Supporting Information for

Porous organic polymer with in situ generated palladium nanoparticle as a phase-transfer catalyst for Sonogashira cross-coupling reaction in water

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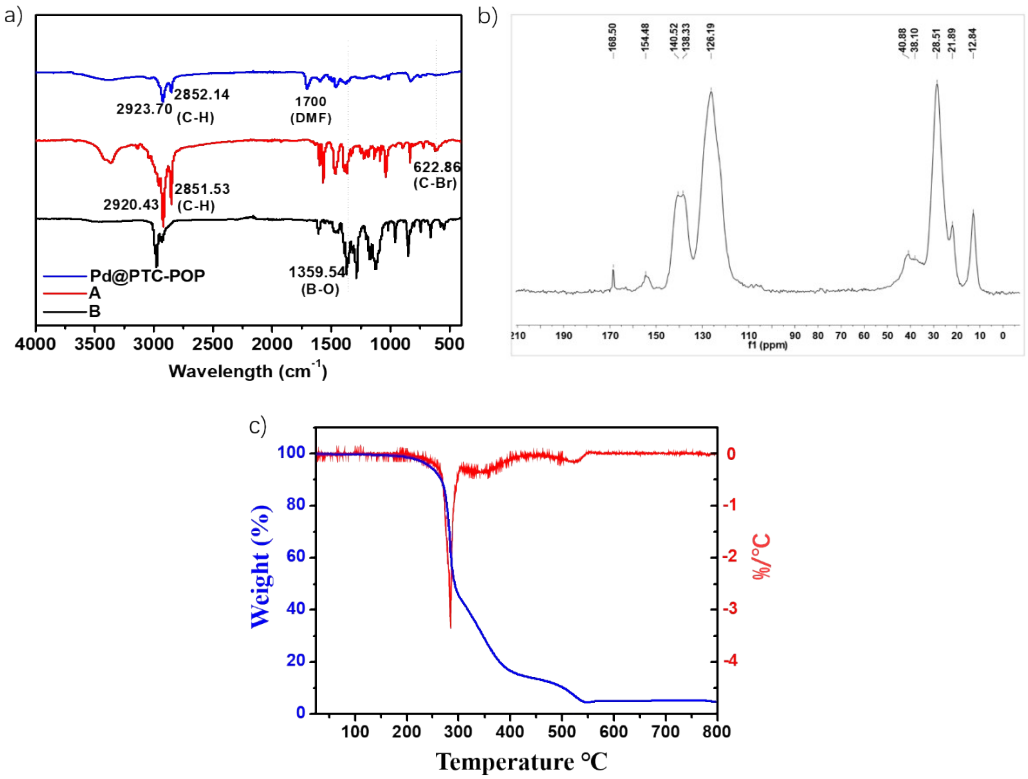


Fig. S1 IR spectrum of **Pd@PTC-POP**. Solid-state ^{13}C NMR of **Pd@PTC-POP**. The peak at 1700 cm^{-1} should be ascribed to the residual DMF in the POP during preparation process, which was further confirmed by the solid-state ^{13}C NMR (ca. 169 ppm) and the TGA analysis (ca. 3% weight loss below 220°C).

