

Supporting Information

A Graphdiyne-Based Carbon Material for Electroless Deposition and Stabilization of Sub-Nanometric Pd Catalysts with Extremely High Catalytic Activity

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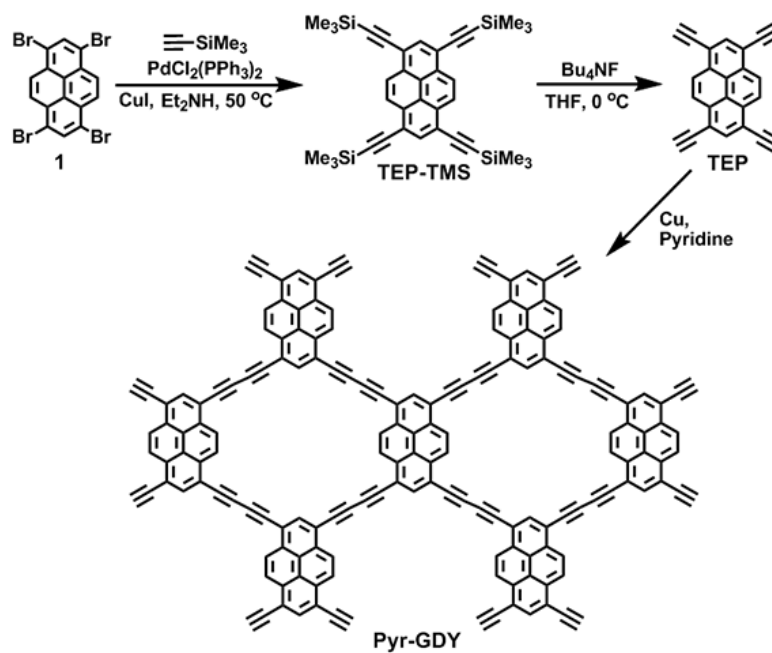
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Experimental Section

Materials and Methods. All the solvents and reagents are commercially available and used without further purification, unless otherwise noted. NMR spectra were recorded on Bruker 400 MHz instrument in D₂O, and chemical shifts were recorded in parts per million (ppm). High resolution mass spectra were performed on Q-TOF LC-MS with an ESI mode. UV-vis spectra were carried out on a Lambda 750 UV/vis/NIR spectrophotometer. Raman spectra were recorded on a high-resolution laser confocal fiber Raman spectrometer (HORIBA EVOLVTION, HORIBA Jobinyvon, France). XPS (X-ray photo-electron spectroscopy) were detected with Al K α as the excitation source on an ESCALAB 250 Xi spectrometer (Thermo Scientific, America). TEM (Transmission electron microscope) and high-resolution TEM (HRTEM) images were performed on Talos F200X, FEI, America using 200 kV acceleration voltage.

Computational Details. The B3LYP hybrid functional as implemented in the Gaussian 09 program ^[1] was used. For the optimization of all the structures, the 6-31G(d) basis set was applied to the C and H atoms, while the LANL2DZ pseudopotential and its corresponding basis set was applied for the Pd atoms. Frequency analysis calculations were performed at the same level of theory as the structural optimizations to confirm the structures with no imaginary frequency. In order to obtain more accurate binding energies between Pd single atom, Pd₄ cluster and Pyr-GDY, the basis set superposition error (BSSE) correction ^[2] was performed based on the optimized structures.



Scheme S1. The synthesis route for Pyr-GDY

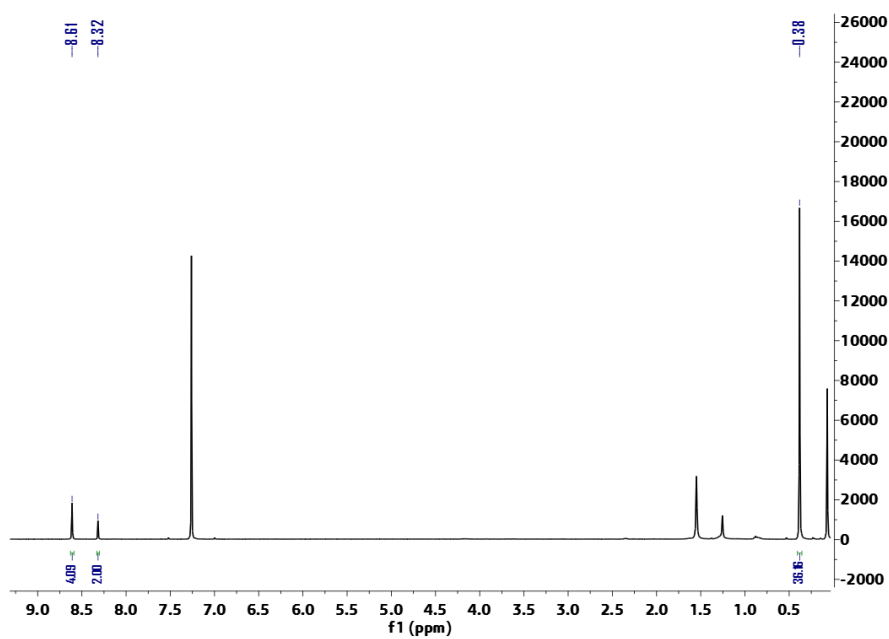


Figure S1. ^1H NMR spectrum of TEP-TMS (CDCl_3 , 400 MHz, 25 $^\circ\text{C}$).

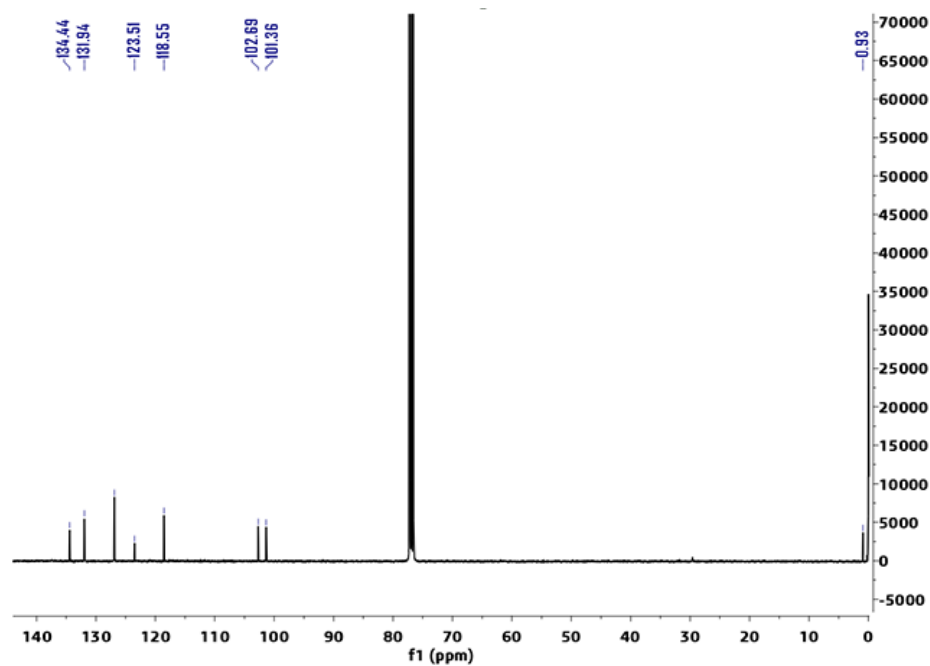


Figure S2. ¹³C NMR spectrum of TEP-TMS (CDCl₃, 100 MHz, 25 °C).

