



# Making metal–organic frameworks electron-deficient for ultrasensitive electrochemical detection of dopamine

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## ABSTRACT

Two metal–organic frameworks (MOFs) containing bipyridinium moieties, UiO-67-MQ and UiO-67-DQ (MQ = *N,N'*-dimethyl-2,2'-bipyridinium, DQ = *N,N'*-ethylene 2,2'-bipyridinium), prepared by post-synthetic *N*-alkylation of the Zr-MOF with 2,2'-bipyridyl-4,4'-dicarboxylate (UiO-67-bpy, bpy = 2,2'-bipyridyl), were used as electrode modifiers for detection of dopamine. Compared with UiO-67-bpy, UiO-67-MQ and UiO-67-DQ significantly enhance the voltammetric sensitivity of dopamine, which is attributed to the donor–acceptor interactions between the electron-deficient bipyridinium moieties and the electron-rich analyte. The detection limits are further lowered by an order of magnitude by the introduction of multi-walled carbon nanotubes, demonstrating remarkable synergy in promoting electron-transfer kinetics. This work is the first report of the use of electron-deficient MOFs in electrochemical sensors.

## 1. Introduction

Dopamine (DA) is an important neurotransmitter in the central nervous system, as well as in the renal and hormonal systems. Abnormal DA concentration causes various diseases such as schizophrenia and Parkinson's disease [1–3], so accurate determination of DA is important for disease diagnosis and monitoring. Electrochemical detection is the best choice for this redox-active analyte [2–4]. Unfortunately, DA has a poor response at conventional electrodes owing to sluggish interfacial electron transfer, and coexisting species may interfere by giving overlapping signals. To address these issues, various materials have been used to modify electrodes, including metal nanoparticles [5–7], oxides [8,9], carbon materials [10–12], and composites [13–16].

Metal–organic frameworks (MOFs) have become a vigorous field of research because their diversity and ease of modification in terms of structure, porosity and properties suggest that they are suitable for applications such as adsorption, catalysis and sensors [17–19]. The use of MOFs as electrode modifiers for chemo- and biosensors has emerged rapidly in the last five years [20]. To improve their performance, MOFs have been composited with different materials [21–28]. Possessing intriguing features such as excellent electronic conductivity, large surface area and tunable surface properties [29], carbon nanotubes, single- or multi-walled (SWCNTs or MWCNTs), have often been used in combination with MOFs [30–36]. However, the use of MOFs in

electroanalytic chemistry is still in its infancy. Only a few MOFs have been used for detection of DA [36–40]. Structure–property correlations needed for the rational choice and optimization of MOFs are still lacking. Generally, stronger electrode–analyte interactions enhance the electron transfer rate and lead to a more sensitive response. In principle, MOFs can be specifically functionalized to increase the interactions through pre-synthetic, or more powerfully, post-synthetic modification [41]. Post-synthetic strategies have been successful in the study of MOFs as sorbents, catalysts, and chemical sensors [42–44]. UiO-67-bpy (bpy = 2,2'-bipyridyl), a Zr-MOF with 2,2'-bipyridyl-4,4'-dicarboxylate, has recently been post-synthetically *N*-alkylated to give bipyridinium-functionalized MOFs UiO-67-MQ (MQ = *N,N'*-dimethyl-2,2'-bipyridinium) [45–47] and UiO-67-DQ (DQ = *N,N'*-ethylene 2,2'-bipyridinium) – see Fig. 1 [48]. Bipyridinium species are well known for their electron-deficient character, which allows them to form donor–acceptor (D–A) charge-transfer (CT) complexes with electron-rich species. We have demonstrated that CT complexation of UiO-67-MQ/UiO-67-DQ with electron-rich anions [48] and of UiO-67-MQ with alkylamines [45] can result in colorimetric and fluorescence sensing properties. Inspired by these results and considering that dopamine contains two electron-rich groups (ethylamine and catechol), we envision that electrodes modified with electron-deficient MOFs should enable sensitive DA detection. As a proof-of-concept, here we report that, compared with UiO-67-bpy, UiO-67-MQ and UiO-67-DQ do indeed afford high voltammetric sensitivity to dopamine owing to

