

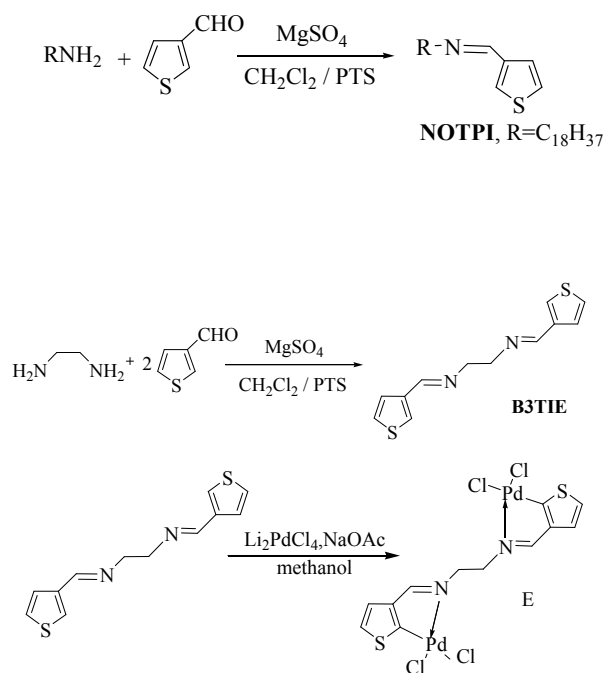
Supporting Information

Electrochemical polymerized and assembled cyclopalladated bi-thiophene imine for catalyzing coupling reaction: A modern strategy to enhancing catalytic activity

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Scheme S1 Synthesis of NOTPI, B3TIE and CPDTDI (E)

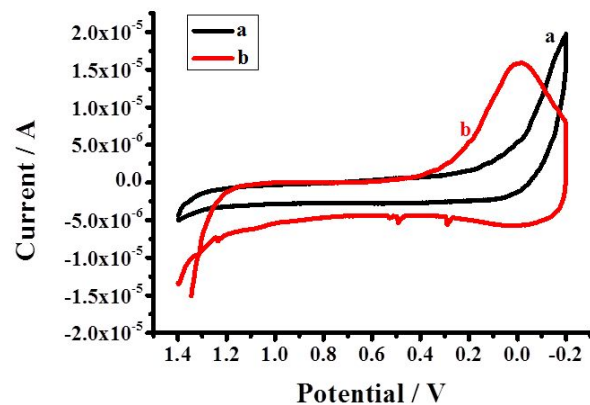


Figure S1 Cyclic voltammograms of (a) hydrophilic ITO and (b) **B3TIE** monolayer. (SP=12mN/m)

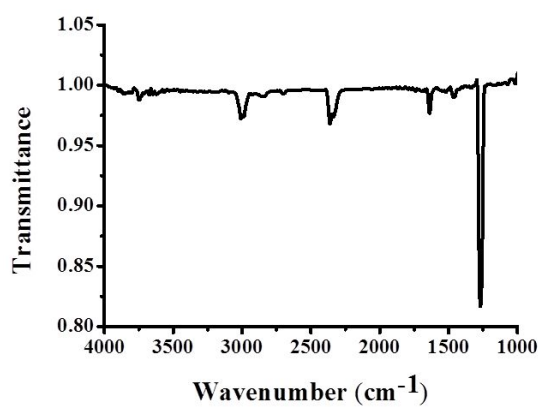


Figure S2 IR spectrum of two-layer LB films of **B3TIE** transferred onto CaF₂. (SP = 12 mN/m)

