Supporting Information for

Hydrogen-Bonding 2D Coordination Polymer for Enzyme-Free Electrochemical Glucose Sensing

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1 General Methods and Instrumentation

All starting materials were purchased from Sigma Aldrich and were used as received without further purification. The solvents were reagent grade.

1.1. Powder X-ray Diffraction (PXRD): PXRDs

Powder X-ray diffraction (PXRD) patterns were recorded with a PANalytical X'Pert MPD (Cu K α , λ =1.5418 Å) within the 2 θ range 5-50° at room temperature.

1.2. Thermogravimetric analysis (TGA)

Thermogravimetric analysis (TGA) was carried out in a nitrogen stream using Hiden-Isochema IGA-002 gravimetric equipment with heating from room temperature up to 700 °C at a heating rate of 10 °C·min⁻¹.

1.3. Electrochemistry

The electrochemical performance was measured with a Bioanalytical Systems (BASi) Potentiostat for cyclic voltammetry (CV) and differential pulse voltammetry (DPV). CV and DPV measurements were performed in 0.1 mM K₃[Fe(CN)₆]/K₄[Fe(CN)₆] (1:1) solution containing 0.5 mM KCl at a scan rate of 100 mV/s (for CV) scanning the potential from 0 V to +0.5 V and back to 0 V. The parameters for DPV were: pulse width 50 ms, pulse period 200 ms, pulse amplitude 50 mV and step E 4 mV, scanning the potential from 0 V to 0.5 V. All experiments were carried out at room temperature with a three-electrode system. The glassy carbon electrode (GC) (3.0 mm diameter) was used as the working electrode, a Ag/AgCl electrode (3 M KCl) as a reference electrode, and a platinum wire (0.1 mm wire diameter) as the auxiliary electrode (all electrodes were purchased from BASi USA).

1.4. Raman Spectroscopy and VT Raman Spectroscopy

Raman spectra were collected using an inVia Renishaw Raman Spectrometer with 785 nm laser excitation (Argon ion). In situ variable temperature Raman (VT- Raman spectra) were collected using Linkam stage, temperature points from 25 to 50, 75, 100, 125, 150, 175, 200, 225, 250 °C with a rate of ~7 °C /min. All the samples were sealed in glass capillary (diameter 1 mm).

1.5. Electrochemical Sensing and Fabrication of modified GC Electrodes.

The ground CP1 (10 mg) was dispersed in DMF (1 mL) to achieve a 10 mg/mL suspension and was sonicated for 5 minutes to form a homogeneous dispersion. The GC electrode (3 mm diameter) was polished with 0.3 um Al_2O_3 slurry for 5 minutes, then sonicated in ethanol/water (1:1, v/v) solution for 1 minute, repeat for 3 times. 10 µL of the suspension was drop-casted onto the surface of the GCE overnight and left to dry in air.

2 Synthesis

2.1. Synthesis of [Zn₂(BPDC)₁Mel_{0.5}-Mel_{0.5}] · (DMF_{0.6}) {denoted CP1}.

 $Zn(CH_3COO)_2 \cdot 2H_2O(0.4 \text{ mM}, 87.8 \text{ mg}), 1,3,5$ -triazine-2,4,6-triamine (0.4 mM, 47.3 mg) and biphenyl-4,4'-dicarboxylic (0.6 mM, 145.3 mg) were added to a mixture of DMF and MeOH (in a ratio of 4:1=v/v, 10 ml) before the addition of 1% H₂O. The mixture was heated in the oven to 90 °C for 72 hours. The solution was cooled down to room temperature and the yellow hexagonal crystals were collected and sorted in DMF. Anal. Calcd (%) for $[Zn_2(BPDC)_1Mel_{0.5}-Mel_{0.5}] \cdot (DMF_{0.6})$ C, 44.236; N, 18.061; H, 4.641. Found (%): C, 47.010; N, 12.200; H, 3.587. The difference between the predicted and calculated elemental analysis results is not uncommon for CPs and reflects the porous nature of the materials that are susceptible to adsorption and desorption of guests (S.I. Figure. S2). Crystal structure data can be obtained from the Cambridge Crystallographic Data Center (CCDC 2036487).

2.2. Synthesis of Gold Nanoparticles (AuNPs).

The AuNPs were synthesized according to the literature procedure with no modifications.1 According to the literature, the size of the nanoparticles was 20 nm.