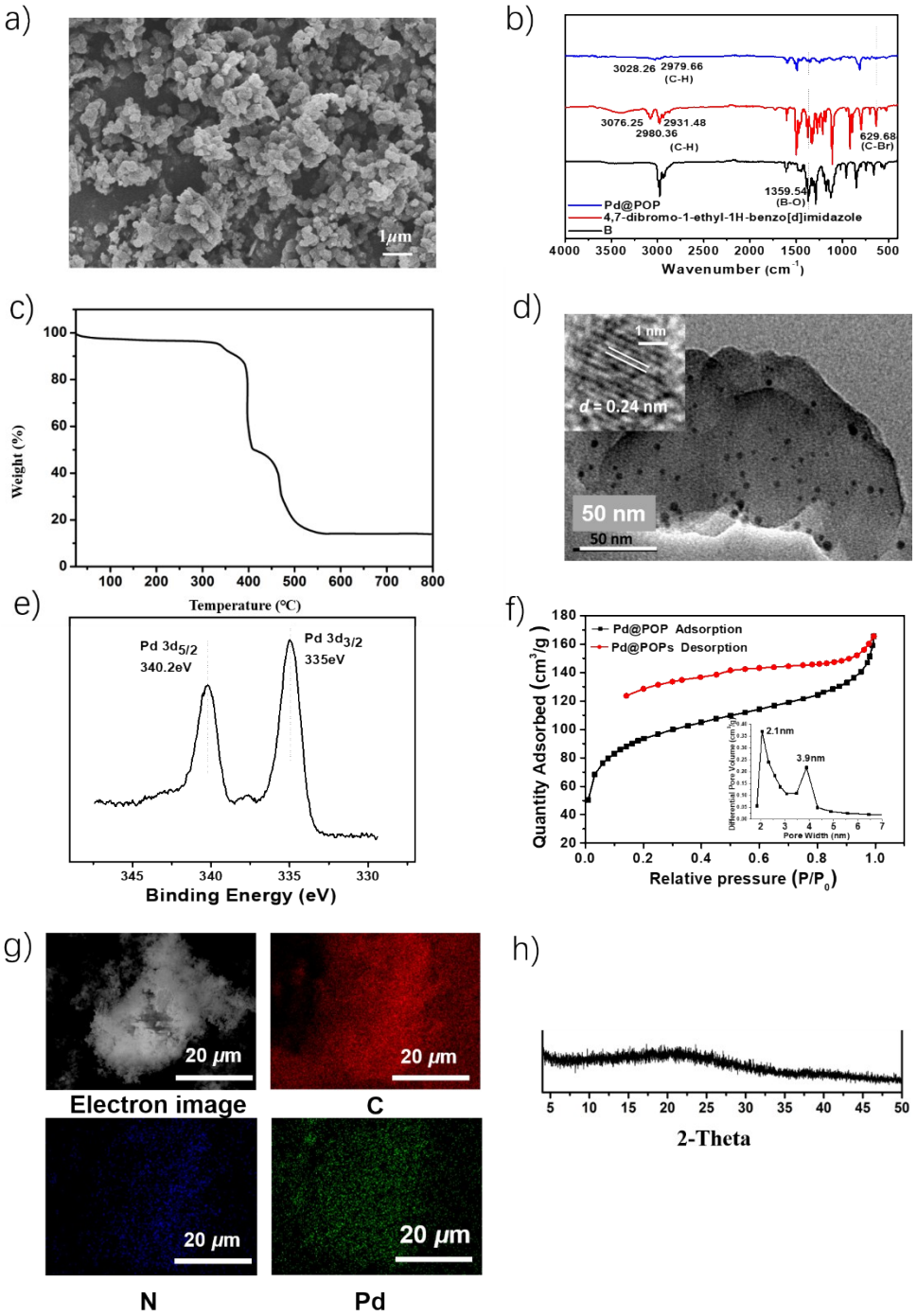


Fig. S2 a) SEM image of **Pd@POP**. It was obtained as the irregular granular particles. b) IR spectra of **Pd@POP** and its precursors. It showed that the characteristic peaks at ca.1359 cm^{-1} and 629 cm^{-1} for the B-O and C-Br species significantly decreased after the coupling reaction, meanwhile the bands at 3028 and 2979 cm^{-1} for the alkyl groups appeared, indicating the formation of **Pd@PTC-POP**. c) TGA trace of **Pd@POP**. No significant weight loss was observed before ca. 300 °C. d) HRTEM image of **Pd@POP**. The Pd NPs (2–6 nm) were homogeneously distributed in the POP matrix, and the atomic lattice fringes with an interplanar spacing of 0.24 nm for face-centred cubic (fcc) Pd NPs were clearly observed. e) XPS spectrum of **Pd@POP**, indicating the valence of Pd species in the POP is zero. f) N_2 sorption isotherm of **Pd@POP**. Its surface area is 331.9 $m^2\ g^{-1}$. Its pore size distribution plot is shown as the inset. g) SEM-EDX spectrum of **Pd@POP**. h) PXRD pattern of **Pd@POP**, suggesting its amorphous nature.

