Supplementary Information for

Flexible-Functionalized Cd-MOFs for Photocatalytic CO_2 Reduction: Tuning Framework Flexibility via Ligand Design

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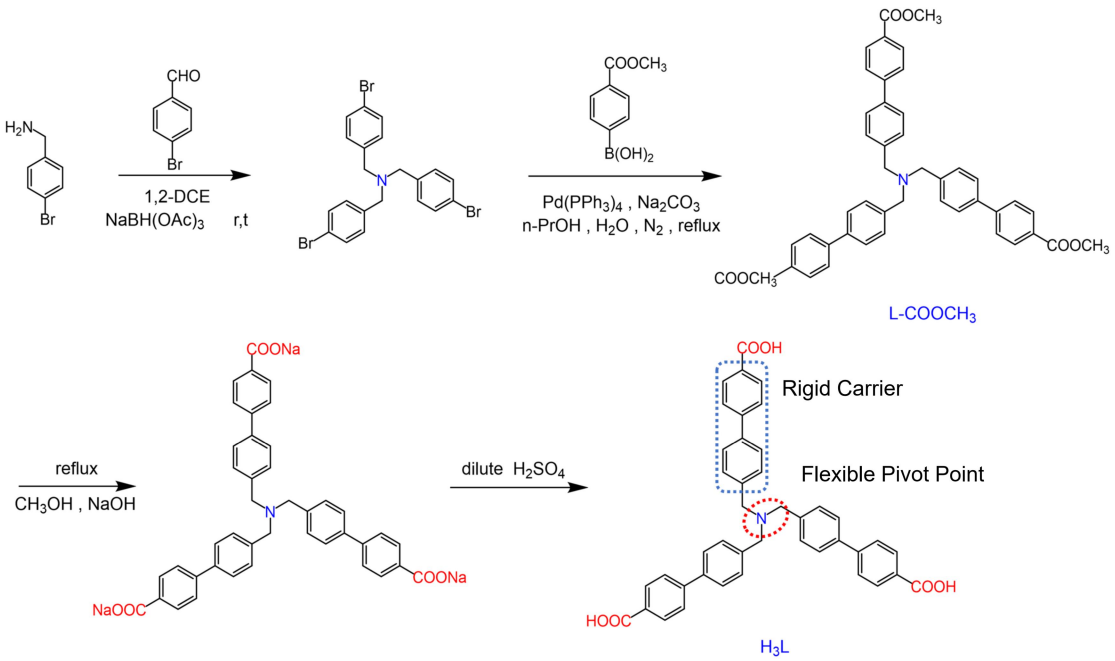

Fig. S1 Synthetic route to the semirigid triangular carboxylic acid H_3L.

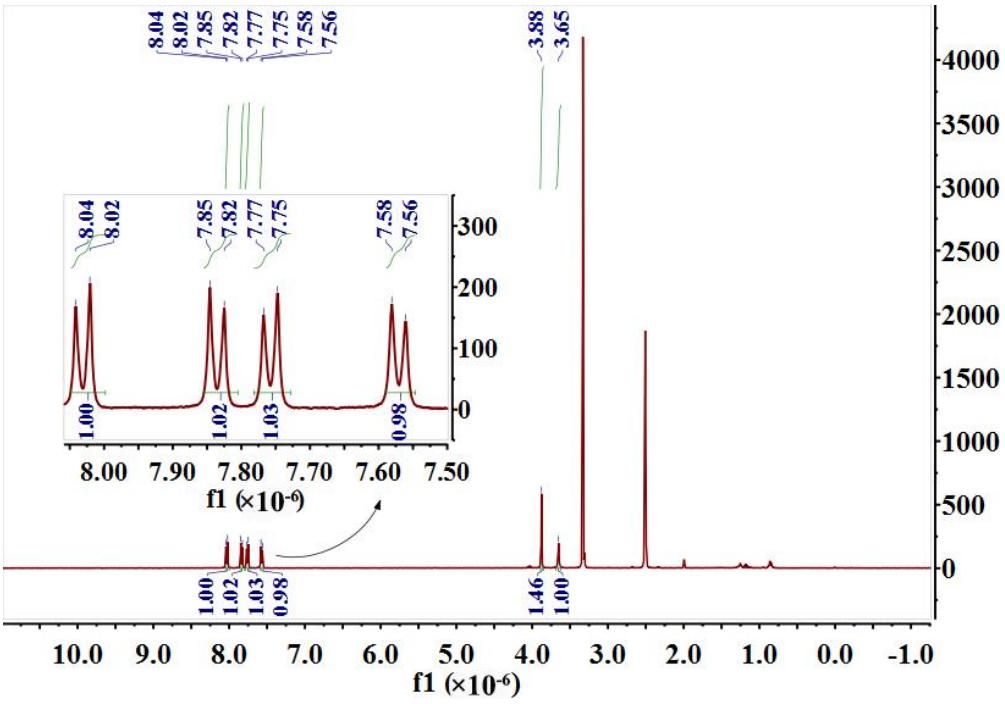

Fig. S2 ^{1}H NMR hydrogen spectrum of L-$COOCH_3$.