2.3. Synthesis of Platinum Nanoparticles (PtNPs).

The PtNPs were synthesized according to the literature procedure with no modifications.² According to the literature, the size of the nanoparticles was 4.1 nm.

3 Crystal Structure

3.1. Single Crystal X-Ray Diffraction

 Table S1. Crystallographic parameters (CCDC 2036487)

Empirical formula	C ₂₀ H ₂₂ N ₁₂ O ₄ Zn
Formula weight	559.86
Temperature/K	100.01(10)
Crystal system	orthorhombic
Space group	Abm2
a/Å	17.5983(4)
b/Å	24.5934(3)
c/Å	18.2648(2)
$\alpha/^{\circ}$	90
β/°	90
$\gamma/^{\circ}$	90
Volume/Å ³	7905.0(2)
Z	12
$\rho_{calc}g/cm^3$	1.411
µ/mm ⁻¹	1.730
F(000)	3456.0
Radiation	$CuK\alpha (\lambda = 1.54178)$
2Θ range for data collection/°	7.188 to 145.164
Index ranges	$-21 \le h \le 13, -18 \le k \le 30, -22 \le l \le 22$
Reflections collected	16740
Independent reflections	7498 [$R_{int} = 0.0244, R_{sigma} = 0.0310$]
Data/restraints/parameters	7498/1/342
Goodness-of-fit on F ²	1.036
Final R indexes [I>=2 σ (I)]	$R_1 = 0.0461, wR_2 = 0.1255$
Final R indexes [all data]	$R_1 = 0.0482, wR_2 = 0.1271$
Largest diff. peak/hole / e Å ⁻³	0.82/-0.53
Flack parameter	0.28(2)



b

а



Figure S1. (a) Image of the unit cell of CP1; (b) ORTEP diagram of CP1.

3.2. Powder X-Ray Diffraction



Figure S2. The refined PXRD of CP1 pattern in red), the experimental PXRD pattern for CP1 in black) and the differences plot in gray.

The comparation of the simulated and experimental PXRD patterns are shown in Figure S2. The close correspondences of peak positions illustrate the structure is correct. The blue (refined) plot of Figure S2 indicates an acceptable fitted degree with $R_p = 6.648\%$, $wR_P = 10.307\%$, where the R_p and wR_P are agreement factors.

Due to the favorable coordination between Zn(II) and carboxylate-based ligands, the IRMOF-10 2D sheet structure (CCDC 186896) was initially considered as a structural component. To further confirm we incorporated melamine into the crystal structure, we compared the PXRD of pure [Zn(BPDC)] (IRMOF-10) with that of our CP. We found that IRMOF-10 decomposed in H₂O immediately, but the chemical stability of our CP (i.e. stability under aqueous conditions) has been significantly enhanced by incorporating melamine into the framework. We envisage that the H-bonding within the framework may contribute to the enhanced stability.

4 Thermogravimetric analysis (TGA)

The thermogravimetric analysis (TGA) curve shows a weight loss of 25% from 25 to 250 °C, which could be attributed to the loss of the DMF, MeOH and coordinated DMF molecules in the molecular unit. After a plateau until 370 °C, the samples begin to decompose with complete collapse at 550 °C.



Figure S3. (a) The TGA of CP1 (under N₂, up to 700 °C) shows a multi-step decomposition. The 1st decrease between 20-250 could be the solvent (MeOH and H₂O) loss before 250 °C; then the 2nd step which is in the range between 250-350 °C due to the loss of DMF molecule³; the 3rd step could be the collapse of the melamine structure⁴; and the significant 4th weight loss over the range370-550 °C could due to framework collapse. (b) DTG of CP1.

5 Raman spectrum analysis

Raman spectra were collected using an inVia Renishaw Raman Spectrometer with 785 nm laser excitation (Argon ion). In situ variable temperature Raman (VT- Raman spectra) were collected using a Linkam stage, with temperature points at 25, 50, 75, 100, 125, 150, 175, 200, 225, 250 °C with a heating rate of ~7 °C /min. All of the samples were sealed in glass capillaries (diameter 1 mm).