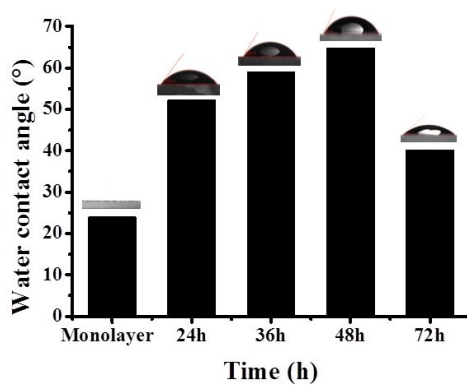


Figure S3 WCA histogram of different self-assembly time of **SABM**

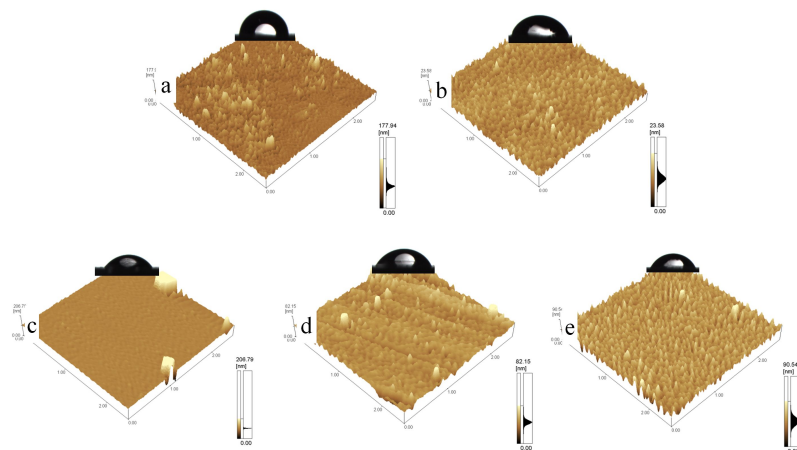


Figure S4 AFM images of **SABM** on silicon at (a) 8 mN/m, (b) 10 mN/m, (c) 12 mN/m, (d) 14 mN/m and (e) 16 mN/m.

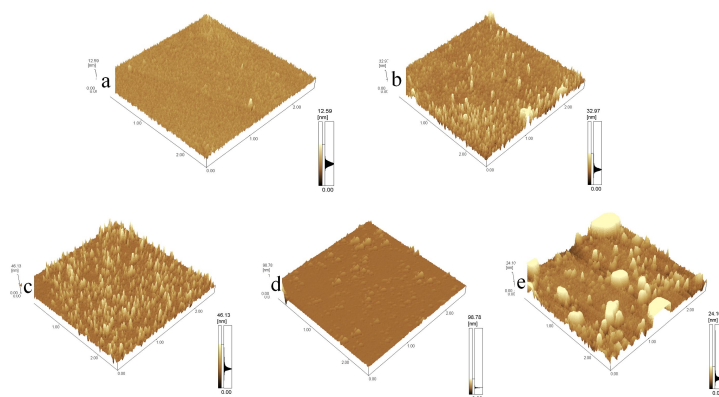


Figure S5 AFM images of **SABM** at different time (a, 0 h; a, 24h; c, 36h; d, 48h; e, 72h).

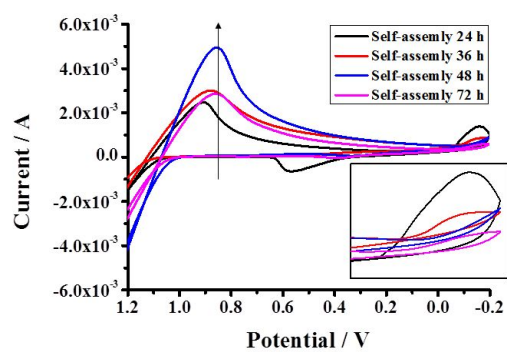


Figure S6 Cyclic voltammograms of different assembly time of **SABM** on ITO electrode.