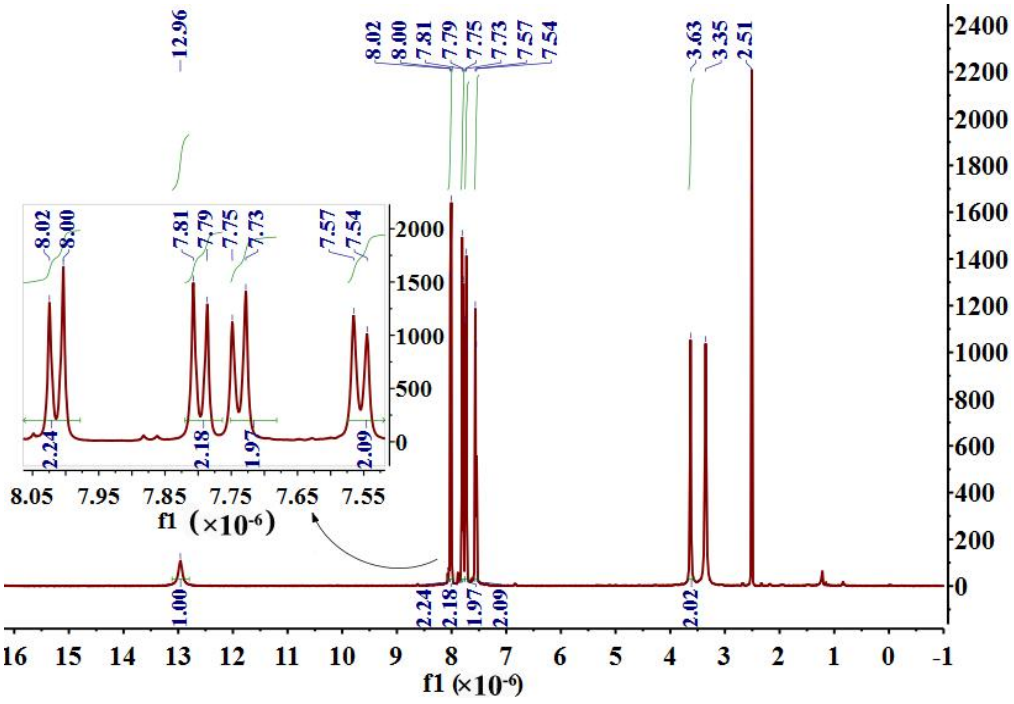

Fig. S3 ^{1}H NMR hydrogen spectrum of H_3L.

Tab. S1 Crystal data and structural refinements parameters of **AQNU-10**.

Complex	**AQNU-10**
Empirical formula	$C_{84}H_{68}Cd_3N_2O_{16}$
Formula weight	1698.60
Crystal system	Monoclinic
Space group	*Cc*
a / Å	46.4009(19)
b / Å	6.3419(2)
c / Å	22.6130(9)
α / °	90
β/ °	91.9630(10)
γ/ °	90
V / Å^3	6650.4(4)
Z	4

D_{calcd} / mg m^{-3}	1.696
μ / mm^{-1}	1.029
F(000)	3432
θ min-max / °	1.978, 26.372
Tot., uniq. data	26008, 10758
R(int)	0.0346
R_1, wR_2 [$I > 2\sigma(I)$]	0.0307, 0.0741
GOF on F^2	1.021
Min. and max resd dens (e·Å^{-3})	-0.583, 1.412

$R_1=\Sigma||F_o|-|F_c||/\Sigma|F_o|$; $wR_2=\{\Sigma[w(F_o^2-F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$; $w=1/[\sigma^2(F_o^2)+(aP)^2+bP]$,$P=(F_o^2+2F_c^2)/3$.

Tab. S2 Selected Bond Lengths (Å) and Angles (deg) for **AQNU-10**.

