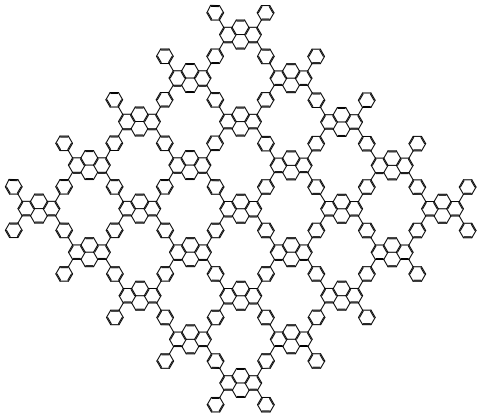
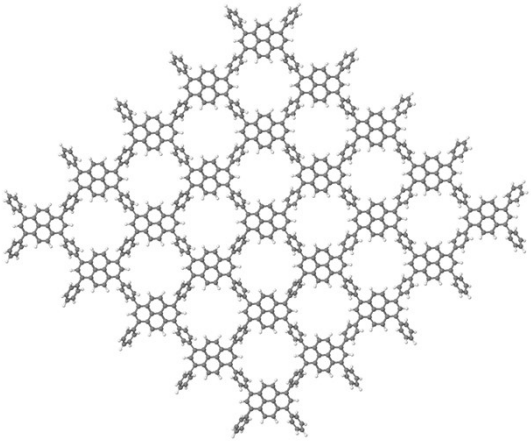
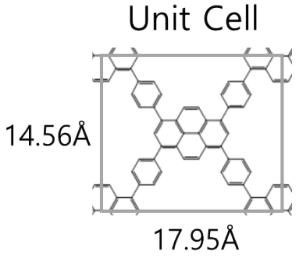
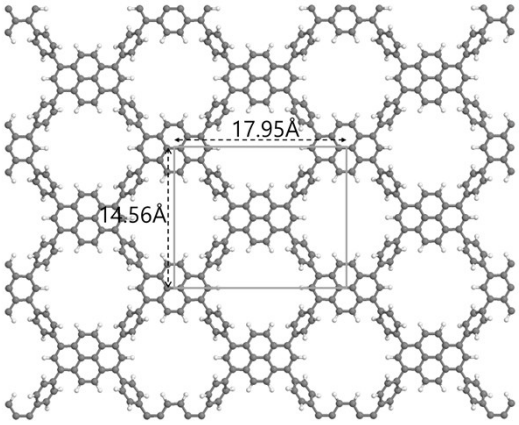
	Model systems of St-MOP	Optimized structures
I		
II		
III		
□		

Fig. S6 The cartesian coordinates (in Å) of optimized geometries for St-MOP model systems.

I

66

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H	14.14619688	4.41049469	-2.12864601
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H	11.67070082	2.28486643	0.29260377
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H	12.71697495	0.06319022	0.25231143
H	13.83971004	0.66826749	-3.83227365
C	13.51168780	10.17520907	-2.48768399
C	15.72505953	9.07728612	-2.63756214
C	11.44565301	11.53123261	-2.35607875
H	14.03706575	11.10725669	-2.64587271
C	16.59845967	8.67850954	-1.61933920
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C	10.43973562	11.80886027	-3.28766497
C	11.82892074	12.55385011	-1.48133624
C	17.97438487	8.80317545	-1.77431989
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H	15.60636792	9.91414167	-4.61120045
C	9.83720058	13.05933020	-3.33789251
H	10.14029990	11.04483951	-3.99209358
C	11.22689102	13.80387298	-1.53181056
H	12.59256135	12.35957193	-0.74028154
C	18.50287593	9.32671736	-2.95027714
H	18.63327947	8.49556203	-0.97377670
H	18.04650830	10.13387600	-4.88782682
C	10.21920453	14.08094297	-2.46171307
H	9.07369165	13.25358380	-4.07910189
H	11.52672111	14.56838671	-0.82802053
H	19.57327735	9.42204611	-3.07071630
C	0.80506055	7.40813279	-0.83569387
C	1.14399882	8.41651572	0.07302990
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C	-0.41860789	9.95792717	-0.95927714
H	0.80792524	10.42057172	0.74264912
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C	1.65936202	13.70693629	-1.58638276
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C	-3.22402071	14.98354270	-0.90638697
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C	-2.56471450	16.15547341	-1.07342167
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C	-6.63844406	12.84307755	0.84653125
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C	-7.46411504	12.17052605	-0.05973607
H	-7.49400782	11.11456187	-1.93030181
H	-7.06869244	13.26266995	1.74608483
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C	-1.13639792	18.73553246	-1.49984446
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C	-2.05883597	19.04980256	-2.50427358
C	-0.82994283	19.71239109	-0.54654748
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C	5.06772133	17.04628387	-3.05785480
H	3.03525242	17.30684159	-3.67313787
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C	-1.43350497	20.96469762	-0.59112370
H	-0.12348458	19.48224589	0.23969767
C	5.94762467	16.53908522	-2.09578141
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H	5.46465179	17.52290142	-3.94391386
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H	-3.36467002	20.52964080	-3.33851102
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H	-3.11381620	-0.09267194	-1.45048933
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C	12.29148737	9.50900457	-2.32998250
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C	13.67101125	9.47321047	-2.51800337
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C	16.40468166	8.95908918	-3.85917551
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H	12.75745244	11.65383061	-0.75030575
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III

