Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A.

Supporting Information

Introduction of Secondary Ligand in Titanium-Based Metal-Organic Frameworks for Visible-Light-Driven Photocatalytic Hydrogen Peroxide Production from Dioxygen Reduction

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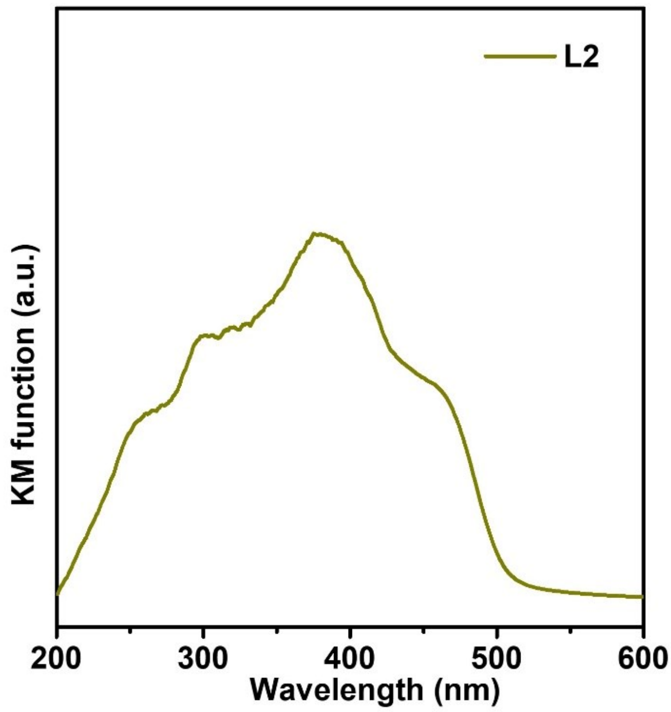
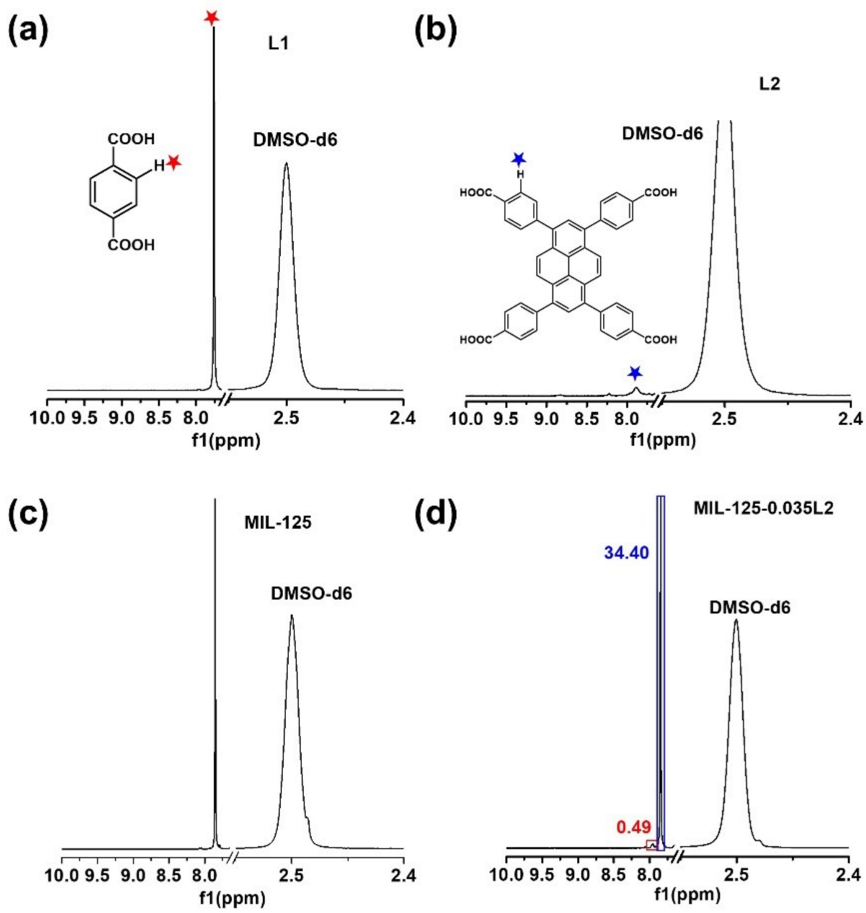


Fig. S1 UV-vis DRS of L2.