Length	Å	Length	Å
Cd(1)-O(7)	2.160(5)	Cd(1)-O(2W)	2.218(5)
Cd(1)-O(1W)	2.236(4)	Cd(1)-O(1)	2.237(5)
Cd(1)-O(9)#7	2.313(6)	Cd(2)-O(4W)	2.221(5)
Cd(2)-O(11)	2.287(4)	Cd(2)-O(10)#4	2.298(5)
Cd(2)-O(6)#5	2.374(5)	Cd(2)-O(1)#6	2.381(5)
Cd(2)-O(9)#4	2.526(5)	2.537(5)	2.537(5)
Cd(2)-C(70)#4	2.745(6)	Cd(3)-O(3W)	2.244(5)
Cd(3)-O(5)	2.296(4)	Cd(3)-O(8)#1	2.302(5)
Cd(3)-O(3)#2	2.348(4)	Cd(3)-O(4)#2	2.394(5)
Cd(3)-O(12)#3	2.436(5)	Cd(3)-O(6)	2.505(4)
Cd(3)-C(28)#2	2.733(6)		
Angle	deg	Angle	deg

O(7)-Cd(1)-O(2W)	105.00(19)	O(7)-Cd(1)-O(1W)	107.5(2)
O(2W)-Cd(1)-O(1W)	90.7(2)	O(7)-Cd(1)-O(1)	128.5(2)
O(2W)-Cd(1)-O(1)	88.10(19)	O(1W)-Cd(1)-O(1)	122.26(17)
O(7)-Cd(1)-O(9)#7	89.42(19)	O(2W)-Cd(1)-O(9)#7	165.58(16)
O(1W)-Cd(1)-O(9)#7	85.3(2)	O(1)-Cd(1)-O(9)#7	82.44(17)
O(4W)-Cd(2)-O(11)	147.54(18)	O(4W)-Cd(2)-O(10)#4	76.0(2)
O(11)-Cd(2)-O(10)#4	136.12(18)	O(4W)-Cd(2)-O(6)#5	100.0(3)
O(11)-Cd(2)-O(6)#5	88.89(16)	O(10)#4-Cd(2)-O(6)#5	86.09(17)
O(4W)-Cd(2)-O(1)#6	89.3(2)	O(11)-Cd(2)-O(1)#6	80.74(17)
O(10)#4-Cd(2)-O(1)#6	100.85(17)	O(6)#5-Cd(2)-O(1)#6	169.60(15)
O(4W)-Cd(2)-O(9)#4	122.06(18)	O(11)-Cd(2)-O(9)#4	85.25(15)
O(10)#4-Cd(2)-O(9)#4	53.95(18)	O(6)#5-Cd(2)-O(9)#4	103.29(17)
O(1)#6-Cd(2)-O(9)#4	75.27(16)	O(4W)-Cd(2)-O(12)	97.70(17)
O(11)-Cd(2)-O(12)	54.01(14)	O(10)#4-Cd(2)-O(12)	159.84(17)
O(6)#5-Cd(2)-O(12)	76.06(15)	O(1)#6-Cd(2)-O(12)	98.16(17)
O(9)#4-Cd(2)-O(12)	139.16(14)	O(4W)-Cd(2)-C(70)#4	100.5(2)
O(11)-Cd(2)-C(70)#4	110.25(19)	O(10)#4-Cd(2)-C(70)#4	27.0(2)
O(6)#5-Cd(2)-C(70)#4	92.76(16)	O(1)#6-Cd(2)-C(70)#4	90.16(17)
O(9)#4-Cd(2)-C(70)#4	27.20(18)	O(12)-Cd(2)-C(70)#4	160.07(17)
O(3W)-Cd(3)-O(5)	140.39(16)	O(3W)-Cd(3)-O(8)#1	96.58(19)
O(5)-Cd(3)-O(8)#1	88.13(17)	O(3W)-Cd(3)-O(3)#2	79.04(17)
O(5)-Cd(3)-O(3)#2	139.70(15)	O(8)#1-Cd(3)-O(3)#2	96.21(16)
O(3W)-Cd(3)-O(4)#2	133.73(17)	O(5)-Cd(3)-O(4)#2	85.06(16
O(8)#1-Cd(3)-O(4)#2	92.06(18)	O(3)#2-Cd(3)-O(4)#2	54.83(15)
O(3W)-Cd(3)-O(12)#3	78.25(17)	O(5)-Cd(3)-O(12)#3	92.92(16)

O(8)#1-Cd(3)-O(12)#3	173.03(17)	O(3)#2-Cd(3)-O(12)#3	87.45(16)
O(4)#2-Cd(3)-O(12)#3	94.89(17)	O(3W)-Cd(3)-O(6)	86.03(17)
O(5)-Cd(3)-O(6)	54.48(15)	O(8)#1-Cd(3)-O(6)	99.55(16)
O(3)#2-Cd(3)-O(6)	159.40(15)	O(4)#2-Cd(3)-O(6)	137.04(16)
O(12)#3-Cd(3)-O(6)	75.59(15)	O(3W)-Cd(3)-C(28)#2	106.0(2)
O(5)-Cd(3)-C(28)#2	112.54(19)	O(8)#1-Cd(3)-C(28)#2	96.06(17)
O(3)#2-Cd(3)-C(28)#2	27.20(19)	O(4)#2-Cd(3)-C(28)#2	27.70(19)
O(12)#3-Cd(3)-C(28)#2	89.90(17)	O(6)-Cd(3)-C(28)#2	159.03(17)