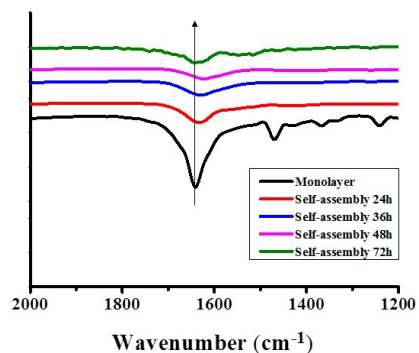


Figure S7 Infrared spectra of different assembly time of SABM on CaF₂ with Li₂PdCl₄

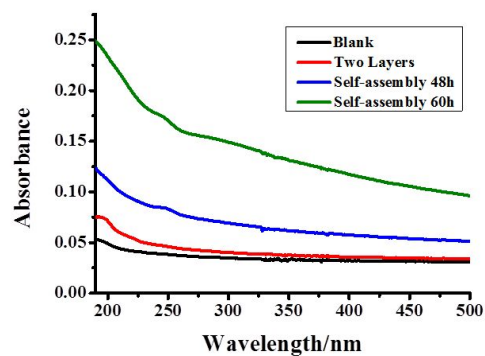


Figure S8 UV spectra of SABM for 48h and 60h.

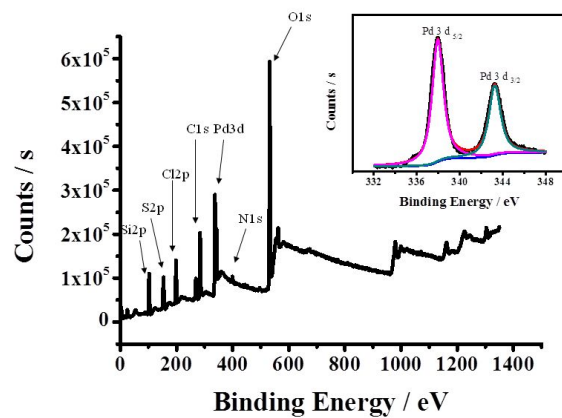


Figure S9 XPS spectra of SABM for 48h

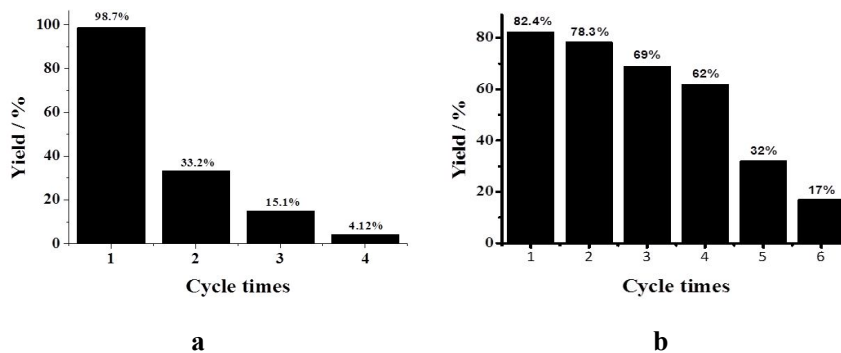


Figure S10 Yields obtained by SABM with (a) and without stirring (b)

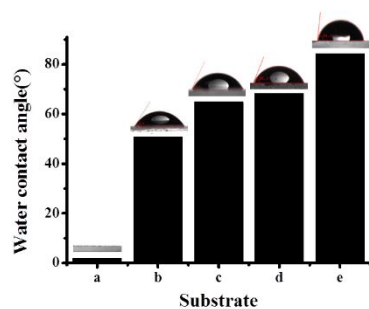
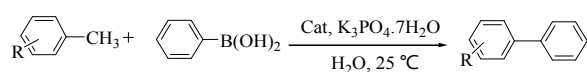


Figure S11 Water contact angles of a: hydrophilic silicon, b: **B3TIE** monolayer, c: **ECP B3TIE** monolayer, d: **SABM** and e: **ECP-SABM**.