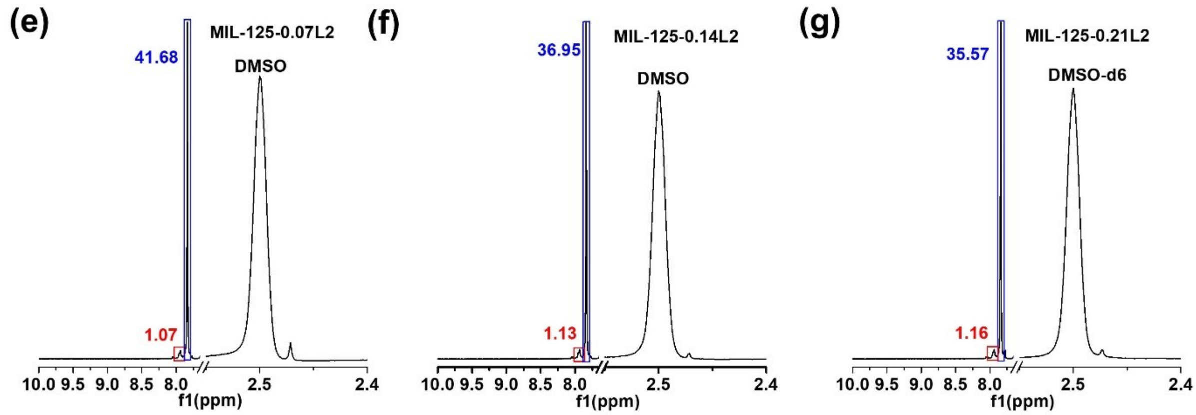


Fig. S2 ^{1}H NMR spectra of (a) L1, (b) L2, (c) MIL-125, and (d-g) MIL-125-xL2 (x = 0.035, 0.07, 0.14, and 0.21).

Table S1. The ligand ratios (L1/L2) calculated from ^{1}H NMR data of digested samples. Molecular formula of MIL-125: $Ti_8O_8(OH)_4(L1)_6$.

Samples	L1/L2	
MIL-125		$Ti_8(L1)_6$
MIL-125-0.035L2	6:0.04	$Ti_8(L1)_6(L2)_{0.04}$
MIL-125-0.07L2	6:0.08	$Ti_8(L1)_6(L2)_{0.08}$
MIL-125-0.14L2	6:0.09	$Ti_8(L1)_6(L2)_{0.09}$
MIL-125-0.21L2	6:0.10	$Ti_8(L1)_6(L2)_{0.10}$

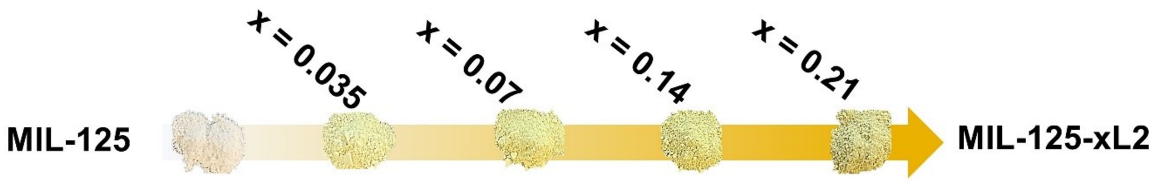


Fig. S3 Photos of MIL-125 and MIL-125-xL2 (x = 0.035, 0.07, 0.14, and 0.21).