Symmetry Codes for 1: #1 *x*+1/2,-*y*+1/2,*z*+1/2; #2 *x*+1/2,-*y*+3/2,*z*+1/2; #3 *x*+1,-*y*+1,*z*+1/2; #4 *x*-1/2,-*y*+1/2,*z*-1/2; #5 *x*-1,-*y*+1,*z*-1/2; #6 *x*-1/2,-*y*+3/2,*z*-1/2; #7 *x*,*y*+1,*z*; #8 *x*,*y*-1,*z*

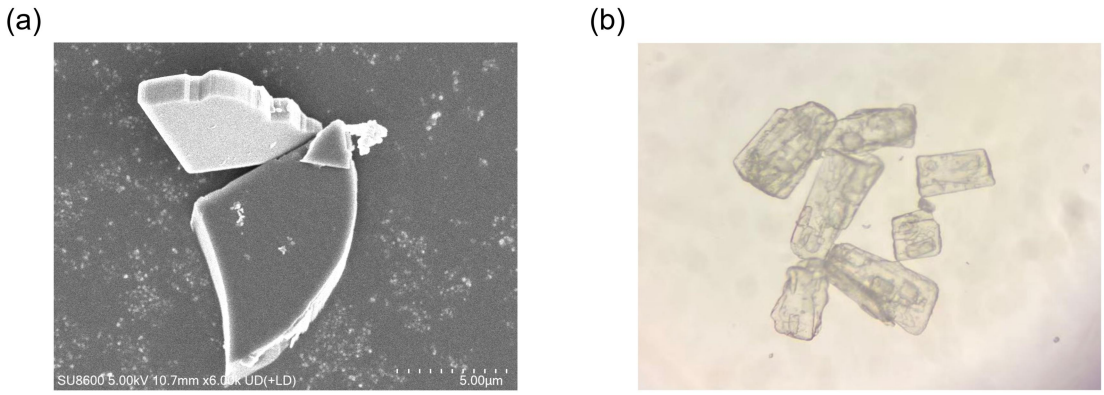

Fig. S4 (a) SEM image and (b) the optical microscope photograph of **AQNU-10.**

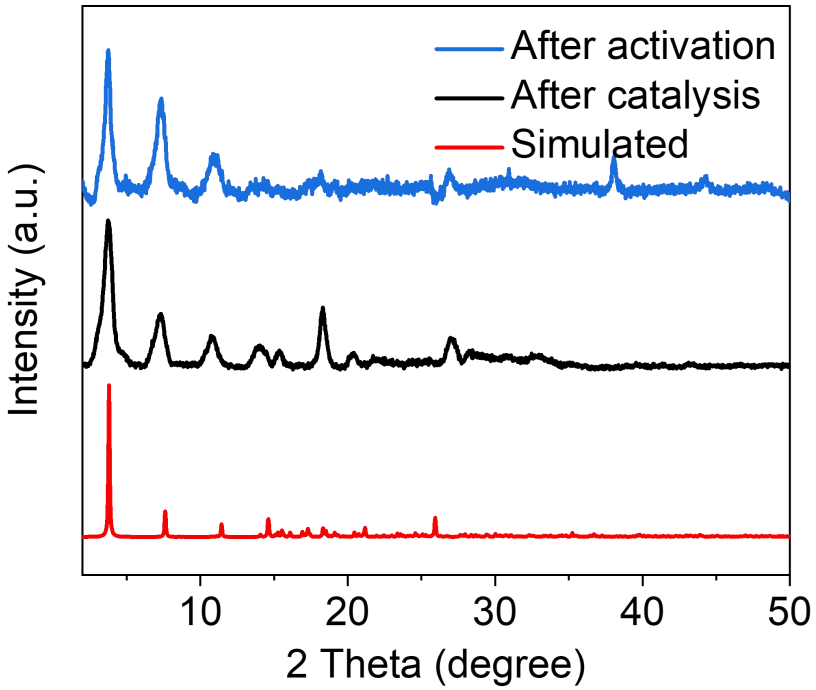