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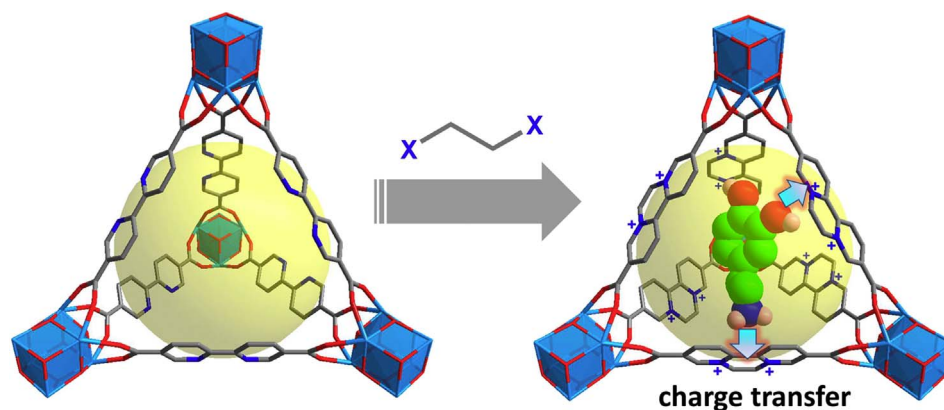


Fig. 1. Creation of electron-deficient UiO-67-DQ from UiO-67-bpy. A DA molecule and its interactions with the framework are shown schematically in UiO-67-DQ.

donor–acceptor interactions. Incorporation of MWCNTs further increases the sensitivity by an order of magnitude because of strong synergistic effects.

## 2. Experimental

### 2.1. Materials and characterization

UiO-67-bpy [46], ethylene ditriflate [49] and UiO-67-MQ [45] were synthesized according to literature procedures. UiO-67-DQ was prepared by a reported procedure [48] with minor modification: UiO-67-bpy (100 mg) and ethylene ditriflate (0.5 mL) were stirred in  $\text{CHCl}_3$  (2 mL) for 4 h at room temperature. The solid was isolated by filtration, washed with ethanol, and dried at  $100^\circ\text{C}$  for 2 h in a vacuum (yield > 90%). The MOFs were characterized by powder X-ray diffraction (XRD, Rigaku D/Max-2500), FT-IR spectroscopy (Nicolet NEXUS 670), NMR (Bruker Advance 400 MHz), scanning electron microscopy (SEM, Hitachi S-4800) and UV–vis spectroscopy (SHIMADZU UV-2700, reference:  $\text{BaSO}_4$ ).

### 2.2. Electrochemistry

Cyclic voltammetry (CV) and differential pulse voltammetry (DPV) were performed on a CHI660E workstation (Shanghai CH) in 0.1 M phosphate buffer solution (PBS) using a three-electrode system (a modified glassy-carbon electrode (GCE,  $\phi 3$  mm), a saturated Ag/AgCl electrode and a platinum wire). The positive and negative initial scan directions make no essential difference in peak currents and potentials in the CVs of DA. For electrode modification, 1.0 mg MOF [and 0.5 mg MWCNTs (98%, diameter 3–20 nm, length 0.5–2  $\mu\text{m}$ ), if used] was ultrasonically suspended in 0.1 mL water and 10  $\mu\text{L}$  Nafion (5 wt% in lower aliphatic alcohols and water). A GCE was polished with slurry alumina (1.0, 0.3 and 0.05  $\mu\text{m}$ , successively), ultrasonically washed with water, coated with 2.5  $\mu\text{L}$  of the suspension and dried at  $40^\circ\text{C}$ .

