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# Engineering pH-switchable UiO-66 via In-situ Amino Acid Doping for Highly Selective Adsorption of Anionic Dyes

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## Abstract

The pH-switchable UiO-66 were engineered via in-situ amino acids (AA) doping for the highly selective adsorption of anionic dyes (i.e. sunset yellow FCF (SY)). Three AA doped samples, i.e. UiO-66-V (valine), UiO-66-T (threonine), and UiO-66-Y (tyrosine), have fabricated hierarchical structure and endowed -NH<sub>2</sub> surface in framework structure concurrently. These AA doped UiO-66s awarded highly selective adsorption and fast diffusivity towards the mentioned anionic dyes. More interestingly, enriched -NH<sub>2</sub> groups endowed AA doped UiO-66s a significant pH-responsive character for selectivity of anionic/cationic dyes. Textural characterization and adsorption measurement confirmed that high surface areas (>1070 m<sup>2</sup>/g) with defected pores and -NH<sub>2</sub> surface significantly enhanced adsorption uptake (352.8 mg/g) and diffusion rate (168×10-3 min-1) for SY on AA doped UiO-66s, about 1.9 and 5.9 times respectively as that on pristine UiO-66. The AA doped UiO-66s exhibited one order of magnitude higher selectivity (> 390) for SY against MB than that of original UiO-66. More importantly, the alteration in surface charge  $(-NH_2 \stackrel{H^+}{\approx} -NH_3^+)$  endorsed a great variation in the selectivity of AA doped UiO-66s to dyes when adjusting pH from 4 to 8, showing an excellent pH on-off switchable property. Also, it realized a stable self-adsorption/desorption recycling process via pH-switching for 6 consecutive cycles. With these features, the pH-switchable defected UiO-66 realized highly efficiency adsorption and non-thermal separation/regeneration process for anionic dyes.

**Keywords:** pH-switchable UiO-66; amino acid doping; anionic dye selectivity; non-thermal separation/regeneration

## 1. Introduction

The extensive use of organic dyes in paper, food and textile industries has significantly expanded their market demand [1]. Their high solubility and improper usage/disposal, however, have resulted in water pollution [2, 3]. According to statistics, printing and dyeing industries are responsible for almost tenth of all the dyes discharge in wastewater, which have reached up to 2-3 billion tons per year in China [4]. These dyes are toxic, non-biodegradable and carcinogenic, and thus pose serious havoc to the environment [5-7] even at a concentrations of <100 mg/L. Some classical dyes, including rhodamine B (RhB), sunset yellow FCF (SY), and methylene blue (MB), are widely used in textile printing and dyeing [8, 9]. Due to their less than 10 % recovery and reuse in the entire country, they are causing serious obnoxious environmental impacts and hence it requires urgent concerns for their efficient removal and recovery from polluted water [10]. Among the many approaches for the removal of these dyes, adsorption is envisioned the most vital method attributed to its cost-effectiveness, easy regeneration of the spent adsorbent, and operation at mild reaction conditions. In addition, in such processes, high adsorption capacity, high selectivity and low-energy regeneration are the critical factors for adsorbents [11].

Metal-organic frameworks (MOFs) are a class of porous materials, which possess ordered three-dimensional crystal structure with ultra-high surface, chemical flexibility, tunable functional and structural features [12-14]. Hence, MOFs have been widely used for gas storage, dye adsorption and separation processes [15]. Yang et al. applied Fe<sub>3</sub>O<sub>4</sub>-doped ZIF-67(Co) in adsorption removal of methylene orange (MO), which could selectively adsorb MO from the mixture solution of MO and MB [16] with separation efficiency of 96%. Tan et al. reported to use MIL-100(Fe) to remove MB in wastewater, obtained a supreme adsorption capacity of 1105 mg/g [17]. Besides, many other MOFs, including MOF-235 [18], MIL-101(Cr) and MIL-53(Cr) [19], have been to use as adsorbents for the removal of MO and MB. As seen, high specific

surface area and large total pore volume enable MOFs to have great potential in pollutant disposal in aquatic environment [20].

For the adsorption process in water purification, structural stability of MOFs is the primary issue to be considered. Among the various MOFs, Zr-based UiO-66 has a relatively high thermal and chemical stability [21, 22]. Notably, UiO-66 is reported to have good structure stability in water. Moreover, it has a wide acid and alkali adaptive range compared to many other MOFs [23]. However, their ultra-microporous size distribution would cause a low adsorbed amount, slow diffusion of guest molecules and energy-intensive regeneration, and thus has seriously hindered their applications in treating organic contaminants with larger molecules in liquid environment [24]. Many researchers proposed various strategies to expand pore size and decorate surface properties of UiO-66(Zr), including hard-templating, pre- and post-modification along with hybridizing strategies [25, 26]. For example, J. F. Yao used HCl to etch UiO-66, and obtained higher adsorption capacity (84.8 mg/g) than that of pristine one (70.4 mg/g) [10]. P. Hu et al. used alkaline heterocycles to modify UiO-66 via in-situ approach to enhance the surface alkalinity. The pyrrole doped UiO-66 showed three times increase in adsorption capacity for cationic RhB (384 mg/g) than that of parent UiO-66 (108 mg/g) [6]. X. T. Liu et al. reported an ammonia modified UiO-66 resulting in enhanced adsorption capacity and selectivity for cationic MB against anionic dyes [27]. Thus, introducing small molecules or chemical groups into UiO-66 can simultaneously expand pore size, modify surface properties and crystal structure, and in turn leads to enhanced adsorption performance.