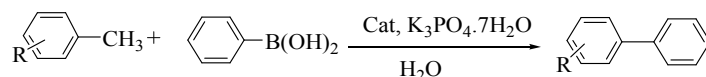
Table S1 Effect of **SABM** deposited at different SP for Suzuki coupling reaction



Entry	Surface pressure (mN/m)	Isolated yield (%)
1	8	26.7
2	10	23.8
3	12	57.0
4	14	11.7
5	16	25.2

Reaction conditions: PhB(OH)₂ (0.30 mmol), 4-bromotoluene (0.25 mmol), Base (0.30 mmol), H₂O (10 mL), TBAB (0.3 mmol). Isolated yield, based on the product. Reaction time 24 h.

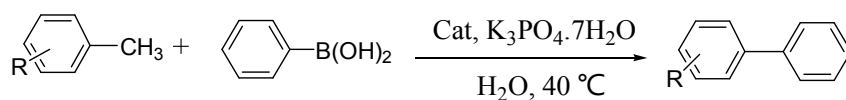
Table S2 Selection of condition for Suzuki coupling reaction



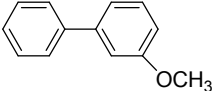
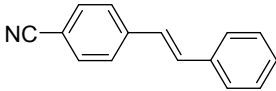
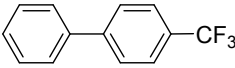
Entry	Reaction time (h)	Self-assembly time (h)	T (°C)	Isolated yield (%)	TON
1	24	24	25	57	4563
2	36	48	40	50.4	4114
3	24	48	40	73.6	6007
4	48	48	50	42.2	3444
5	48	24	40	68	5550
6	48	48	40	82.4	6726
7 ^a	48	48	40	76.4	5840

Reaction conditions: PhB(OH)₂ (0.30 mmol), 4-bromotoluene (0.25 mmol), Base (0.30 mmol), H₂O (8 mL), TBAB (0.3 mmol). Deposition SP: 12mN/m; a: **SAMB** deposited at 16 mN/m.

Table S3 Substrate expansion for Suzuki coupling reaction



Entry	ArX	Product	Isolated yield (%)
1	<i>p</i> -CH ₃ C ₆ H ₄ Br		82.4
2	<i>p</i> -CH ₃ OC ₆ H ₄ Br		85.6
3	<i>p</i> -CF ₃ C ₆ H ₄ Br		88
4	<i>p</i> -CHOC ₆ H ₄ Br		62.4
5	<i>p</i> -NO ₂ C ₆ H ₄ Br		81.2
6	<i>o</i> -CH ₃ C ₆ H ₄ Br		82.8
7	<i>o</i> -CHOC ₆ H ₄ Br		87.8
8	<i>m</i> -CHO-C ₆ H ₄ Br		62.4
9	<i>o</i> -COOCH ₃ -C ₆ H ₄ Br		99
10	<i>m</i> -CH ₃ C ₆ H ₄ Br		86.4

11	<i>p</i> -CNC ₆ H ₄ Br		81.7
12	<i>m</i> -CNC ₆ H ₄ Br		62.8
13	<i>o</i> -CNC ₆ H ₄ Br		13.9

Reaction conditions: PhB(OH)₂ (0.30 mmol), ArBr (0.25 mmol), Base (0.30 mmol), H₂O (8 mL), TBAB (0.3 mmol), 40°C for 48h.

The reaction of substrates with a strongly electron repulsive group, such as *p* or *m*-substituted of bromobenzene with styrene gave good yields (Table S3, entries 1-2, 10). Good yields were also obtained with strongly electron withdrawing group of *p* or *m*, *o*-substituted of bromobenzene (Table S3, entries 3, 5-7, 9-11). The yields were moderate with withdrawing or repulsive group in *p* or *m*-position (Table S3, entries 4, 8, 12). In the reaction system, the yield of 2-bromo-benzonitrile was only 13% because of steric effect (Table S3, entries 13).

Table S4 Content of palladium after recycling with **SABM**

Entry	0	1	2	3	4
Substrate Pd count ($\times 10^{-7}$ mmol)	7.09	6.09	5.31	4.61	3.68