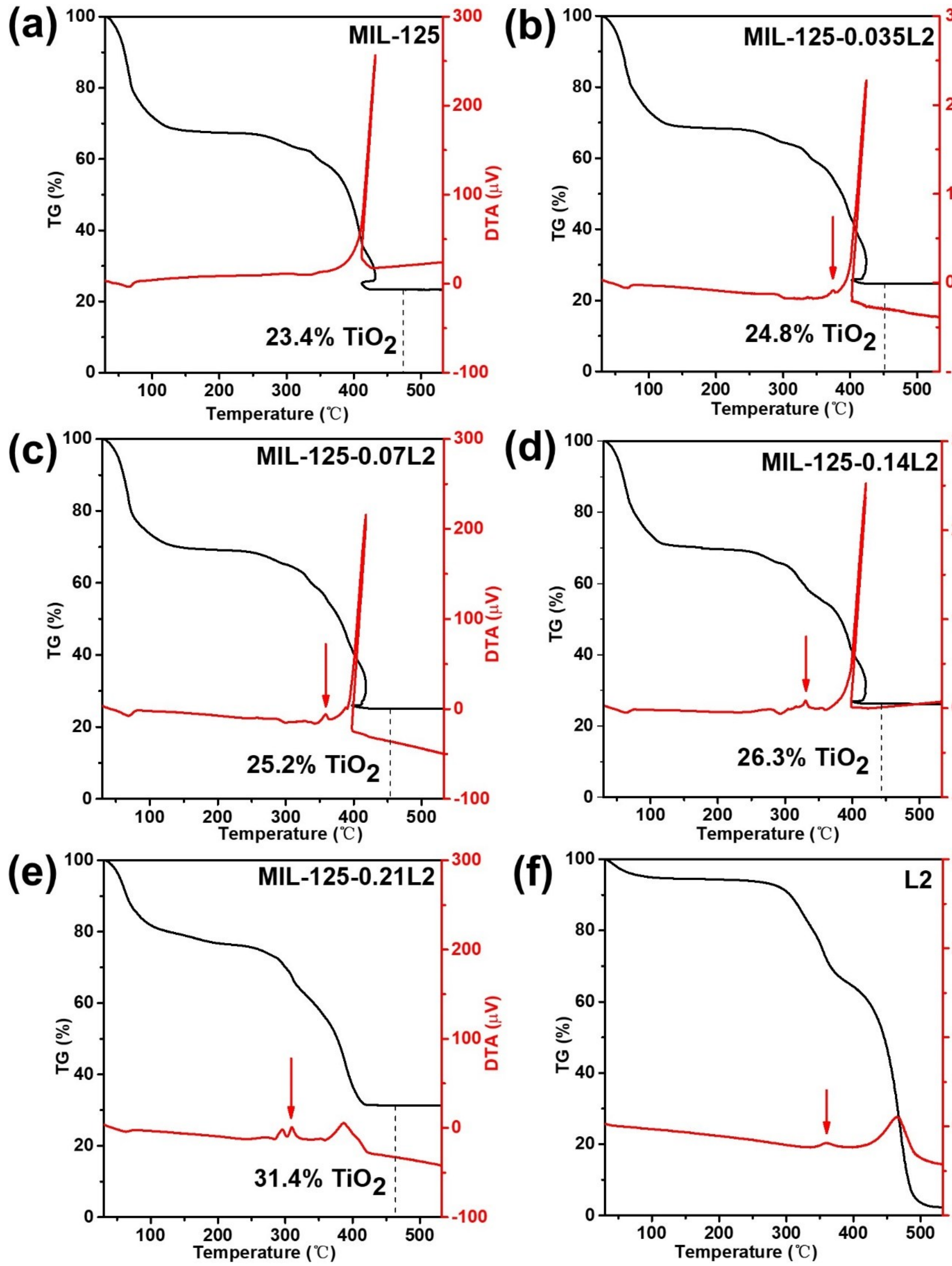


Fig. S4 TG and DTA profiles of (a) MIL-125, (b-e) MIL-125-xL2 (x = 0.035, 0.07, 0.14, and 0.21), and (f) L2.