## 3. Results and discussion

### 3.1. Materials characterization

UiO-67-DQ was prepared by post-synthetic N-alkylation of UiO-67-bpy. XRD (Fig. 2a) confirms that the UiO-67-type framework is retained after modification. SEM (inset) suggests an octahedral morphology typical of this class of MOFs. UiO-67-DQ shows several new IR bands (Fig. 2b) that confirm successful functionalization: the ethylene group is responsible for the band at  $3090\text{ cm}^{-1}$ , and the triflate counteranion is reflected by the strong absorption at  $1265$ ,  $1170$  and  $1032\text{ cm}^{-1}$  [50]. NMR (Fig. 2c) reveals that 61% of the bpy linkers are modified to DQ. The ratio is similar to that (66%) for UiO-67-MQ [45] and to that (65%)

for UiO-67-DQ prepared by a similar procedure [48].

CT complexes are typically identified by new spectral absorption that is not characteristic of either the donor or the acceptor alone [51]. Solid-state UV–vis spectroscopy (Fig. 2d) shows that new absorption appears in the visible region after treating UiO-67-DQ with DA, catechol or 1-butylamine in PBS (pH = 6, optimal for DA detection, see below), accompanied by a color change from white to yellow or red-brown. The DA-treated sample shows more intense absorption and color than others. UiO-67-bpy does not show any chromogenic properties. The results confirm CT complexation of DA with the bipyridinium moieties through both catechol and amino groups. Although DA is expected to be mostly in the ammonium form at pH = 6, it is assumed that the amino-based CT complexation moves the acid–base equilibrium toward neutral DA.

### 3.2. Electrochemical behaviors on modified GCEs

UiO-67-DQ, UiO-67-MQ and UiO-67-bpy were used to modify GCEs, with Nafion (NF) as binder. As can be seen from Fig. 3a, DA gives weak CV signals at the bare GCE, reflecting the sluggish redox kinetics. Modification with NF enhances the peak currents by 4–5 times, because the cation-exchange polymer allows effective permeation of DA and promotes electron transfer [52]. Introduction of UiO-67-bpy leads to minor changes in peak currents, indicating that the unmodified MOF does not significantly interfere with the kinetics. However, UiO-67-DQ/NF/GCE and UiO-67-MQ/NF/GCE produce obviously increased currents. The comparison clearly confirms that the N-alkylating modification is advantageous to DA–electrode electron transfer. Because UiO-67-DQ and UiO-67-MQ have smaller pores than UiO-67-bpy owing to the presence of alkyl groups and counteranions [45], the signal amplification cannot be simply ascribed to the porosity. The main reason could be the electron-deficient nature of the MOFs, as we anticipated. In other words, the electron-deficient bipyridinium moieties provide donor–acceptor interaction sites for adsorbing the electron-rich dopamine molecules at the electrode.

The fact that UiO-67-DQ/NF/GCE gives a higher current response than UiO-67-MQ/NF/GCE can also be justified by donor–acceptor interactions. The bipyridinium moiety is quasi-coplanar in UiO-67-DQ but highly twisted in UiO-67-MQ because of the steric hindrance between the two *N*-methyl groups in MQ. The interannular angles are  $> 50^\circ$  in  $\text{MQ}^{2+}$  derivatives [53,54] and  $< 24^\circ$  for  $\text{DQ}^{2+}$  [55,56]. The more planar structure reduces the energy of the lowest unoccupied molecular orbital (LUMO). This is confirmed by CVs of the MOFs (Fig. 3b). UiO-67-DQ shows  $\text{DQ}^{2+}/\text{DQ}^{\cdot+}$  reduction at  $E_{1/2} = -0.36\text{ V}$ , while  $\text{MQ}^{2+}/\text{MQ}^{\cdot+}$  reduction occurs at a more negative potential. The LUMO energy for UiO-67-DQ ( $-4.44\text{ eV}$ , estimated from CV [57]) is lower than that for UiO-67-MQ ( $-4.24\text{ eV}$ ). A lower LUMO means higher electron-deficiency and enables stronger D–A interactions. The difference is also

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