Electronic Supplementary Material (ESI) for RSC Advances.

Supporting Information

Anchoring Ultrasmall Pd Nanoparticles by Bipyridine Functional Covalent Organic Frameworks for Semihydrogenation of Acetylene

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Table S1 Experimental conditions for the synthesis of TbBpy in different solvents.

Serial number	Solvent type and amount	Other synthesis conditions
1	Dioxane, 2 ml	0.2 mmol of 1,3,5-tribenzaldehyde; 0.3 mmol of 5,5-diamino-2,2-bipyridine; 0.4 ml of acetic acid aqueous solution (3 mol/L); temperature of 120℃; synthesis time It takes 72 h.
2	N-butanol, 2 ml	
3	Mesitylene, 2 ml	
4	Ethanol, 2 ml	

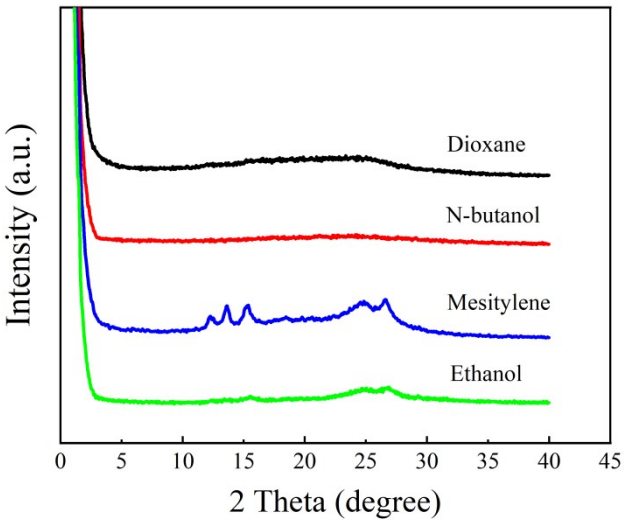

Figure S1. XRD patterns of TbBpy synthesized in 4 different solvents.

Table S2 Experimental conditions for the synthesis of TbBpy in ethanol/mesitylene with different volume ratio.

Serial number	Solvent ratio and dosage	Other synthesis conditions

1	Ethanol/Mesitylene=4:1,2 ml	0.2 mmol of 1,3,5-tribenzaldehyde; 0.3 mmol of 5,5-diamino-2,2-bipyridine; 0.4 ml of acetic acid aqueous solution (3 mol/L); temperature of 120 ℃; synthesis time for 72 h.
2	Ethanol/Mesitylene=1:1,2 ml	
3	Ethanol/Mesitylene=1:4,2 ml	

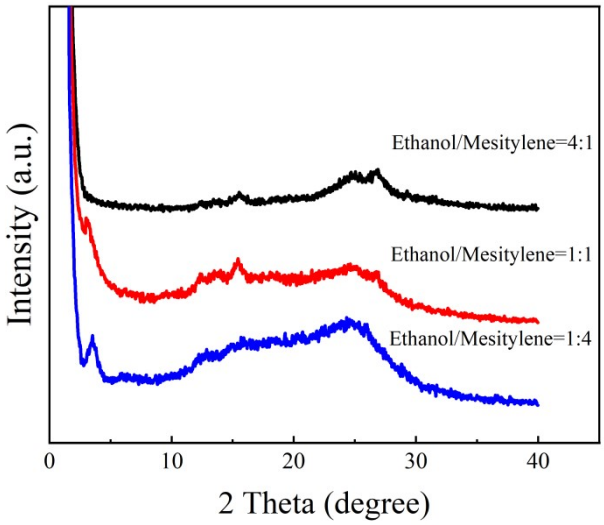

Figure S2. XRD patterns of TbBpy synthesized in ethanol/mesitylene with different volume ratios.

Table S3 Experimental conditions for synthesizing TbBpy with different concentrations of acetic acid aqueous solution.