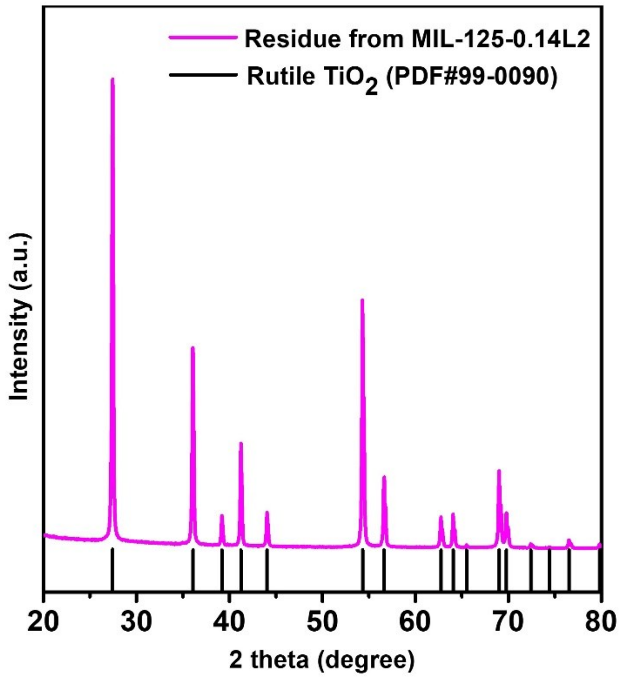


Fig. S5 XRD patterns of MIL-125-0.14L2 after being heated with temperature ramp of 1.0 ℃ min^{-1} up to 800 ℃ in air.

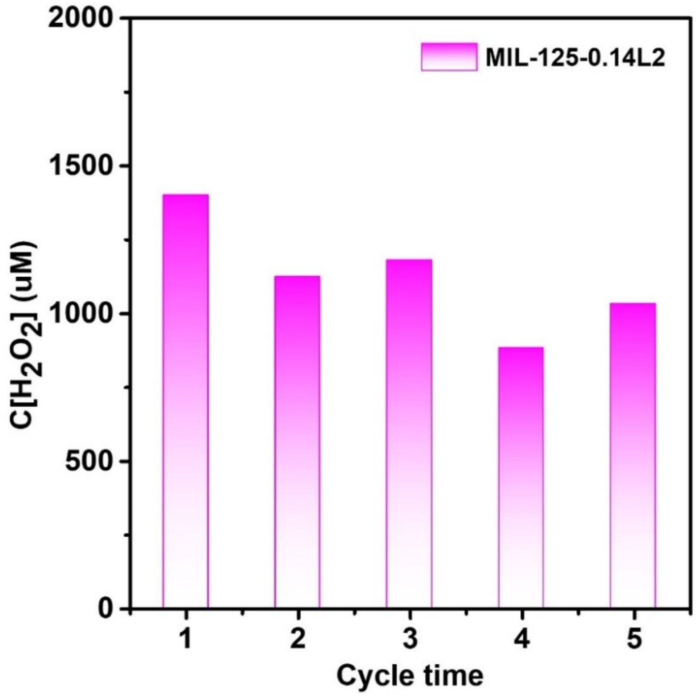


Fig. S6 Recycling tests of H_2O_2 in O_2-saturated CH_3CN solution (10 mL) of TEOA (2 mL) under photoirradiation ($\lambda > 400$ nm) using 10 mg of MIL-125-0.14L2.