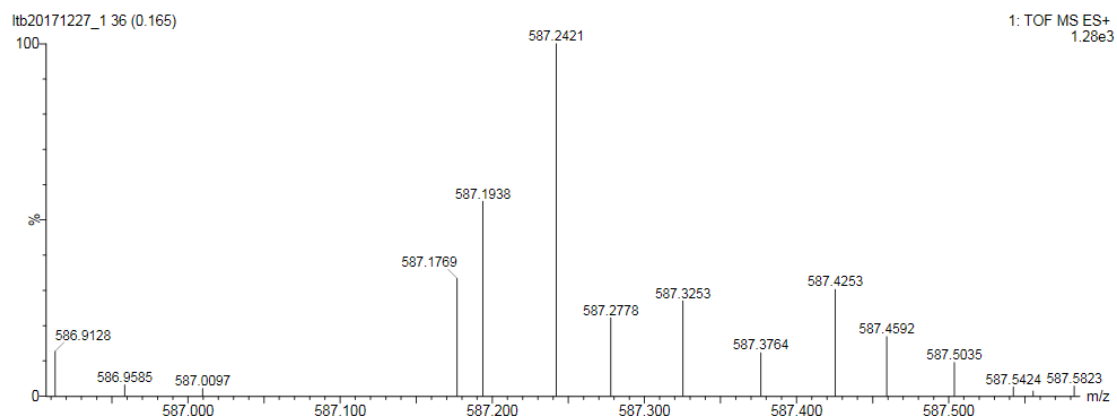


Figure S3. HRMS (ESI) pattern for TEP-TMS

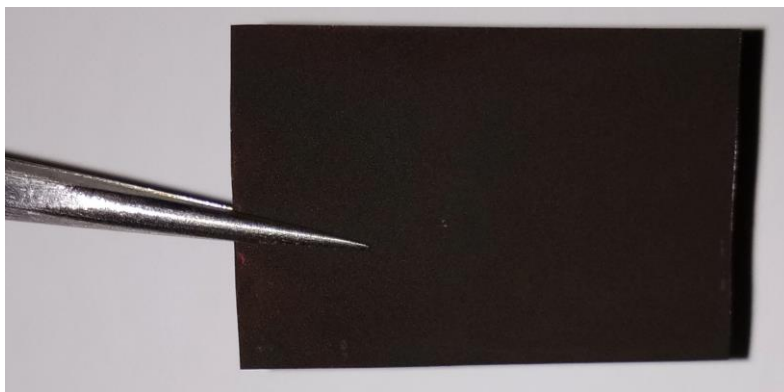


Figure S4. The photograph of Pyr-GDY grown on the surface of copper foil.

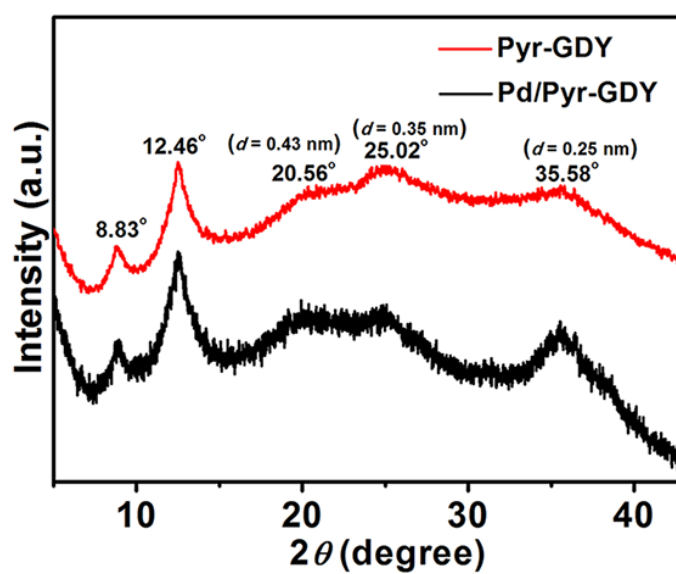


Figure S5. PXRD patterns of Pyr-GDY and Pd/Pyr-GDY.

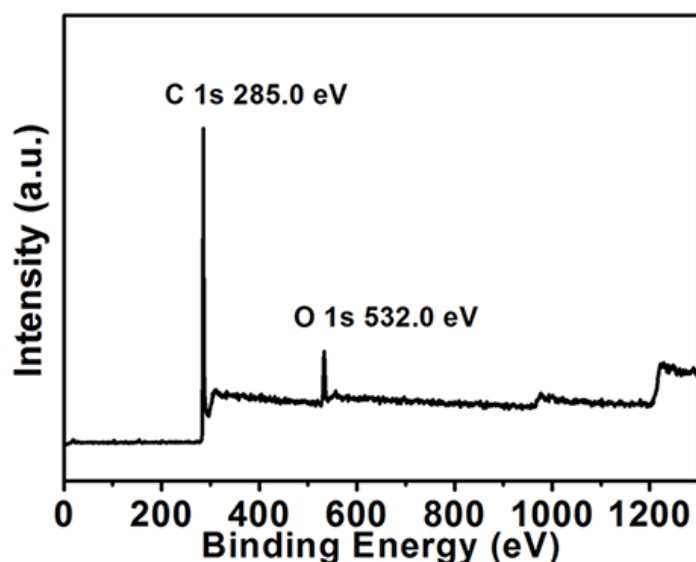


Figure S6. XPS pattern of Pyr-GDY (survey scan).

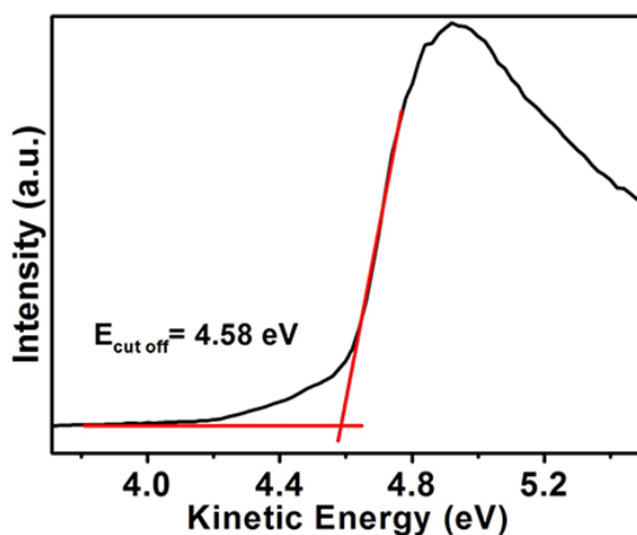


Figure S7. UPS of Pyr-GDY. The work function (Φ) was calculated through the equation: $\Phi = h\nu - E_{\text{Fermi}} + E_{\text{cutoff}} = 4.67 \text{ eV}$, where $h\nu$, E_{Fermi} , and E_{cutoff} are the photoenergy of the excitation light (21.22 eV), the Fermi level edge (21.13 eV), and the inelastic secondary electron cutoff (4.58 eV), respectively. The reduction potential was obtained from the equation, $\Phi/e = E_{(\text{vs SHE})} + 4.44 \text{ V}$, where Φ is the work functions, E is the reduction potential versus standard hydrogen electrode (SHE). On the basis of these equations, the reduction potential of Pyr-GDY can be calculated as +0.23 V vs SHE.