Serial number	**Concentration and dosage of acetic acid aqueous solution**	**Other synthesis conditions**
1	6 mol/L, 0.4 ml	0.2 mmol of 1,3,5-tribenzaldehyde; 0.3mmol of 5,5-diamino-2,2-bipyridine; ethanol/mesitylene mixed solvent with a volume ratio of 1:4; temperature is 120 ℃; The synthesis time is 72 h.
2	9 mol/L, 0.4 ml	
3	12 mol/L, 0.4 ml	

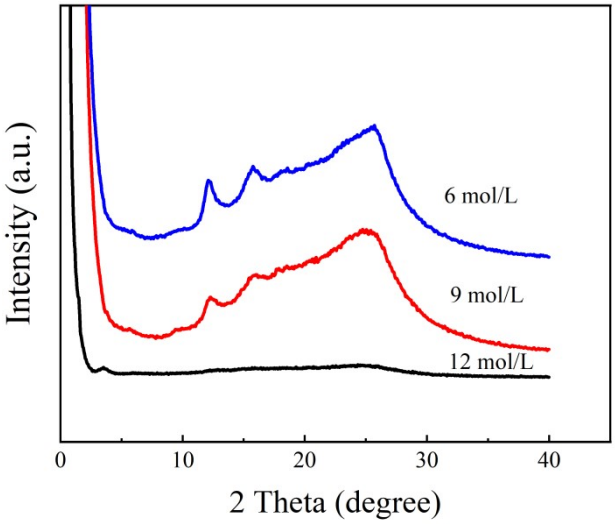

Figure S3. XRD patterns of TbBpy synthesized from 1: 4 volume ratio of ethanol/mesitylene mixed solvents with different concentrations of acetic acid solution.

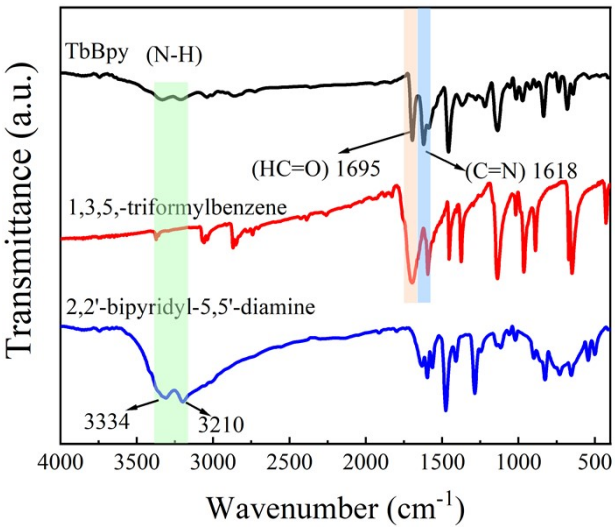

Figure S4. Infrared spectra of TbBpy, 1,3,5-triphenylaldehyde and 5,5-diamino-2,2-bipyridine.

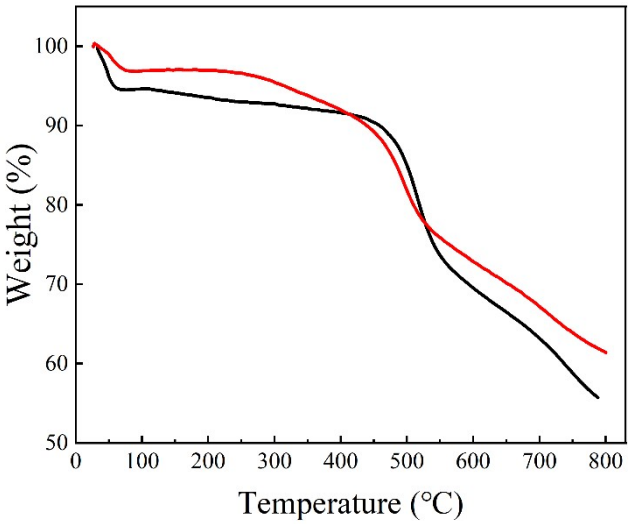

Figure S5. TGA curves of TbBpy (black) and Pd@TbBpy (red).