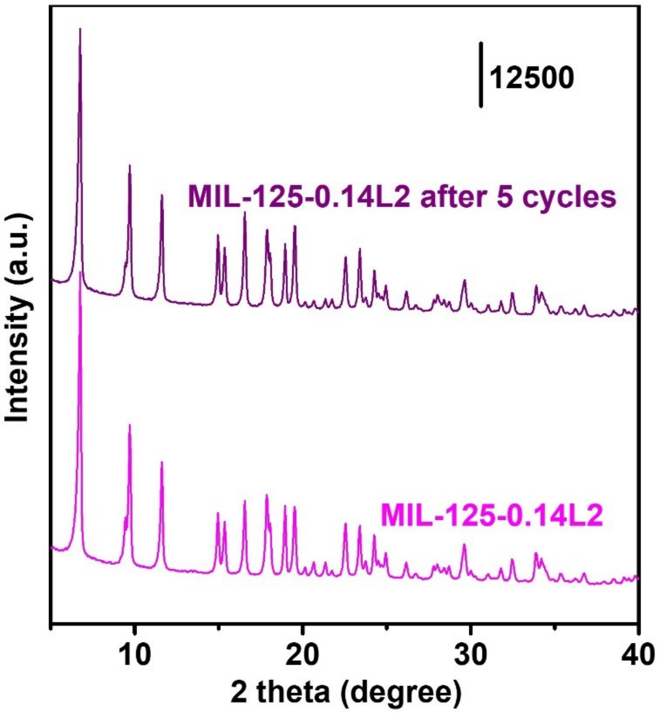


Fig. S7 XRD patterns of MIL-125-0.14L2 after 5 recycling tests.

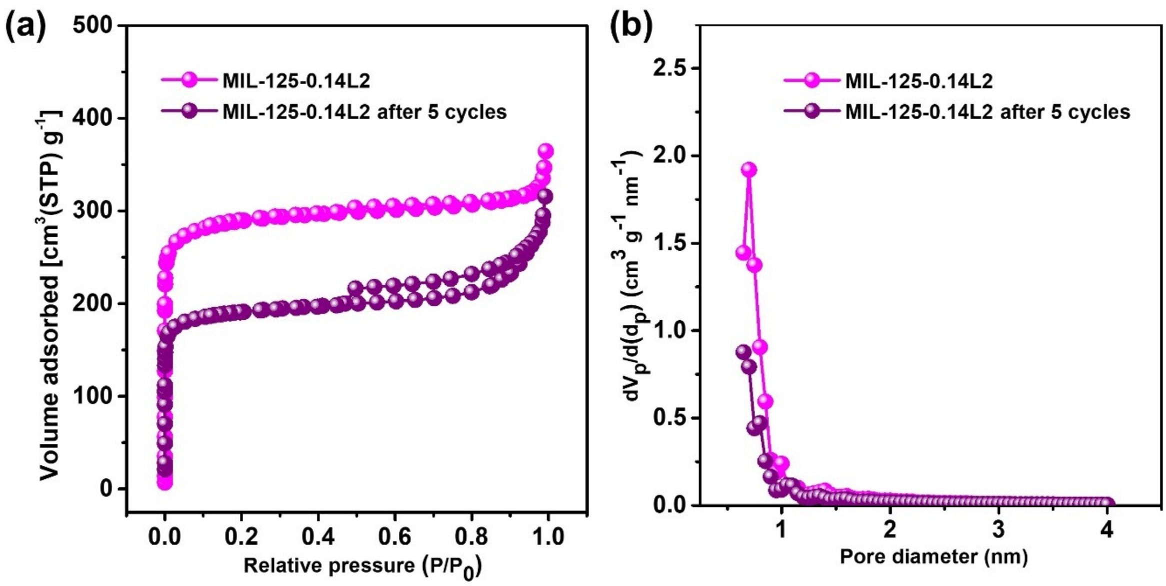


Fig. S8 (a) N_2 adsorption/desorption isotherms and (b) pore diameter distribution of MIL-125-0.14L2 after 5 recycling tests.

Table S2. BET surface area and V_p of MIL-125-0.14L2 after 5 recycling tests.