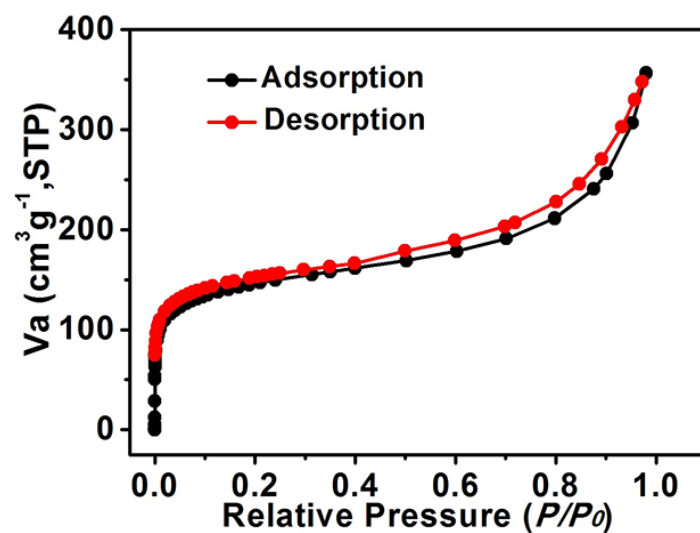


Figure S8. Nitrogen adsorption-desorption isotherm of Pyr-GDY.

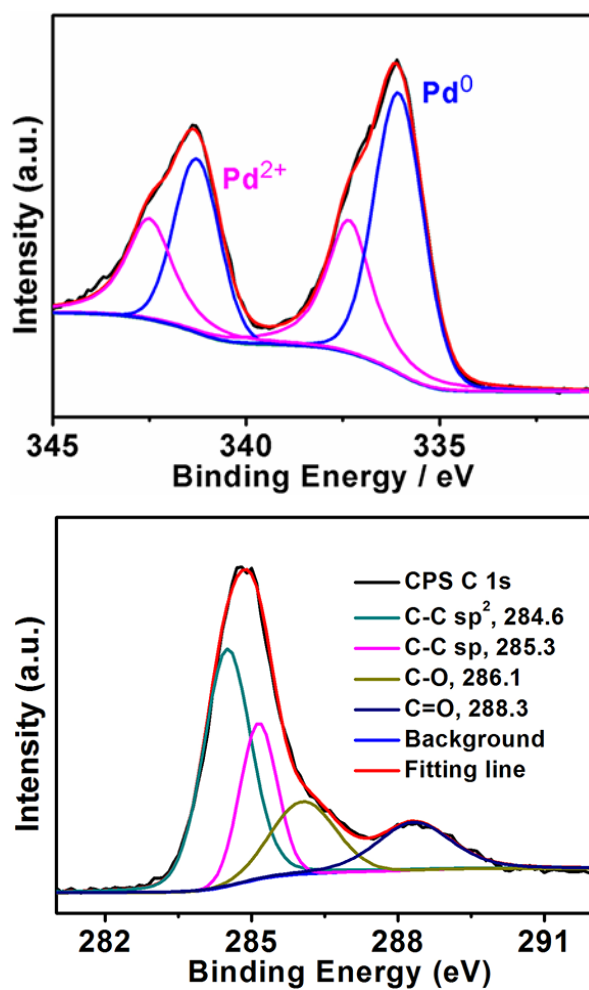


Figure S9. XPS patterns of Pd in Pd/Pyr-GDY (up), and C 1s in Pyr-GDYO (down).

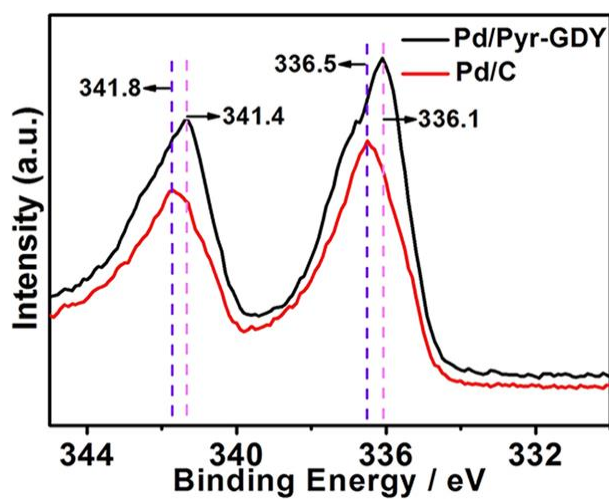
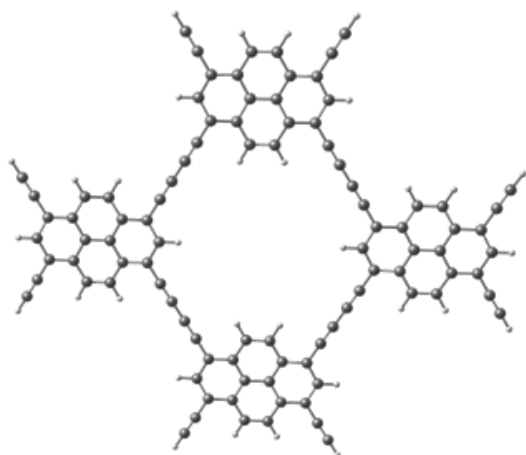


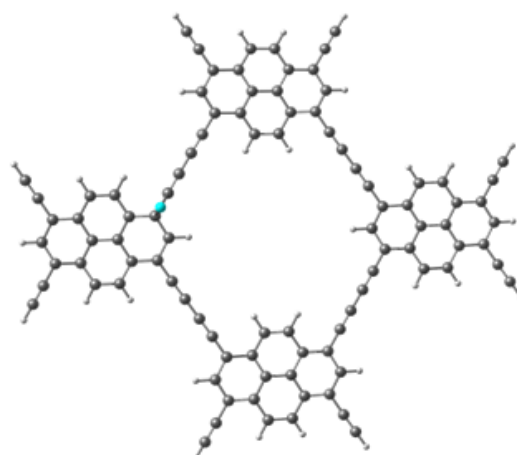
Figure S10. XPS patterns of Pd in Pd/Pyr-GDY (black line) and Pd/C (red line).

Table S1. C 1s XPS data for Pyr-GDY, Pd/Pyr-GDY and Pyr-GDYO.