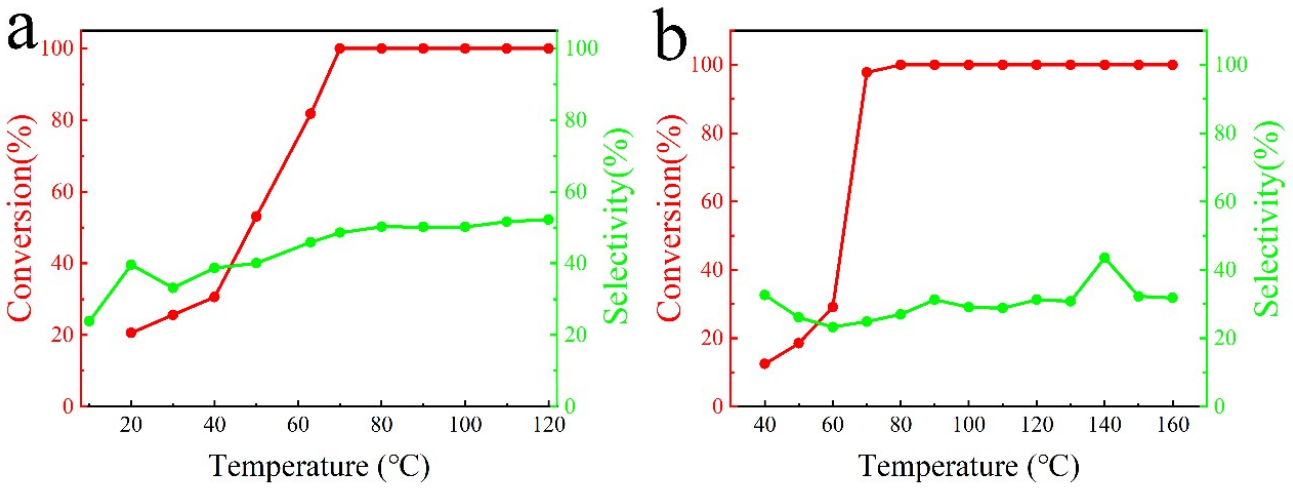

Figure S6. Catalytic activity of different reduction reactions: acetylene conversion (red) and ethylene selectivity (green) of (a) 1wt%Pd@TbBpy-$NaBH_4$ and (b) 1wt%Pd@TbBpy-H_2 at 40000 h^{-1}.