Fig. S5 After activation and catalysis powder XRD patterns of **AQNU-10.**

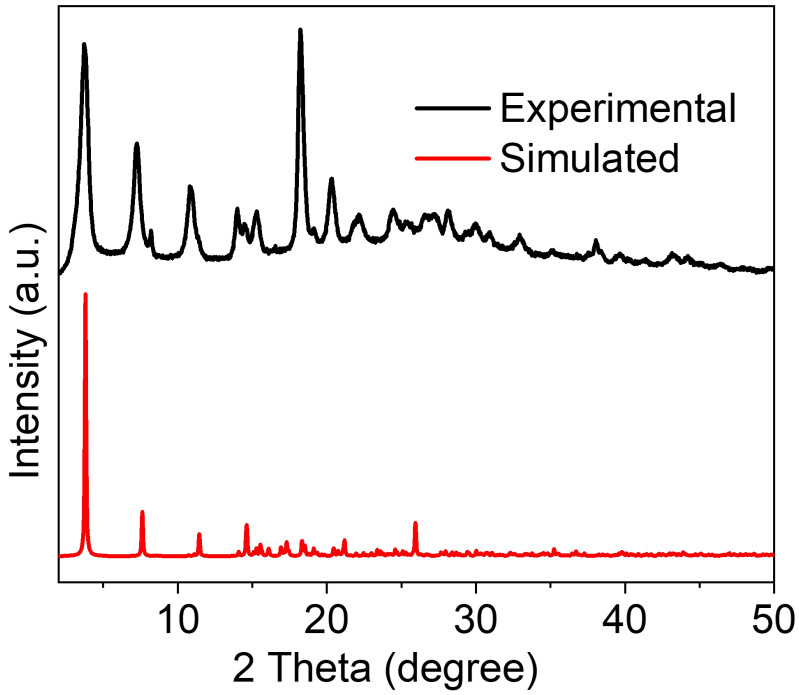

Fig. S6 Simulated and experimental powder XRD patterns of **AQNU-10**.

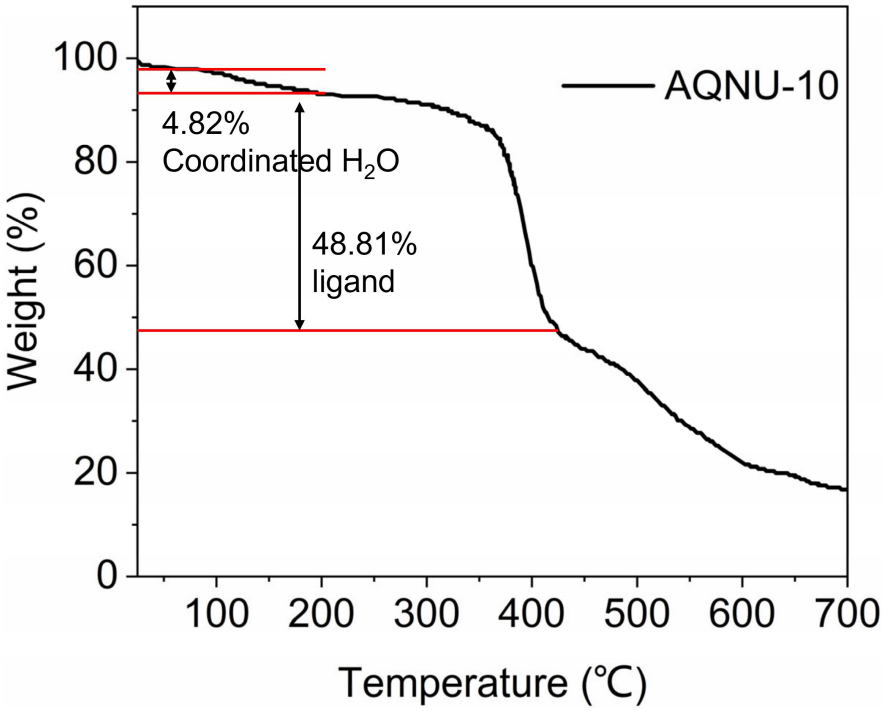

Fig. S7 Thermogravimetric curve of **AQNU-10**.

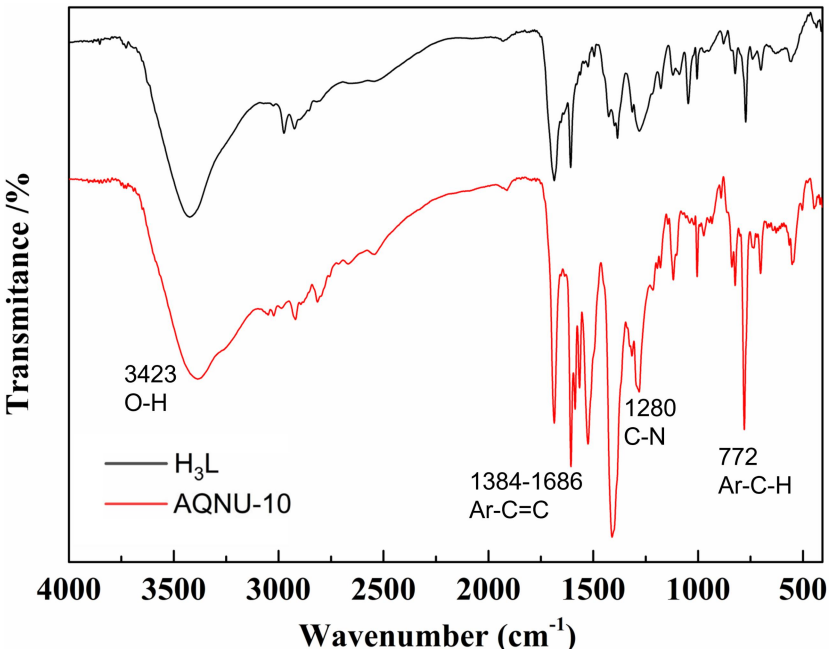

Fig. S8 Infrared spectra of H_3L ligand and **AQNU-10**.