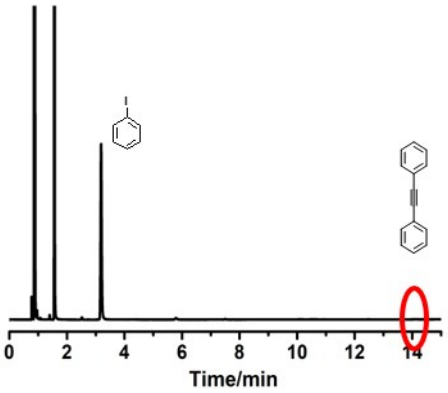
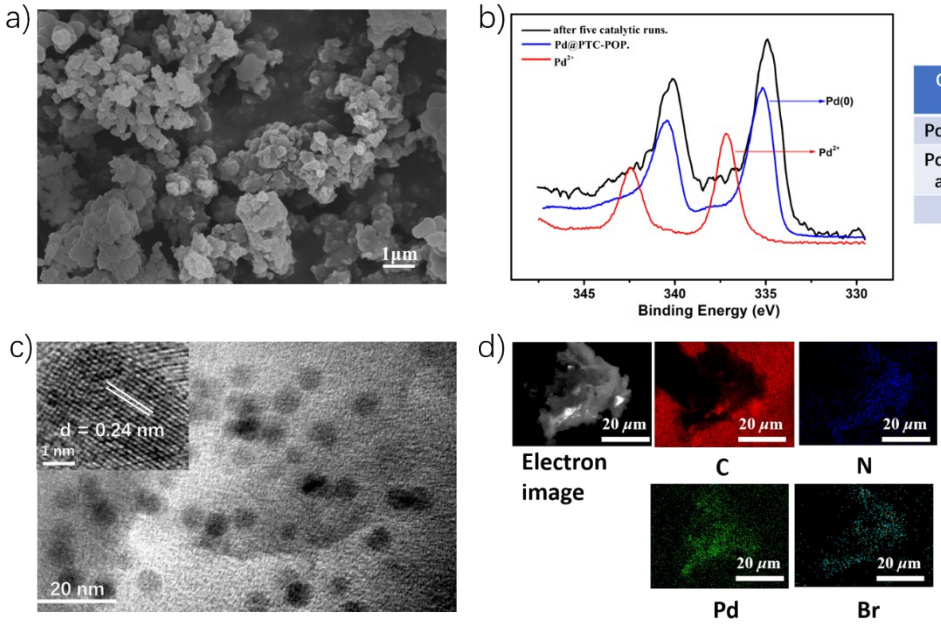


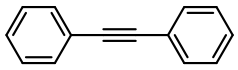
Fig. S3 GC analysis for the model Sonogashira coupling reaction between iodobenzene and phenylacetylene catalyzed by **PTC-POP** (for Table 1, entry 11).



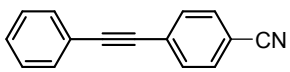
Compound	Pd $3d_{5/2}$ (eV)	Pd $3d_{3/2}$ (eV)
Pd@PTC-POP	340.4	335.2
Pd@PTC-POP after 5 runs	340.1	334.9
$Pd(NO_3)_2$	342.5	337.2

Fig. S4 SEM (a), XPS (b), HRTEM (c) and SEM-EDX (d) spectra of the **Pd@PTC-POP** after five catalytic runs.

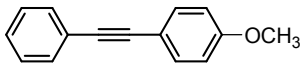
Product characterization (for Table 2)



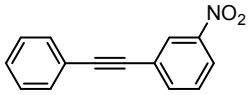
3a: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 (dd, *J* = 7.3, 2.3 Hz, 4H), 7.46-7.31 (m, 6H).; ^{13}C NMR (101 MHz, $CDCl_3$) δ 131.6 (4C), 128.4 (4C), 128.3 (2C), 123.3 (2C), 89.4 (2C).; HRMS (ESI-TOF) calcd for $C_{14}H_{10}$ ([M+H]$^+$) 179.0863, found 179.0891.



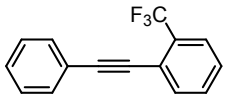
3b: 1H NMR (400 MHz, $CDCl_3$) δ 7.66-7.62 (m, 2H), 7.62-7.58 (m, 2H), 7.55 (dd, *J* = 6.5, 3.2 Hz, 2H), 7.39 (d, *J* = 2.2 Hz, 2H), 7.37 (d, *J* = 1.4 Hz, 1H).; ^{13}C NMR (101 MHz, $CDCl_3$) δ 132.1 (2C), 132.1 (2C), 131.8 (2C), 129.2, 128.5 (2C), 128.3, 122.2, 118.6, 111.5, 93.8, 87.7.; HRMS (ESI-TOF) calcd for $C_{15}H_9N$ ([M+Na]$^+$) 226.0635, found 226.0622.