Figure S4. Raman spectrum of CP1 at room temperature



Figure S5. Raman Comparation of CP1 in D₂O and H₂O glucose solution at room temperature

6 Computational studies of CP1

Density functional theory (DFT) calculations³⁻⁶ were performed with VASP 5.4.4 including Van der Walls dispersion corrections using the D3 and Becke-Jonson approximation [DFT-D3(BJ)]^{7,8} to represent hydrogen bonding. The generalized gradient approximation of Perdew, Burke and Ernzerhof (PBE)¹¹ with the projector augmented-wave (PAW) method was used.^{12,13} The plane-wave energy cut-off was set to 410 eV and the energy convergence criteria was 10⁻⁶ eV. A single k-point at the gamma point⁹ was employed with the Gaussian smearing method¹⁰ and a sigma value of 0.05. The CP structure consisted of the as obtained from the single crystal experiment as in Figure S1b and also Figure 4a; two sets of alternating Zn(BPDC)Mel 2D net work and interstitial melamine layers with hydrogen termination where necessary were selected in Olex2 (Figure 3a in main text).

Since the framework contains Zn, the commonly used Hubbard U-J correction was employed.¹⁶ A value for U-J of 16.2 eV was determined using the variational linear response approach method of Cococcioni.¹⁷ This value is significantly higher than other commonly used values found in the literature of 7.5 eV and 12 eV,^{18–21} which is consistent with literature which predicts the difficulty of using this method for determining U-J for atomic species with fully filled electron shells.²² As a result, all calculations were repeated with a range of U-J values of from 0 eV to 16 eV in 2 eV steps with a few extra U-V values. We found little effect on the final calculated quantities as shown in Figure S9 and as a result, we used the value of U-J of 16.2 eV for the results presented in the main text. Specifically, the relaxed geometries and ELF results were very similar as in Figures S8 and S9.

The Geometry optimizations were performed to reduce the Pulay stress.²³ This method is similar to the relaxation scheme used for other CP/MOFs.²⁴ This resulted in a structure where the positions were optimized until all forces between atoms were smaller than 1 meV/Å.



Figure S6 CP1 backbone in a $1 \times 1 \times 1$ supercell with U = 16.2 eV. grey = carbon, red = oxygen, light blue = zinc, blue = nitrogen.



6.1 Unit cell parameters as a function of U-J

Figure S7 The lattice parameter (a) and volume of unit cell (b) in different U values. The experimental unit cell volume value is shown by the dashed lines (b).

6.2 Geometry optimization with different U values





Figure S8. Geometry Optimization with different U values in the Zn based system (strong corelated system) (U=0, 2, 4, 6, 8, 10, 12, 14, 15, 15.7, 16, 16.2).

6.3 Electron localization function (ELF) optimization with different U values





Figure S9. Optimization of ELF 2d cut plane at face 0,0,1 for different U values for the Zn based system (strong corelated system) (U=0, 4, 6, 8, 10, 12, 15, 15.7, 16, 16.2).

6.4 Table of bond distances

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Bonding Mole	g Source ecule	Bonding Name	Experimental Bond length (Å)	Simulated Bond length (Å)	Differences %
Interstitial Melamine 1 Interstitial Melamine 2		H68 N20	2.22881	1.94044	12.93829443
		N72…H4	2.24942	2.01619	10.36845053
		N80 H24	2.19909	2.06804	5.959283158
		H52 N27	2.15107	1.78657	16.94505525
		N28 H51	2.15107	1.78786	16.8850851
	Interstitial Melamine 2	N79 H23	2.19909	2.06782	5.969287296
		N71…H3	2.24942	2.01526	10.40979452
	H67…N19	2.22881	1.94037	12.94143512	

7 ELECTROCHEMICAL SENSING



Figure S10. (a) DPV performance of bare electrode from 0 mM to 55.56 mM in $K_3[Fe(CN)_6]/K_4[Fe(CN)_6]$ solution containing 0.5 mM KCl at pH 7.5 for glucose detection, detection range from 0.55mM to 55.56mM, limit of detection is 0.55 mM; (b) Plots of the current density versus the concentration of glucose ($c_{glucose}$) (the inset shows the curve of the linear current density on the log value of $c_{glucose}$, $R^2 = 0.9746$ with the linear range from 0.55 mM to 55.56 mM; error bars denote standard deviation for 3 measurements.)



Figure S11. (a) Current densities of CP1/GC to 5 mM glucose for testing of 3 individual CP1/GC electrodes. The error bars denote the standard deviations. (b) Stability of CP1/GC to 5 mM glucose with 15 days measurement over 1 month. The error bars denote the standard deviations.

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