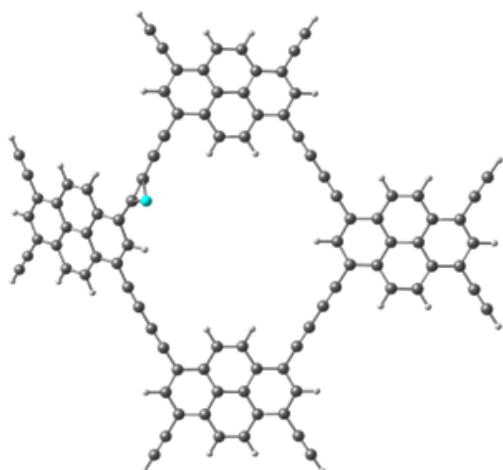
C species Sample	C-C (sp ²)		C-C (sp)		C-O		C=O	
	area	ratio	area	ratio	area	ratio	area	ratio
Pyr-GDY	49033.9	61.7%	23781.2	30.0%	3901.6	4.9%	2724.8	3.4%
Pd/Pyr-GDY	27506.8	58.8%	10721.4	23.7%	5338.2	11.8%	2561.6	5.7%
Pyr-GDYO	11305.2	46.5%	4838.1	19.9%	4254.7	17.5%	3914.3	16.1%



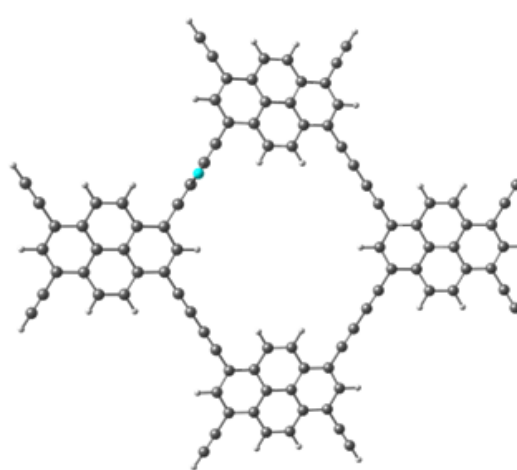
Pyr-GDY



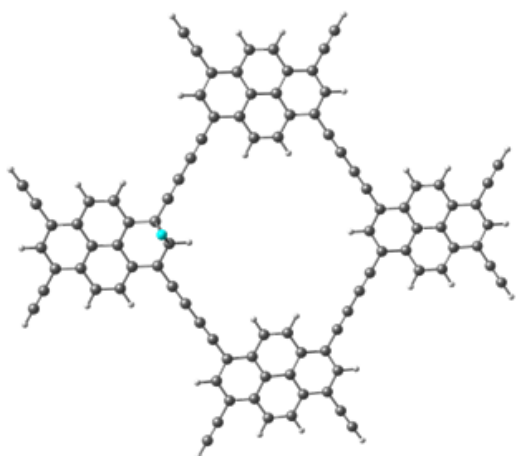
Pd/Pyr-GDY (A)
BE = -17.14 kcal/mol



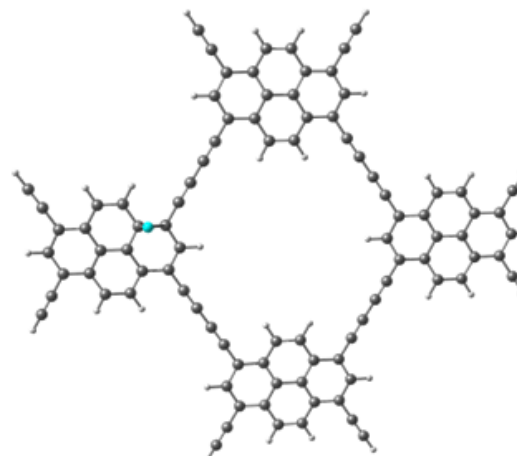
Pd/Pyr-GDY (B)
BE = -35.93 kcal/mol



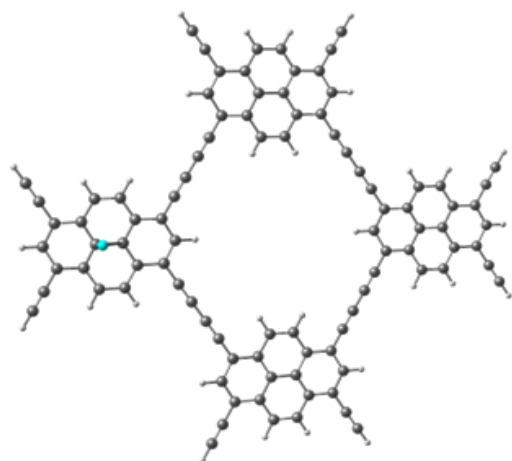
Pd/Pyr-GDY (C)
BE = -18.27 kcal/mol



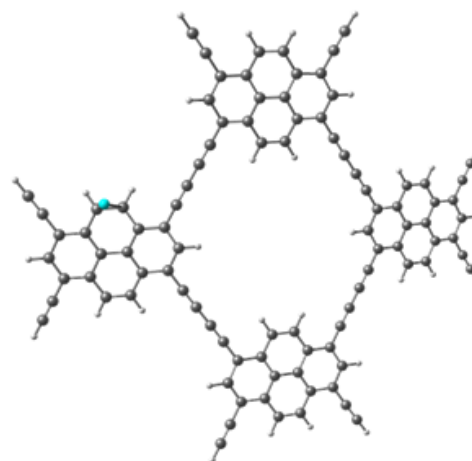
Pd/Pyr-GDY (D)
BE = -20.69 kcal/mol



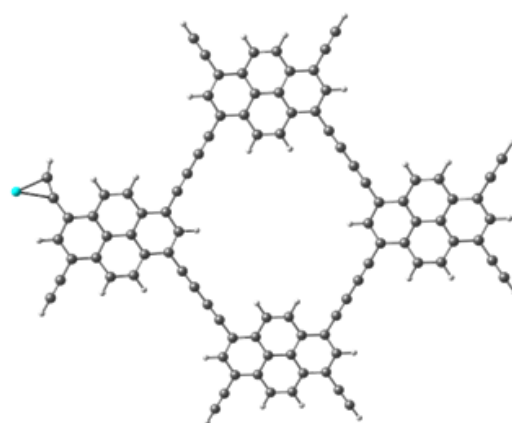
Pd/Pyr-GDY (E)
BE = -16.48 kcal/mol



Pd/Pyr-GDY (F)
BE = -11.16 kcal/mol



Pd/Pyr-GDY (G)
BE = -26.76 kcal/mol



Pd/Pyr-GDY (H)
BE = -38.98 kcal/mol

Figure S11. The binding energies of Pd(0) single atom at various positions in Pyr-GDY.