However, uncoordinated modification strategy cannot effectively construct stable pore structure in MOFs. Also, pore blocking would happen during modification process. It will thus damage adsorption and/or diffusion kinetics properties, and produce energy-extensive

consumption [28] as well. Meanwhile, this will make it more difficult to accurate control in pore size and their number [29, 30]. Transition metals and organic ligands are proposed to modify MOFs [31]. Both modification methods can increase the number of adsorption active sites in MOFs to improve the adsorption capacity of dyes. The doped transition metal elements in MOF lattice donate valence electron and enhance internal adsorption sites [32], while organic ligands (i.e. amino acid) doping can introduce new functional groups into MOFs and provide new external adsorption sites. Amino acids (AA) contain both amino and carboxylic acid functional groups, and hence possess great variety in rigidity, flexibility and amphipathy. Some AAs were proposed to build MOFs as ligands due to their carboxylic acid groups [33, 34]. However, their relative flexible structure cannot construct a rigid topological skeleton, resulting in comparatively low surface area for some novel MOFs [35, 36].

In this work, three AA, i.e. Valine (Val), Threonine (Thr), and Tyrosine (Tyr), with different chemical properties were proposed to induce defective sites in the UiO-66 crystal via in-situ onepot strategy. Asymmetric coordination facilitated to engineer larger pores on UiO-66 surface having -NH<sub>2</sub> groups, which awarded high selectivity and kinetics towards anionic dyes. Moreover, the alteration in surface charge  $(-NH_2 \stackrel{H^+}{\rightleftharpoons} -NH_3^+)$  endorsed a great variation in the selectivity of AA doped UiO-66s to dyes when adjusting pH, showing an excellent pH on-off switchable property. With these features, the pH-switchable defected UiO-66 realized highly efficiency adsorption and non-thermal separation/regeneration process for anionic dyes. Crystal morphology, coordination mode, defected pore structure and thermal stability were characterized by scanning electron microscopy (SEM), powdered X-ray diffraction (PXRD), X-ray photoelectron spectroscopy (XPS), N<sub>2</sub> sorption isotherm and thermogravimetric analysis (TGA).

determined via high performance liquid chromatography (HPLC). The adsorption equilibrium, kinetics, pH-responsiveness, separation and recycling performance of various anionic and cationic dyes (with different molecular 3D structures) including acid orange II (AO), SY, acid red 73 (AR 73), congo red (CR), coomassie brilliant blue R-250 (CBB), MB and RhB, were investigated on the fabricated AA doped UiO-66s.

## 2. Experimental

## 2.1. Materials

All the reagents used in this study were of analytical reagent grade and applied without further processing. Zirconium chloride (ZrCl<sub>4</sub>, > 99.5%) was provided by J & K Chemical Technology Co., Ltd. Beijing, China. Terephthalic acid (H<sub>2</sub>BDC, 99.5%), HCl (48 wt.%), anhydrous methanol (CH<sub>3</sub>OH, 99%), ice acetic acid (C<sub>2</sub>H<sub>4</sub>O<sub>2</sub>, HAc, 99.5%), and N,N-dimethylformamide (C<sub>3</sub>H<sub>7</sub>NO, DMF, 99.8%) were purchased from Guangdong Guanghua Sci-Tech Co., Ltd. Guangdong, China. Val (V), Thr (T) and Tyr (Y) (>99%) were provided by Aladdin Industrial Co., Ltd. Shanghai, China. AO (99.3%), SY (99.5%), AR 73 (99.4%), CR (99.9%), CBB (99.5%), MB (99.3%) and RhB (99%) were supplied by Nanjing Chemical Reagent Co. Ltd. Nanjing, China. Acetonitrile and methanol for HPLC analysis were acquired from Thermo Fisher Scientific Co., Ltd.

## 2.2. In-situ synthesis of AA doped UiO-66s

Parent UiO-66 crystal prepared following the literature [6] were modified via in-situ synthesis approach by incorporating Val (V), Thr (T) and Tyr (Y), respectively. Briefly, 1.0 mmol  $ZrCl_4$ and 1.0 mmol H<sub>2</sub>BDC, 5.0 mmol Val, and 70 mmol HAc were successively dissolved in 70 mL DMF. The resulting solution was transferred to a 50 mL Teflon-lined stainless steel auto clave jar and was heated in an oven at 120 °C for 24 h at a heating rate of 1 °C/min, to obtain the modified UiO-66 crystals. The obtained sample was denoted as UiO-66-V. Similar protocol was followed for doping Thr (T) and Tyr (Y) onto UiO-66 for the synthesis of UiO-66-T and UiO-66-Y. The synthesized samples were then centrifuged and washed thrice with DMF and methanol, respectively. Finally, the produced UiO-66s were activated at 120 °C for 12 h under vacuum, and then stored in inert  $N_2$  environment.