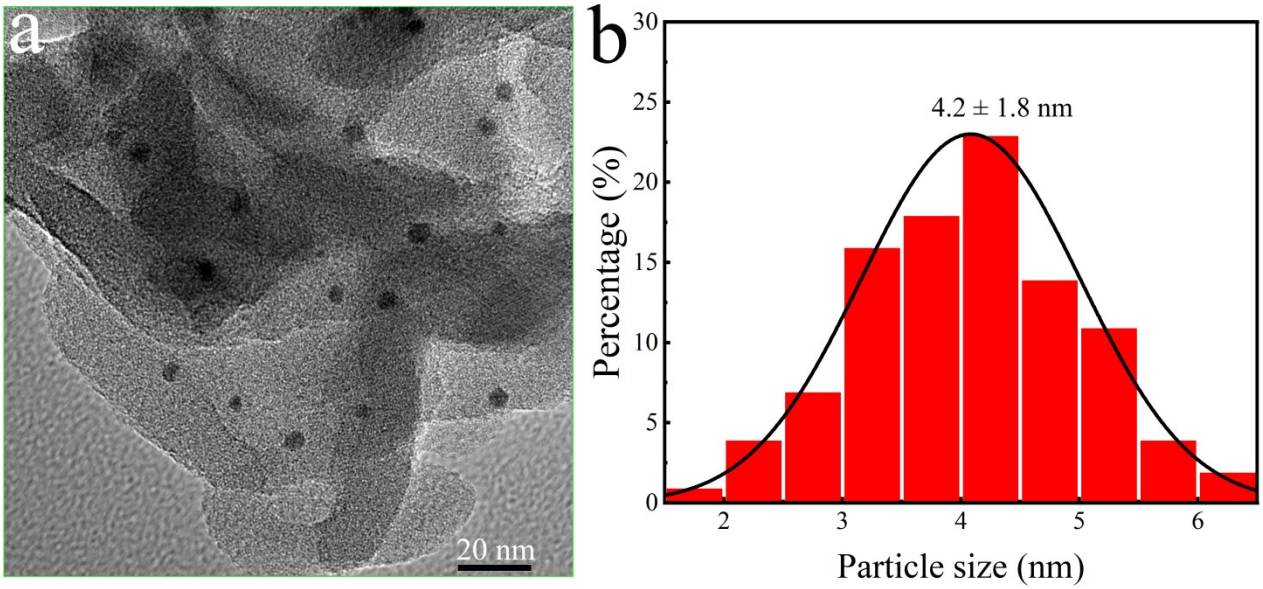

Figure S7. After catalytic testing: (a) HR-TEM images Pd@TbBpy and (b) the Pd particle size frequency distribution histogram.

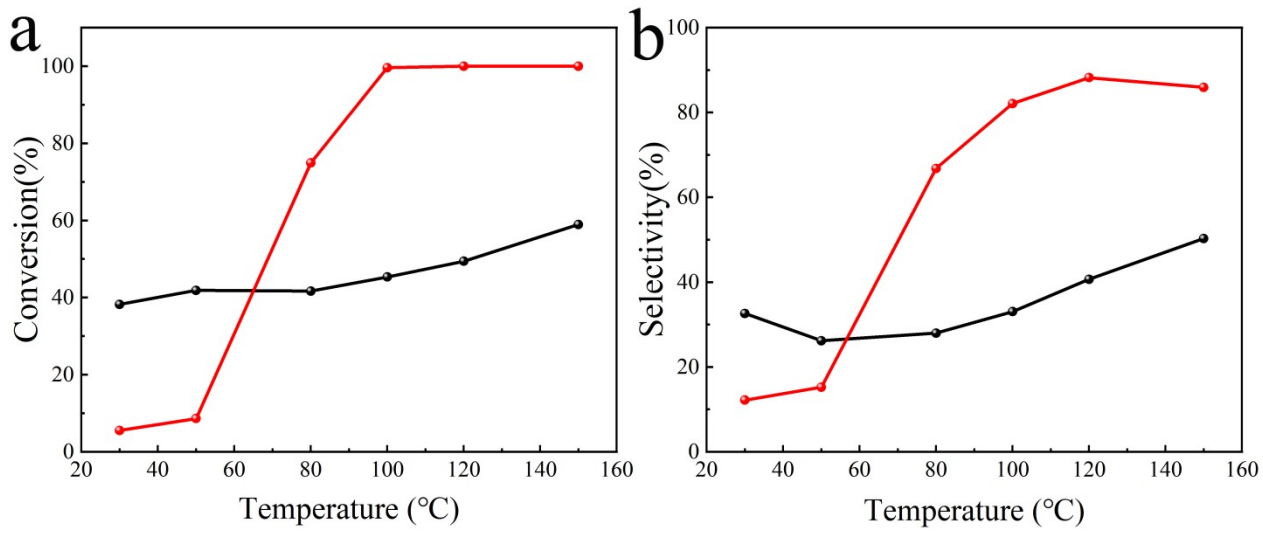

Figure S8. Catalytic activity of 0.75wt%Pd@TbBpy (red) and Pd salt (black) .