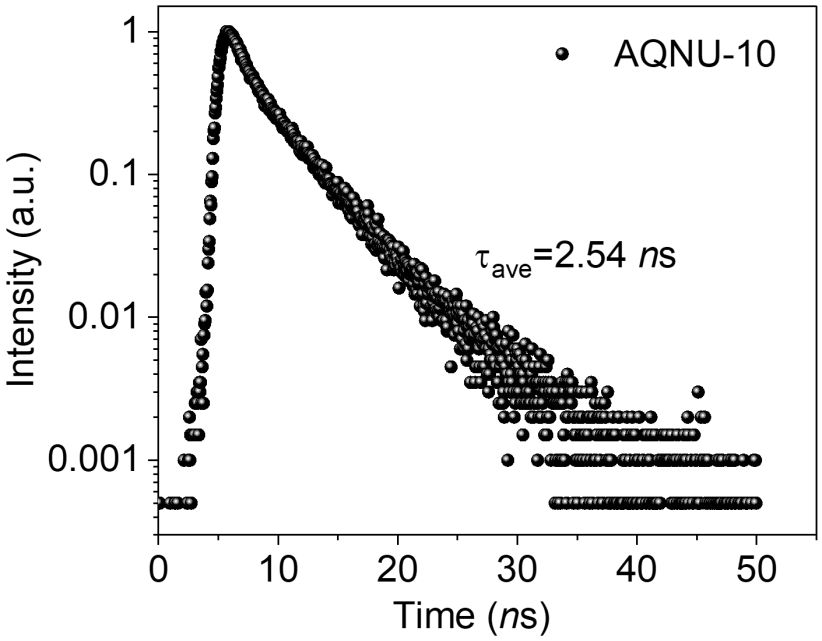

Fig. S9 Fluorescence lifetime decay profile of **AQNU-10**.

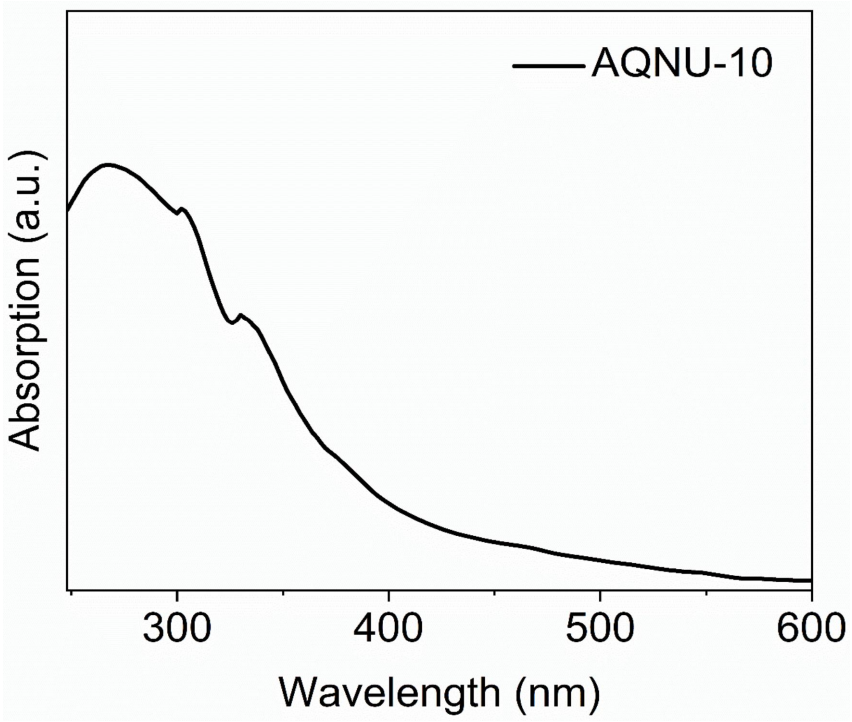

Fig. S10 The solid ultraviolet visible (UV-Vis) absorption spectrum of **AQNU-10**.