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C	-3.38464661	-0.32999761	-0.57129267
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C	0.62122403	0.42018737	0.05938486
C	0.53575122	0.46002584	0.05982206
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C	0.70489200	0.46209809	0.05974290
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C	0.62002825	0.65915114	0.06064206
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C	0.45023249	0.57988385	0.05999364
C	0.36657063	0.53795382	0.06026075
C	0.36662808	0.46187102	0.05993661
C	0.70584305	0.29564289	0.05907316
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C	0.77180654	0.30103548	0.03657789
C	0.79991580	0.19923234	0.08204508
C	0.85024518	0.25641795	0.03685417
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C	0.95132529	0.15913775	0.05974510
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C	0.29978760	0.69934496	0.03770782
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C	0.22132182	0.74388920	0.03796364
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C	0.12005703	0.84088389	0.06073175
C	0.03557637	0.80367212	0.06045500
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C	0.36595340	0.29538487	0.05960566

C	**0.29989936**	**0.30069863**	**0.08207037**
C	**0.35040331**	**0.24352290**	**0.03701212**
C	**0.22138060**	**0.25619600**	**0.08182711**
C	**0.27187630**	**0.19898314**	**0.03677523**
C	**0.20580017**	**0.20438779**	**0.05922079**
C	**0.12024436**	**0.15904672**	**0.05913798**
C	**0.12116796**	**0.07988399**	**0.05949617**
C	**0.03581480**	**0.19633775**	**0.05931152**
C	**0.03569843**	**0.04001497**	**0.05979875**
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H	**0.77001086**	**0.43221771**	**0.05982656**
H	**0.53598250**	**0.24288227**	**0.05901700**
H	**0.76979498**	**0.56831439**	**0.05958202**
H	**0.53552815**	**0.75718664**	**0.06049312**
H	**0.67185327**	**0.23950664**	**0.09967985**
H	**0.76060775**	**0.33968607**	**0.01837613**
H	**0.81119071**	**0.16070901**	**0.10028089**
H	**0.89976943**	**0.26066776**	**0.01890374**
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H	**0.76016961**	**0.66021019**	**0.10116730**
H	**0.67166460**	**0.76098111**	**0.01999258**
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H	**0.81108531**	**0.83971059**	**0.01943800**
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H	**0.39910413**	**0.75998278**	**0.10090517**
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H	**0.25983043**	**0.83877161**	**0.10142356**
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H	**0.40002532**	**0.23919383**	**0.01910199**
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H	**0.26070469**	**0.16039122**	**0.01862382**
H	**0.03593761**	**0.25716247**	**0.05914363**
H	**0.26993760**	**0.06796435**	**0.06032473**

Fig. S7 XPS spectra of Pd 3d orbitals of St-MOP@Pd-2 before and after five successive visible light-driven Suzuki-Miyaura couplings. Reaction conditions: St-MOP@Pd-2 (9.0 mg, 0.14 mol% Pd), 1-acetyl-4-bromobenzene (0.500 mmol), phenylboronic acid (0.625 mmol), K_2CO_3 (0.750 mmol), MeOH, 25°C, 5 h, white LED irradiation (0.9 mW/cm^2).