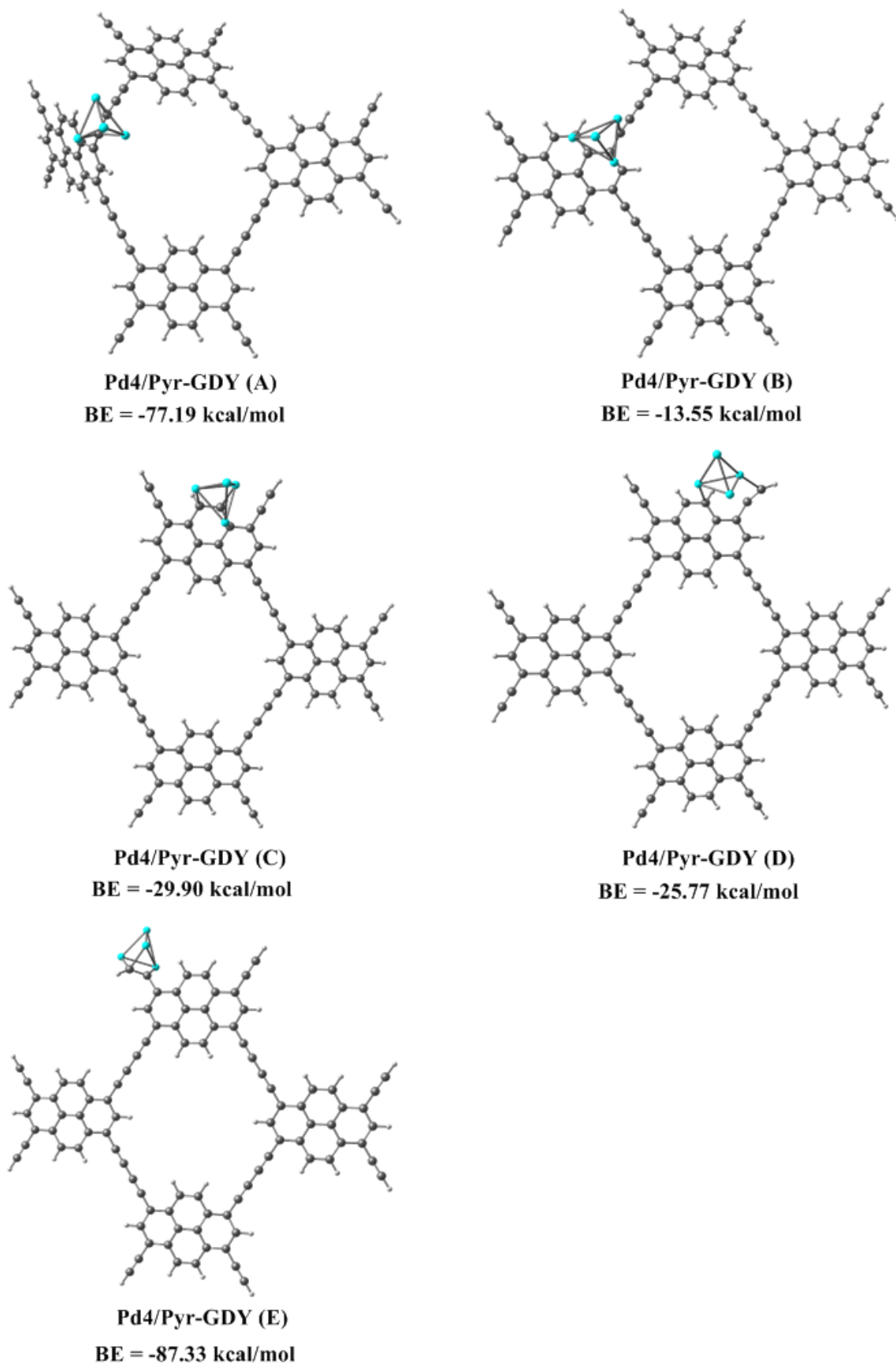


Figure S12. The binding energies of Pd₄ cluster at various positions in Pyr-GDY.

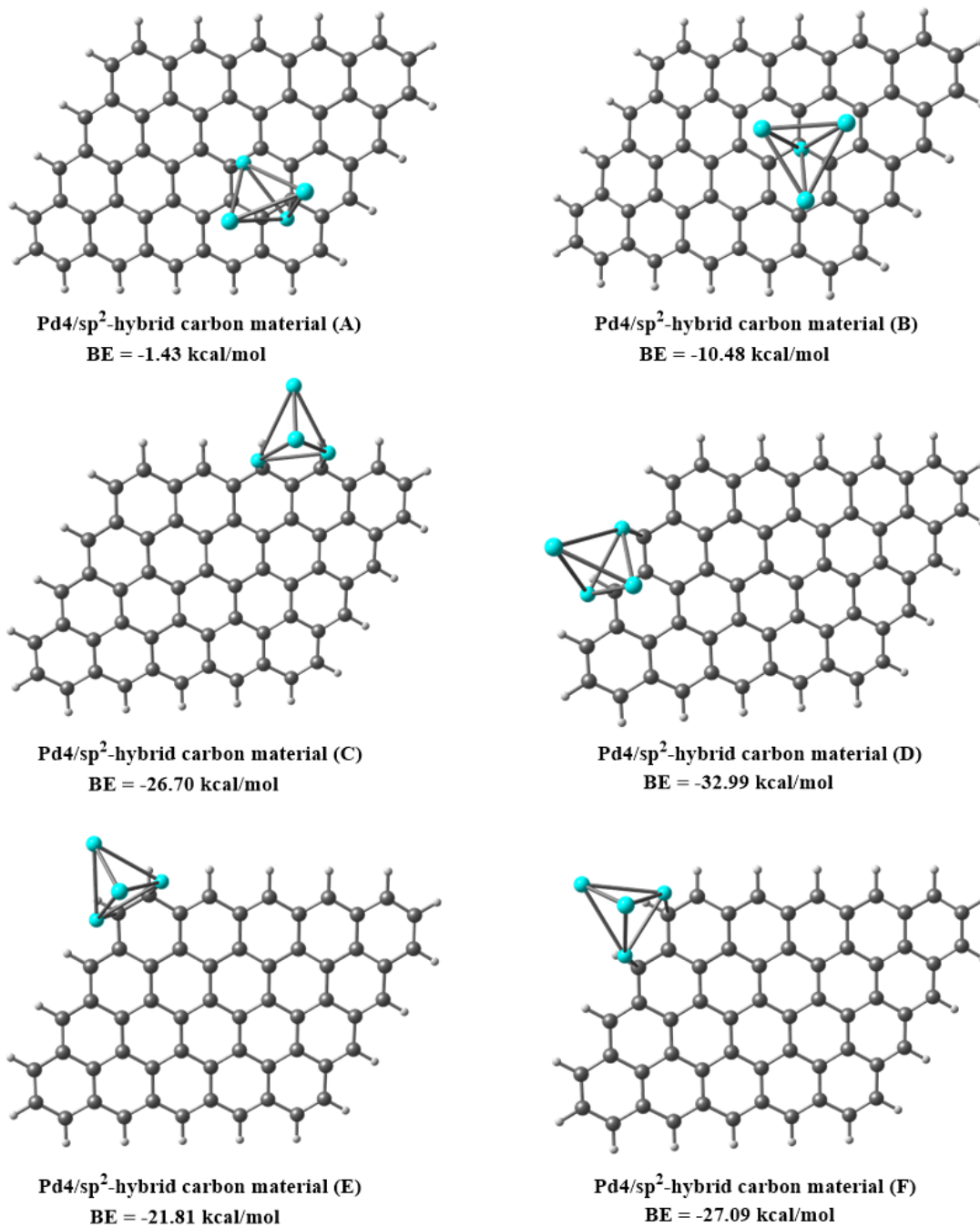


Figure S13. Optimized structures for the sp²-hybrid carbon material bind with the Pd₄ cluster, the binding energies (BE) are given in kcal/mol.