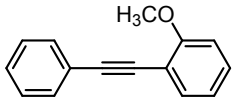
3c and 3i: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 (d, *J* = 2.0 Hz, 1H), 7.53 (d, *J* = 1.5 Hz, 1H), 7.52 (s, 1H), 7.49 (s, 1H), 7.40-7.33 (m, 3H), 6.92 (s, 1H), 6.90 (s, 1H), 3.86 (s, 3H).; ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.6, 133.1 (2C), 131.5 (2C), 128.3 (2C), 128.0, 123.6, 115.4, 114.0 (2C), 89.4, 88.1, 55.3.; HRMS (ESI-TOF) calcd for $C_{15}H_{12}O$ ([M + Na]$^+$) 231.0788, found 231.0766.



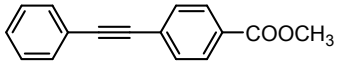
3d: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.34-8.28 (m, 1H), 8.11 (ddd, *J* = 8.3, 2.2, 1.0 Hz, 1H), 7.78-7.72 (m, 1H), 7.48 (dt, *J* = 13.0, 5.2 Hz, 3H), 7.31 (dd, *J* = 4.4, 2.3 Hz, 3H).; ^{13}C NMR (101 MHz, $CDCl_3$) δ 148.2, 137.2, 131.8 (2C), 129.4, 129.1, 128.5 (2C), 126.4, 125.2, 122.9, 122.2, 91.9, 86.9.; HRMS (ESI-TOF) calcd for $C_{14}H_9NO_2$ ([M + Na]$^+$) 246.0533, found 246.0520.



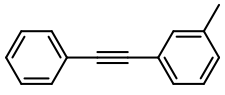
3e: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59 (t, *J* = 7.4 Hz, 2H), 7.50-7.45 (m, 2H), 7.42 (t, *J* = 7.6 Hz, 1H), 7.33 (d, *J* = 7.8 Hz, 1H), 7.30-7.25 (m, 3H).; ^{13}C NMR (101 MHz, $CDCl_3$) δ 133.7, 131.7 (2C), 131.4, 128.8, 128.4 (2C), 127.9, 126.7, 125.9, 125.0, 122.7, 122.3, 121.6, 94.9, 85.4, 29.7.; HRMS (ESI-TOF) calcd for $C_{15}H_9F_3$ ([M+Na]$^+$) 269.0556, found 269.0530.



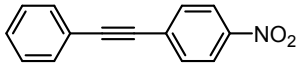
3f: ^{1}H NMR (400 MHz, CDCl3) δ 7.56 (dd, *J* = 7.3, 2.0 Hz, 2H), 7.50 (dd, *J* = 7.6, 1.5 Hz, 1H), 7.37-7.28 (m, 4H), 6.93 (dd, *J* = 17.3, 8.0 Hz, 2H), 3.92 (s, 3H).; ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.9, 133.6, 131.7 (2C), 129.8, 128.3 (2C), 128.1, 123.6, 120.5, 112.4, 110.7, 93.4, 85.7, 55.9.; HRMS (ESI-TOF) calcd for $C_{15}H_{12}O$ ([M+Na]$^+$) 231.0788, found 231.0771.



3g: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03 (d, *J* = 1.8 Hz, 1H), 8.02 (d, *J* = 1.8 Hz, 1H), 7.60 (d, *J* = 1.8 Hz, 1H), 7.58 (d, *J* = 1.7 Hz, 1H), 7.57-7.55 (m, 1H), 7.54 (d, *J* = 2.6 Hz, 1H), 7.39-7.35 (m, 3H), 3.93 (s, 3H).; ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.6, 131.8 (2C), 131.5 (2C), 129.5 (2C), 129.5, 128.8, 128.5 (2C), 128.0, 122.7, 92.4, 88.7, 52.3.; HRMS (ESI-TOF) calcd for $C_{16}H_{12}O_2$ ([M+Na]$^+$) 259.0737, found 259.0723.

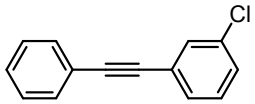


3h and 3k: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 (dd, *J* = 7.3, 2.1 Hz, 2H), 7.43-7.35 (m, 5H), 7.28 (t, *J* = 7.6 Hz, 1H), 7.19 (d, *J* = 7.6 Hz, 1H), 2.40 (s, 3H).; ^{13}C NMR (101 MHz, $CDCl_3$) δ 138.1, 132.2, 131.6 (2C), 129.2, 128.7, 128.4 (2C), 128.3, 128.2, 123.4, 123.1, 89.6, 89.2, 21.3.; HRMS (APCI-TOF) calcd for $C_{15}H_{12}$ ([M+H]$^+$) 193.1019, found 193.1010.