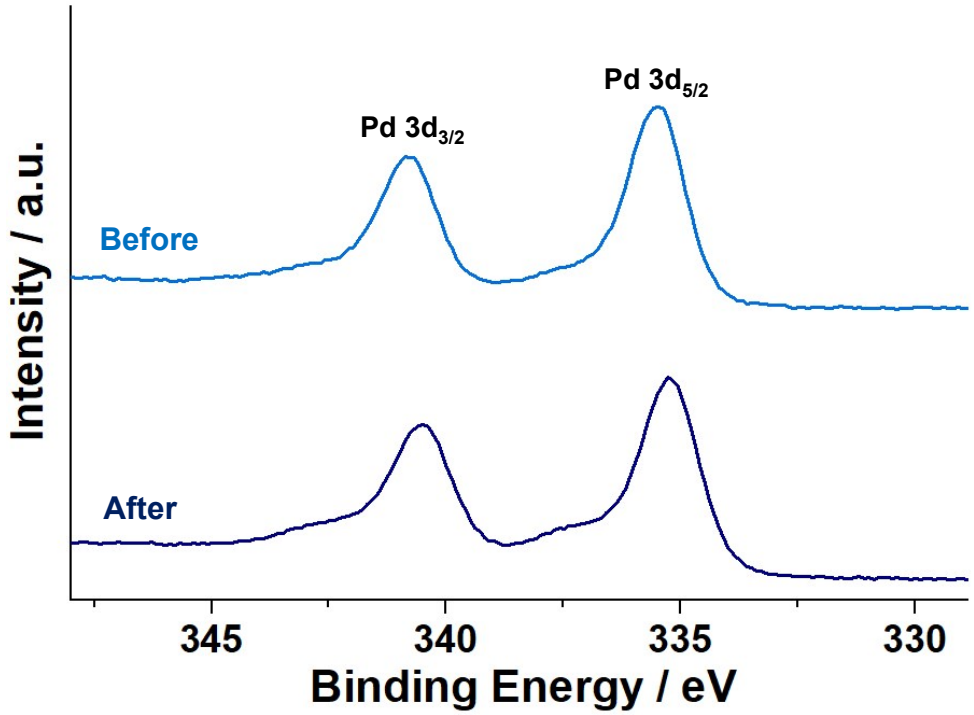
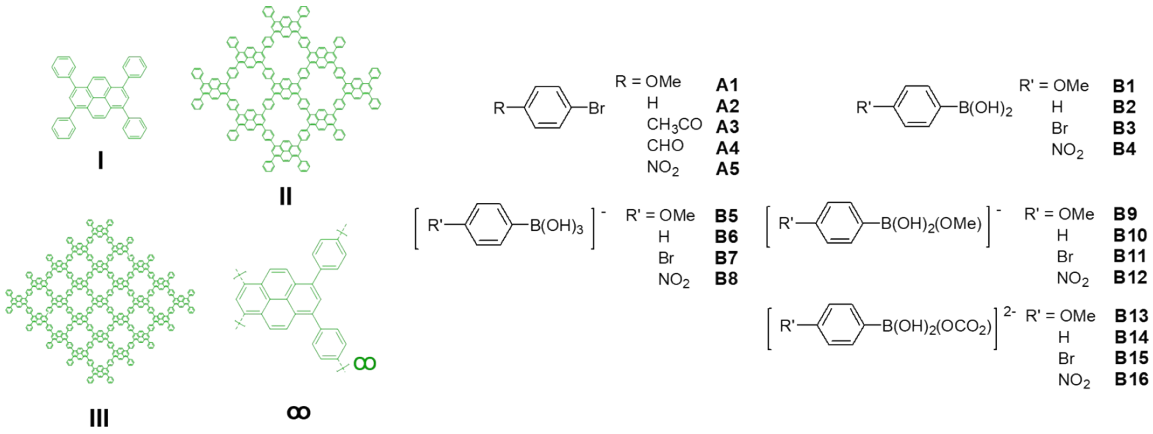


Table S1 Simulated energy levels of model systems of St-MOP, aryl bromides, aryl boronic acids, and aryl borates.



Systems	VB (eV)	CB (eV)
I	-5.50	-2.05
II	-5.41	-2.26
III	-5.40	-2.32
□	-5.60	-2.70
Compounds	HOMO (eV)	LUMO (eV)
A1	-6.31	-0.80
A2	-6.93	-0.83
A3	-7.23	-2.19
A4	-7.38	-2.44
A5	-7.74	-3.13
B1	-6.22	-0.64
B2	-6.96	-0.96
B3	-6.82	-1.26
B4	-7.78	-2.92
B5	-2.08	3.64
B6	-2.22	3.77
B7	-2.49	2.91
B8	-2.91	0.49
B9	-2.07	3.53
B10	-2.15	3.69
B11	-2.42	2.86
B12	-2.82	0.43
B13	2.32	6.09
B14	2.35	6.32
B15	2.11	4.91
B16	1.79	2.65

Table S2 Photocatalytic performance of the recent polymer@Pd materials for the visible light-driven Suzuki coupling in the literature.

Materials	Pd (mol%)	Aryl halide	Aryl boronic acid	Temp. (^{o}C)	Time (h)	Yield (%)	TON	TOF (h^{-1})	Ref
g-C_3N_4@Pd	1.87	Iodobenzene	Phenylboronic acid	25	1	97	52	52	1
Conjugated microporous poly(benzoxadiazole)-Pd Nps	0.56	1-Bromo-4-fluorobenzene	Phenylboronic acid	r.t.	4	96	171	43	2
Conjugated microporous poly(benzoxadiazole)-Pd Nps	0.56	1-Acetyl-2-bromobenzene	Phenylboronic acid	r.t.	16	76	136	8	2
Polydopamine-Pd Nps	0.56	Methyl 4-bromobenzoate	Phenylboronic acid	r.t.	2	95	170	85	3
Conjugated nanoporous polycarbazole-Pd Nps	0.50	1-Acethyl-4-chlorobenzene	Phenylboronic acid	r.t.	48	85	170	4	4
St-MOP@Pd-2	0.14	1-Acethyl-4-bromobenzene	Phenylboronic acid	25	3	92	657	219	This work

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