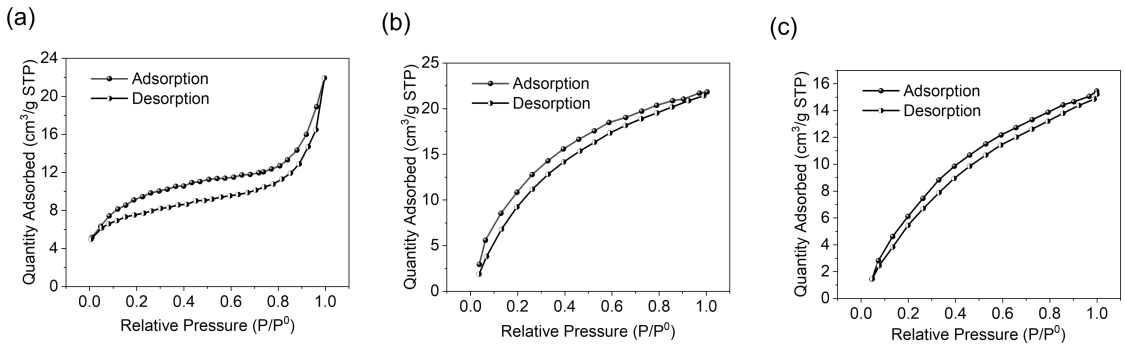

Fig. S11 (a) N_2 adsorption and desorption isotherms of **AQNU-10** measured at 77 K. (b-c) CO_2 adsorption-desorption isotherms of **AQNU-10** at 273 and 298 K

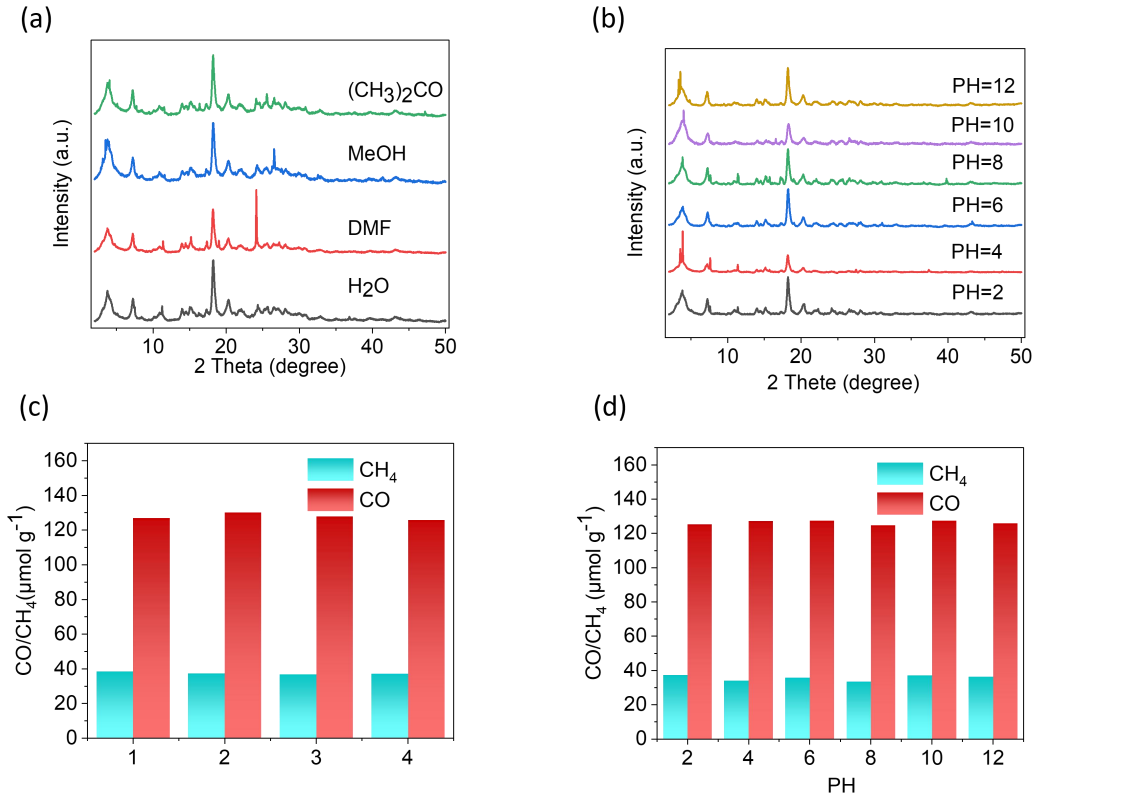

Fig. S12 XRD patterns (a-b) and Photocatalytic CO_2 reduction performance (c-d) of **AQNU-10** in different solvents and PH environments.