Samples	S_{BET} (cm^2 g^{-1})	D_p (nm)	V_p (cm^3 g^{-1})
MIL-125-0.14L2	800	0.70	0.43
After 5 cycles	532	0.70	0.29

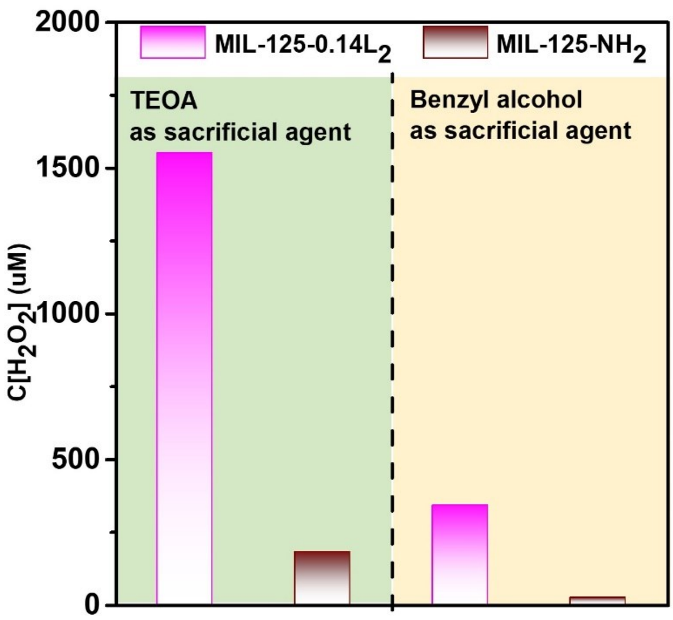


Fig. S9 Activity comparison of MIL-125-0.14L2 and MIL-125-NH_2 using TEOA or benzyl alcohol as sacrificial agent after 1 h of reaction. Reaction conditions: 5 mg of MOFs in O_2-saturated CH_3CN solution (5 mL) of TEOA (1 mL), or 10 mg of MOFs in O_2-saturated CH_3CN solution (10 mL) of benzyl alcohol (2 mL) under photoirradiation ($\lambda >$ 420 nm).

Table S3. Comparison of the photocatalytic H_2O_2 production on some of other typical photocatalysts under similar reaction conditions summarized in the recent review report (Angew. Chem. Int. Ed. **2020**, 59, 17356–17376).

Photocatalyst	Sacrificial reagent or reaction solution	Catalyst concentration	Irradiation conditions	Activity of H_2O_2
mesoporous g-C_3N_4	ethanol	4 mg mL^{-1}	$\lambda > 420$ nm	90 μmol (24 h)
(K,P,O)-g-C_3N_4	ethanol	0.5 mg mL^{-1}	$\lambda \geq 420$ nm	1.7 mM (7h)
CoP/g-C_3N_4	ethanol	1.0 mg mL^{-1}	$\lambda > 420$ nm	140 μM (2 h)
Au/g-C_3N_4	2-propanol	1.0 mg mL^{-1}	UV/Vis	747 μmol (2 h)
KPF_6/g-C_3N_4	ethanol	0.5 mg mL^{-1}	$\lambda > 420$ nm	1.5 mM (5 h)
$[Ru^{II}(Me_2phen)_3]^{2+}$	O_2-saturated aqueous H_2SO_4 solution	1.0 μM	$\lambda > 420$ nm	612 μM (9 h)
silica/graphene oxide/CdS	alcohol	0.5 g L^{-1}	$\lambda = 635$ nm	90 μM (1 h)
CdS-graphene	Water + methanol	1.0 mg mL^{-1}	Solar simulator	128 μM (12 h)
O_V-Bi/$Bi_2O_{2-x}CO_3$	Water + C_2H_5OH	4.0 mg mL^{-1}	$\lambda \geq 420$ nm	1.2 mM (3 h)
MIL-125-0.14L2 Our work	TEOA	1.0 mg mL^{-1}	$\lambda > 400$ nm	1654 μM (1 h)
	Benzyl alcohol			1103 μM (1 h)