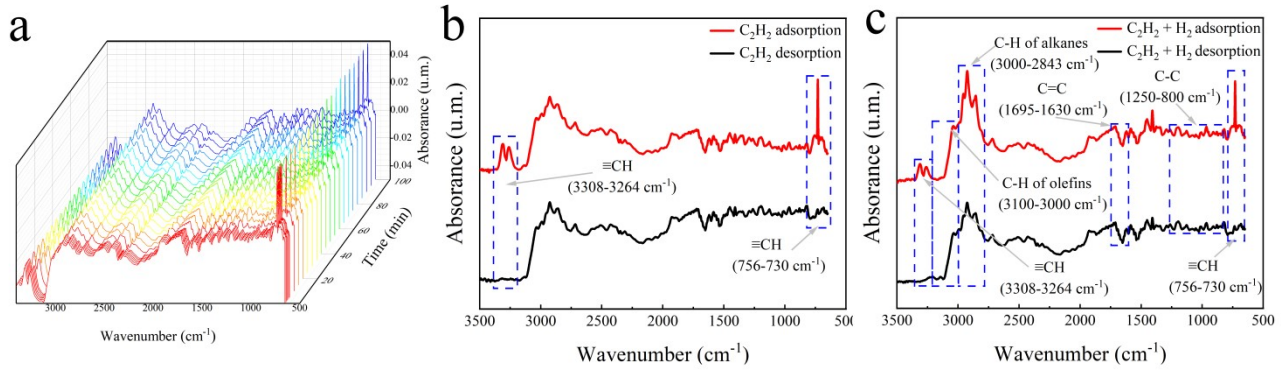

Figure S9. In situ DRIFTS spectra over a 0.75wt% Pd@TbBpy at 120°C: (a) The real-time in situ DRIFTS spectra of C_2H_2 adsorption. (b) The adsorption and desorption spectra of C_2H_2. (c) The absorption and desorption spectra of C_2H_2 hydrogenation.

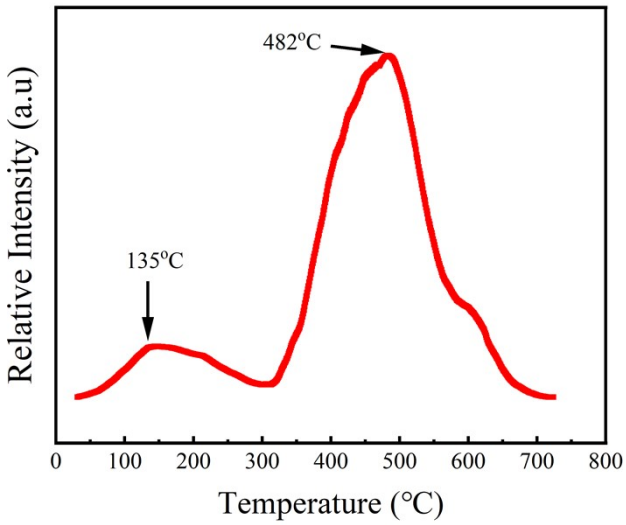

Figure S10. H_2-TPD profiles of Pd@TbBpy catalyst.

Table S4. Conversion and Selectivity of acetylene hydrogenation for Pd-based catalyst.

Catalyst	Pd loading, % /Size,nm	Tempure, °C	WHSV h^{-1}	Conversion, %	Selectivity, %	Reference
Pd@TbBpy	0.75	120	70000	100	88.2	This work
Pd_1/ND@G	0.11	180	60000	100	90	Huang et.al [1]
Pd_1/CeO_2	1	160	90000	100	85%	Guo et.al [2]
Pd/MCN	0.1	120	33000	~90	84.3	Dodangeh et.al [3]
Pd1/MgO-H100	0.16	140	90000	100	70	Guo et.al [4]
Pd/CTS	1	90	90000	100	~90	Guan et.al [5]

Pd/SiC	0.80	100	30000	100	80	Guo et.al [6]
Pd_1/C_3N_4	3.5	~110	60000	99	83	Huang et.al [7]
Pd@NMC-850	0.208	100	12000	66	83	Wang et.al [8]
Pd/α-Al_2O_3@SiC	0.035	130	10000	83	65	Zhang et.al [9]

References

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