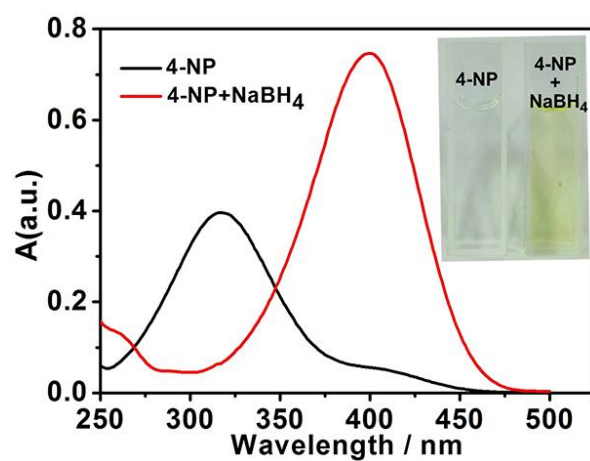


Figure S14. UV-vis spectra of 4-NP (black line) and 4-nitrophenolate ion (red line).

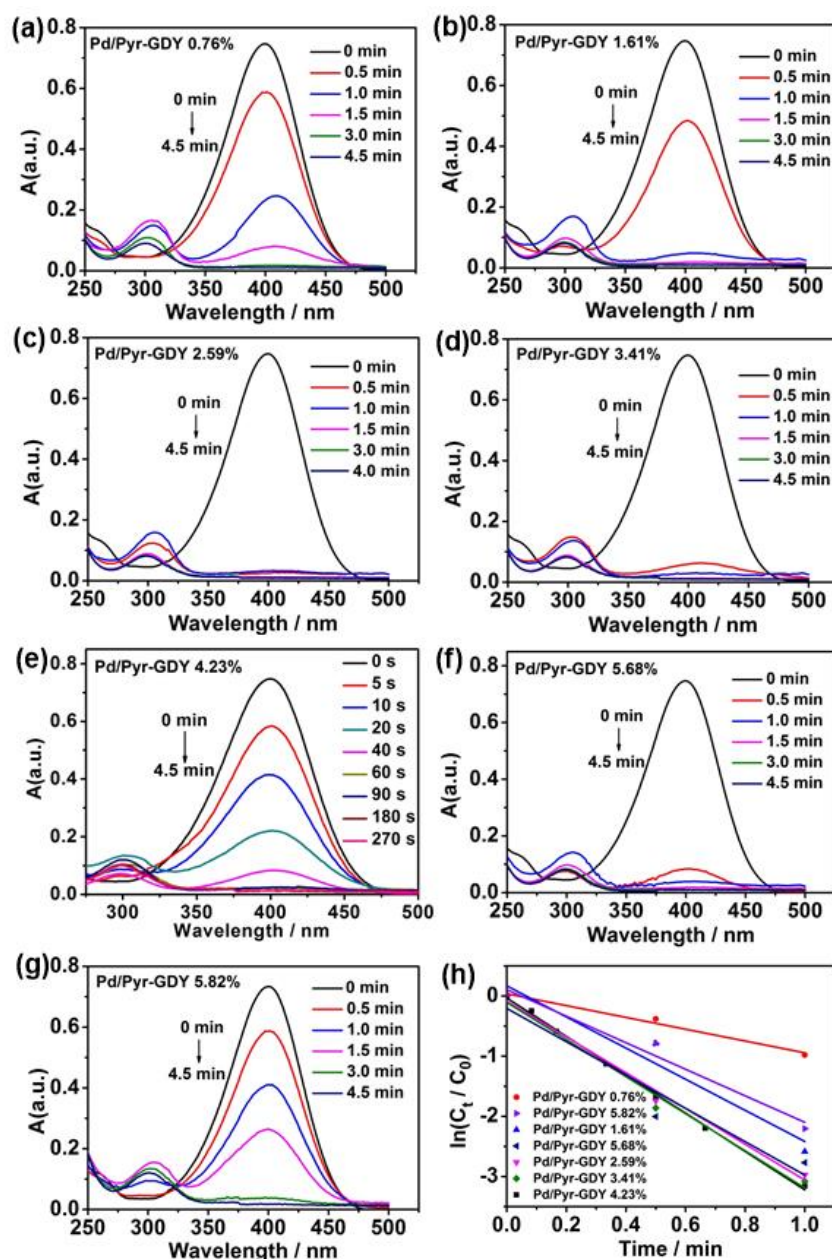


Figure S15. Time-dependent UV-vis absorption spectra recorded during the catalytic reduction of 4-NP with different Pd contents (a) Pd/Pyr-GDY 0.76%, (b) Pd/Pyr-GDY 1.61%, (c) Pd/Pyr-GDY 2.59%, (d) Pd/Pyr-GDY 3.41%, (e) Pd/Pyr-GDY 4.23%, (f) Pd/Pyr-GDY 5.68%, (g) Pd/Pyr-GDY 5.82%, (h) Plots of $\ln(C_t/C_0)$ as a function of the reaction time for the reduction of 4-NP catalyzed by seven different catalysts. The contents of Pd were measured by Inductively Coupled Plasma (ICP).

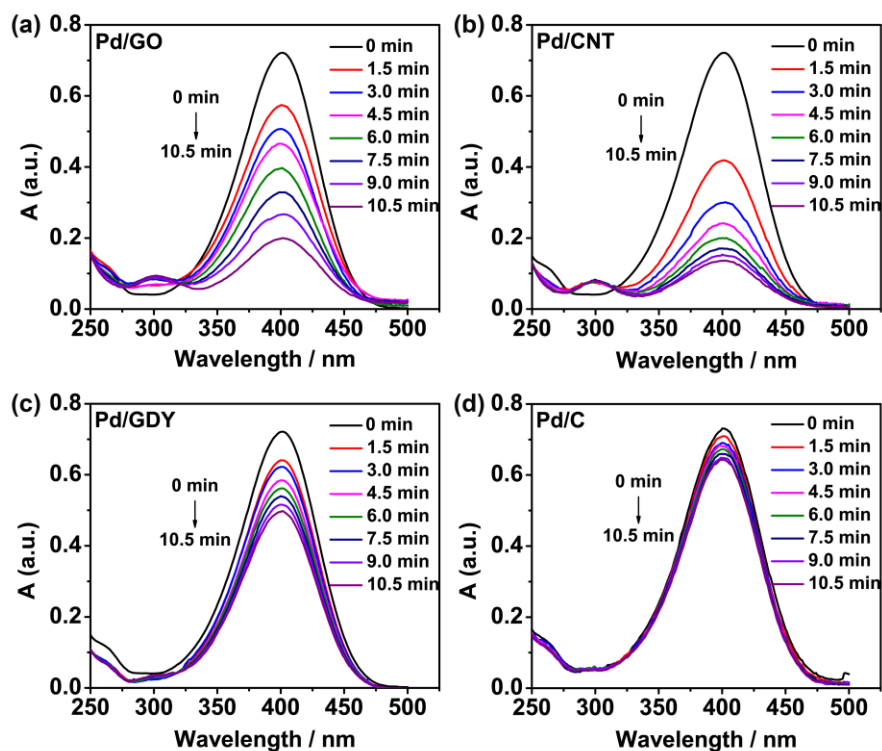


Figure S16. Time-dependent UV-vis absorption spectra recorded during the catalytic reduction of 4-nitrophenol in the presence of (a) Pd/GO, (b) Pd/CNT, (c) Pd/GDY and (d) Pd/C with the same amount of Pd loading (8.2×10^{-5} mg).