Note: (c): 1. Acetone; 2. Methanol; 3. N, N-Dimethylformamide; 4. H_2O

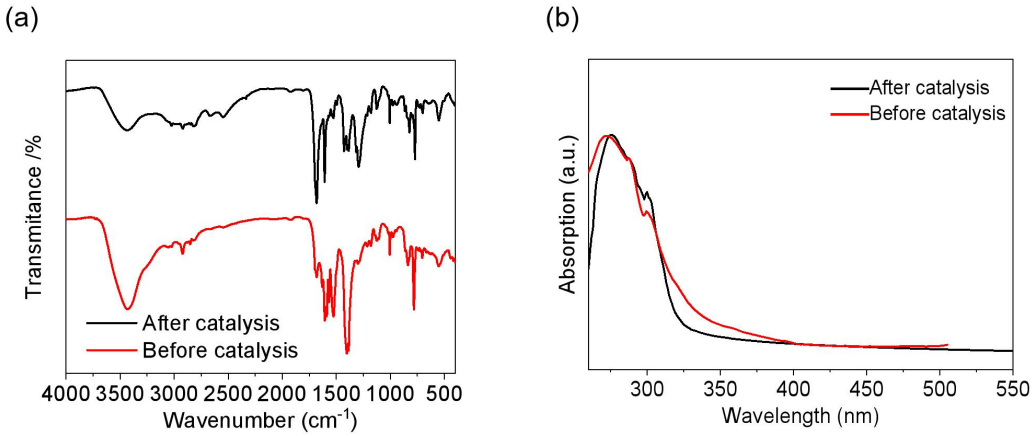

Fig. S13 (a) FT-IR and **(**b**)** UV-vis absorption spectra of **AQNU-10** before and after catalysis.

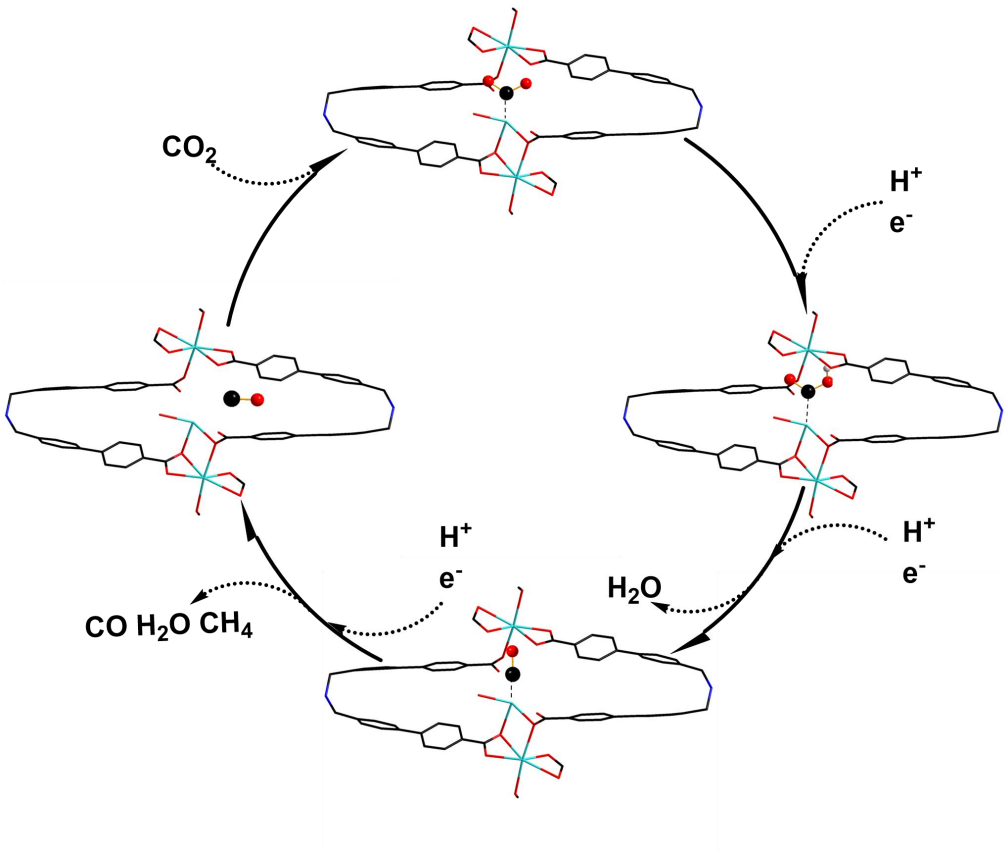

Fig. S14 CO_2RR catalytic cycle.

Calculation of CO production rate.

The CO production rate was calculated using the equation (1).

$$C_{CO}(mmol\ g^{-1}h^{-1}) = \frac{N_{CO}}{M_{photocatalyst} \times T_{illumination}} \quad (1)$$

where the N_{CO} represents the mole numbers of generated CO, $M_{photocatalyst}$ is the quality of the photocatalyst in reaction, $T_{illumination}$ is the illumination time.

Calculation of CO production selectivity.

The selectivity of CO production is evaluated using the equation (2).

$$CO\ selectivity(\%) = \frac{2\varphi_{CO}}{2\varphi_{CO} + 2\varphi_{H_2}} \quad (2)$$

Where the φ_{CO} represents the mole numbers of generated CO, φ_{H2} represents the mole numbers of generated H_2.