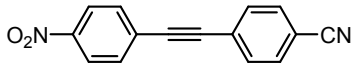


3j: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.17-8.15 (m, 1H), 8.15-8.13 (m, 1H), 7.62-7.59 (m, 1H), 7.59-7.57 (m, 1H), 7.49 (dd, *J* = 6.5, 3.2 Hz, 2H), 7.33 (d, *J* = 2.0 Hz, 2H), 7.31 (d, *J* = 1.8 Hz, 1H).; ^{13}C NMR (101 MHz, $CDCl_3$) δ 146.0,

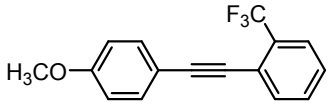
131.3 (2C), 130.8 (2C), 129.2, 128.3, 127.5 (2C), 122.6 (2C), 121.1, 93.7, 86.5.; HRMS (ESI-TOF) calcd for $C_{14}H_9NO_2$ ([M+Na]$^+$) 246.0533, found 246.0516.



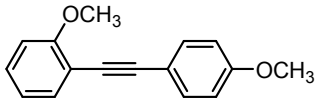
3l: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55-7.48 (m, 3H), 7.39 (dt, *J* = 7.3, 1.3 Hz, 1H), 7.36-7.31 (m, 3H), 7.29 (dt, *J* = 8.0, 1.6 Hz, 1H), 7.25-7.21 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 134.2, 131.7 (2C), 131.5, 129.8, 129.6, 128.7, 128.6, 128.5 (2C), 125.1, 122.8, 90.6, 88.0.; HRMS (APCI-TOF) calcd for $C_{14}H_9Cl$ ([M+H]$^+$) 213.0473, found 213.0468.



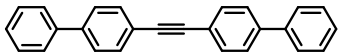
3m: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.29 (s, 1H), 8.27 (s, 1H), 7.72 (dd, *J* = 8.5, 4.4 Hz, 4H), 7.67 (d, *J* = 8.4 Hz, 2H).; ^{13}C NMR (101 MHz, $CDCl_3$) δ 147.5, 132.6 (2C), 132.3 (2C), 132.2 (2C), 129.0, 126.9, 123. 8 (2C), 118.2, 112.6, 92.3, 91.3.; HRMS (ESI-TOF) calcd for $C_{15}H_8N_2O_2$ ([M+Na]$^+$) 271.0486, found 271.0469.



3n: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65 (dd, *J* = 12.4, 7.8 Hz, 2H), 7.53-7.46 (m, 3H), 7.38 (t, *J* = 7.7 Hz, 1H), 6.92-6.89 (m, 1H), 6.89-6.86 (m, 1H), 3.83 (s, 3H).; ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.1, 133.5, 133.2 (2C), 131.4, 131.1, 127.5, 125.8, 125.0, 122.3,121.9, 114.8, 114.1 (2C), 95.1, 84.3, 55.3, 29.7.; HRMS (ESI-TOF) calcd for $C_{16}H_{11}F_3O$ ([M+H]$^+$) 277.0842, found 277.0931.



3o: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54-7.46 (m, 3H), 7.32-7.26 (m, 1H), 6.96-6.84 (m, 4H), 3.91 (s, 3H), 3.82 (s, 3H).; ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.8, 159.5, 133.5, 133.1 (2C), 129.5, 120.5, 115.7, 113.9 (2C), 112.7, 110.7, 93.5, 84.3, 55.9, 55.3.; HRMS (ESI-TOF) calcd for $C_{16}H_{14}O_2$ ([M+Na]$^+$) 261.0894, found 261.0876.



3p: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65-7.49 (m, 5H), 7.49-7.31 (m, 4H).; ^{13}C NMR (101 MHz, $CDCl_3$) δ 141.0, 140.4, 132.1 (4C), 131.6 (4C), 128.8 (4C), 128.4 (4C), 128.3 (2C), 127.6 (2C), 123.4, 122.2, 90.1, 89.3.; HRMS (APCI-TOF) calcd for $C_{26}H_{18}$ ([M+H]$^+$) 331.1489, found 331.1481.