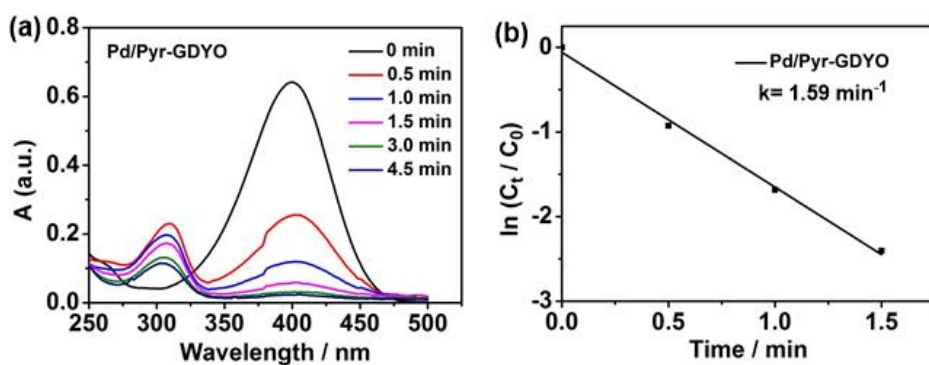


Figure S17 (a) Time-dependent UV-vis absorption spectra recorded during the catalytic reduction of 4-nitrophenol by Pd/Pyr-GDYO. (b) Plots of $\ln(C_t/C_0)$ as a function of the reaction time for the reduction of 4-nitrophenol catalyzed by Pd/Pyr-GDYO.

Table S2. Comparison of 4-nitrophenol reduction by NaBH₄ using various Pd NPs catalysts.

Catalyst	Mass of Pd (mg)	Amount of 4-NP (mmol)	Particle size (nm)	Reduction time (min)	Rate constant (k/min ⁻¹)	Ref.
Pd/Pyr-GDY	8.2×10 ⁻⁵	1×10 ⁻⁴	0.8	1.0	3.18	This work
Pd@RCC3	1.1×10 ⁻³	6.6×10 ⁻⁴	0.72	4	1.25	3
Pd/GDYO	1.25×10 ⁻³	0.67×10 ⁻⁴	1.3	11	0.32	4
CNT-Pd	0.029	3×10 ⁻²	2.2	8	0.38	5
Pd@HCS	0.053	3×10 ⁻⁴	1-8	5	0.93	6
Pd/PdO/OCNTs	0.095	1.5×10 ⁻⁴	3.5	4.6	1.00	7
Pd@NC	5×10 ⁻⁴	3×10 ⁻⁴	8-16	6.5	0.47	8
Pd/Fe ₃ O ₄ @SiO ₂ @KCC-1	2.3×10 ⁻³	3×10 ⁻⁴	4	4.2	1.1	9
Pd /tris-trz-PEG	5.3×10 ⁻³	2.5×10 ⁻⁴	1.5	3.1	1.49	10
Fe ₃ O ₄ @SiO ₂ -Pd	N.A.	3×10 ⁻⁵	2	5	0.76	11
Fe@NC@Pd	4.5×10 ⁻³	3x10 ⁻²	3.7	1.92	2.4	12
Ag ₂ Au ₁ Pd ₂	6.4×10 ⁻³	3×10 ⁻⁴	32	10	0.46	13
AgPd NCs/rGO	0.016	3.5×10 ⁻⁴	2.3	3	2.2	14
Rh@3D GDY	1.25×10 ⁻³	6.7×10 ⁻⁵	2-3	20	0.17	15

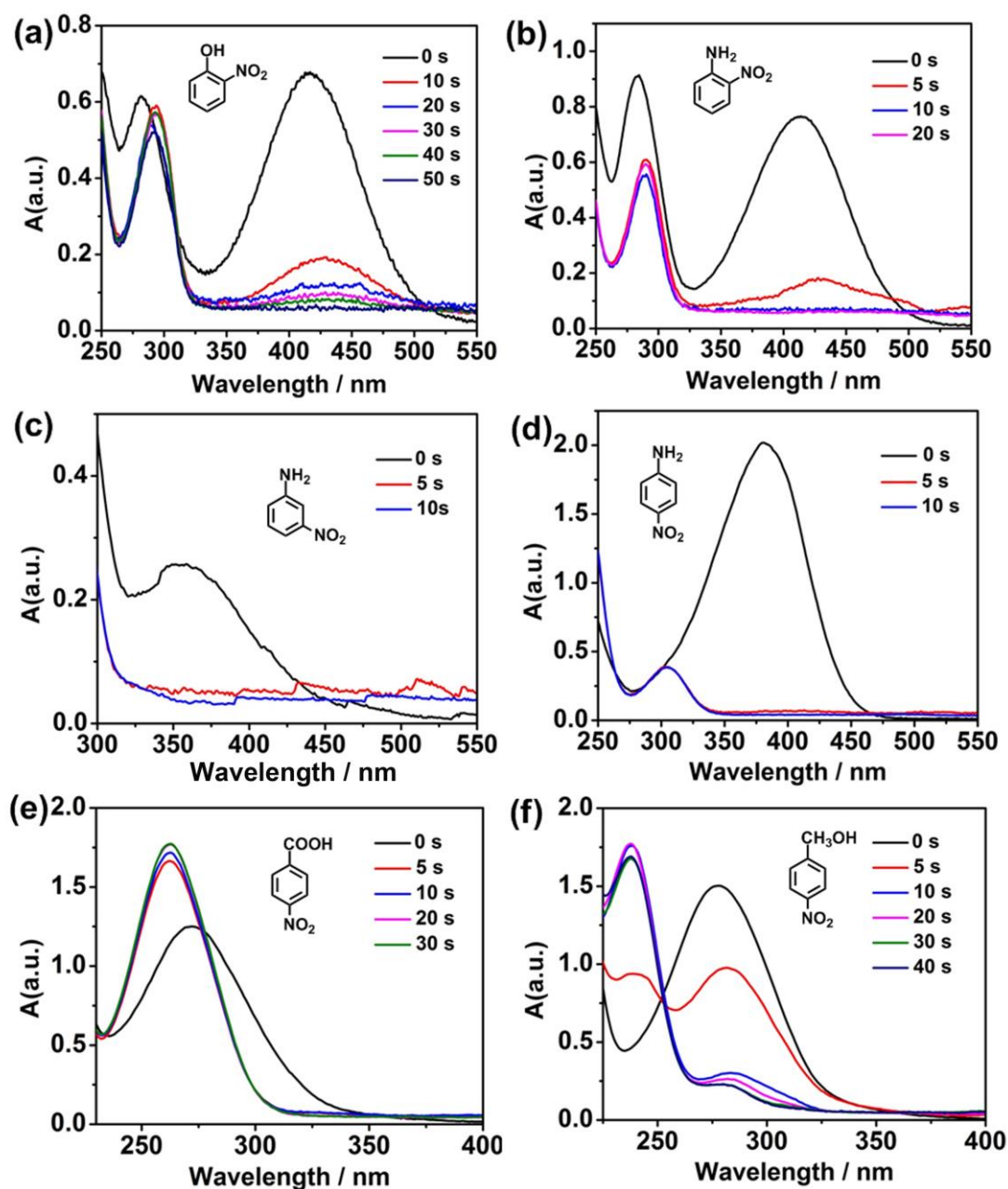


Figure S18. UV-vis spectra recorded during the reduction of (a) 2-nitrophenol, (b) 2-nitroaniline, (c) 3-nitroaniline, (d) 4-nitroaniline, (e) 4-nitrobenzoic acid, (f) 4-nitrobenzyl alcohol (0.167 mM) catalyzed by Pd/Pyr-GDY (3.78×10^{-6} mmol Pd) in H_2O (3 mL) containing NaBH_4 (0.64 mmol).

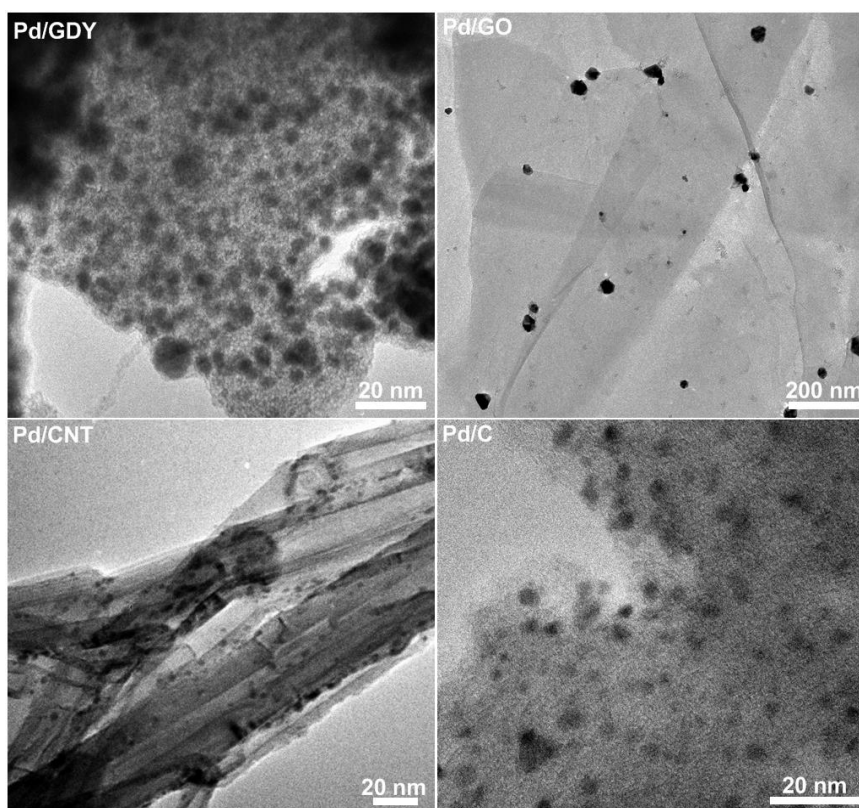


Figure S19. TEM images for Pd/GDY, Pd/GO, Pd/CNT, and Pd/C.

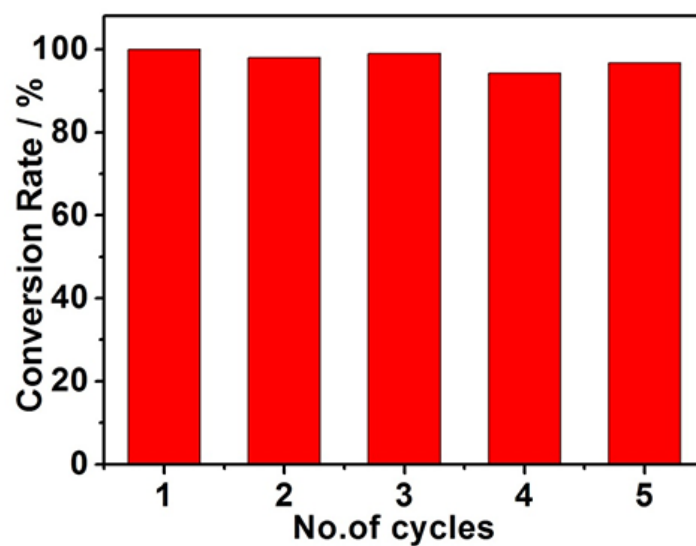


Figure S20. Circulation tests of Pd/Pyr-GDY for Suzuki-Miyaura reaction using bromobenzene and phenylboronic acid as the reactants.

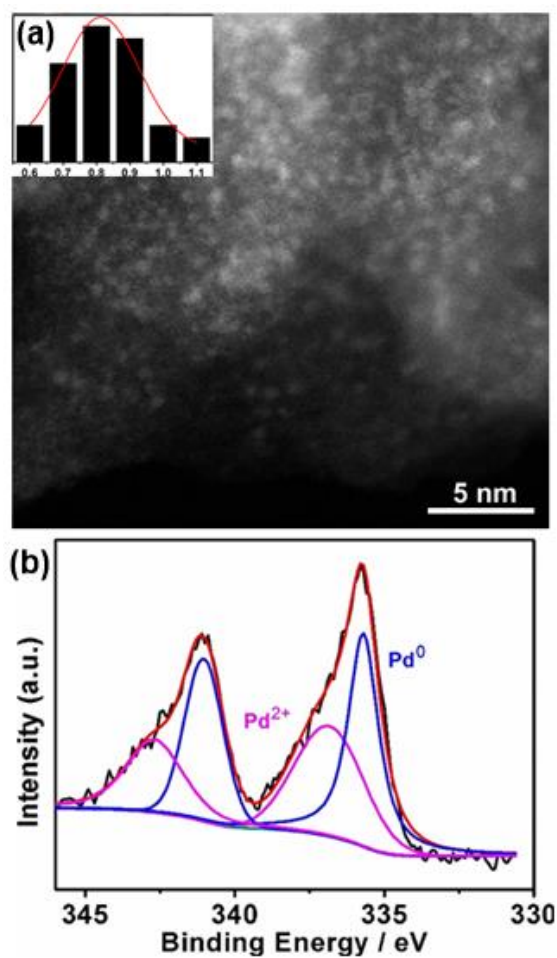


Figure S21. HAADF-TEM image (a) and XPS patterns (b) of Pd in Pd/Pyr-GDY after five cycles of Suzuki-Miyaura reaction.

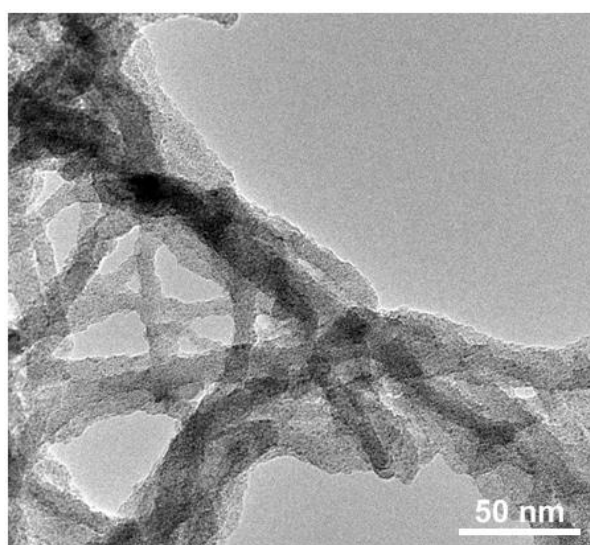


Figure S22. TEM image of Pd/Pyr-GDY after five cycles of Suzuki-Miyaura reaction.

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