## 2.3. Textural characterization

Morphology of the synthesized UiO-66s was characterized by SEM (SU8020). Crystallinity of the synthesized products was analyzed by PXRD (RIGAKU, Japan) at Cu  $K_{\alpha}$  radiation ( $\lambda =$ 1.5406 Å). The specific surface area and pore size distribution parameters were measured by N<sub>2</sub> adsorption/desorption (Micromeritics ASAP 2460). TGA was conducted using TGA/DSC 3+ METTLER TOLEDO STAR system. Temperature-controlled desorption (TPD) was executed in a Rheometric Scientific STA1500 instrument. The electronic states of the surface elemental components were analyzed by XPS (PHI 5000C ESCA). The zeta potentials of the samples were measured using a MALVERN ZETASIZER Nano-ZS90 (Brookhaven NanoBrook Omni) at room temperature.

## 2.4. Evaluation of adsorption performance of AA doped UiO-66s for various dyes

A series of AAs with different dimensions and chemical properties (V, T and Y) (**Table S1**) were used to modify the non-defective pristine UiO-66, named UiO-66-V, UiO-66-T and UiO-66-Y, and in turn applied them for the adsorption performance test of various anionic and cationic dyes. In the adsorption experiments, 5.0 mg of pristine UiO-66 or defected UiO-66s was added to a 50 mL of 0.1 mmol/L dye aqueous solution and was stirred for 24 h. The adsorbent

samples were then segregated via centrifugation and the supernatants were collected and tested for change in dyes concentration by a UV-vis spectrophotometer. The adsorption capacity  $Q_e$ (mmol/g) of the dyes was calculated according to Eq. (1):

$$Q_{\rm e} = \frac{(C_0 - C_{\rm e})}{M} V \tag{1}$$

Where  $C_0$  and  $C_e$  are the initial and equilibrium concentrations of dyes (mmol/L), respectively; *M* is the mass of adsorbent (g), and *V* is the volume of the dye solution (L).

The equilibrium adsorption capacity  $Q_e$  (mmol/g) and transient fractional adsorption capacity  $Q_t$  (mmol/g) were calculated according to Eq. (2) and (3), respectively.

$$Q_{e} = \frac{(C_{0} - C_{e})V}{m}$$
(2)
$$Q_{t} = \frac{(C_{0} - C_{t})V}{m}$$
(3)

Where  $C_0$ ,  $C_e$  and  $C_t$  (mmol/L) are the concentrations of dyes at initial, equilibrium and transient time *t* (min), respectively; *V* is the volume of solution (L).

## 2.5. pH-responsive and regeneration performance of AA doped UiO-66s

pH-responsive experiments of dye adsorption on AA doped UiO-66s were carried out under variable pH 6-10 adjusted by using 0.1 mmol/L NaOH or HCl solution, which was in-situ detected using a pH meter (BPP-7800, Bell Analytical Instruments Co., Ltd.). The interval time was set to 10 min when solution pH increased by 1, while the dye concentration and adsorbent dosage were kept same as those mentioned in Section 2.4. A similar procedure was adopted for testing the recycling performance of the adsorbent.

## 2.6. Selective adsorption performance on AA doped UiO-66s

In order to avoid the mutual interference of binary dyes, concentration standard curves of MB and SY in the mixed dyes were analyzed by UV-vis spectrophotometer. Initially, the concentration of SY was fixed at 0.02 mM, and MB was dissolved to prepare a solution of concentration ranging 0.01~0.05 mM. Similarly, the concentration of MB was fixed at 0.01 mM, while that of SY was varied between 0.01~0.05 mM. Standard curves for both dyes with high correlation coefficient ( $R^2 = 0.999$ ) are shown in Fig. S3.

Certain quantities of MB and SY (corresponding to 0.1 mmol/L) were mixed into 100 mL deionized water under moderate stirring. The molar ratios of SY/MB were varied as 9:1, 7:3, 5:5, 3:7 and 1:9, respectively. Then, 5.0 mg of original or AA doped UiO-66s was added to the 50 mL binary mixture of MB and SY, then stirred on a vibration shaker at 298 K, filtered and the supernatant was analyzed by UV-vis spectrophotometer. Using their standard curves, the competitive adsorption selectivity for MB over SY was determined from Eq. (4) [1]:

$$\alpha_{SY/MB} = \left(\frac{Q_{SY}}{Q_{MB}}\right)\left(\frac{C_{MB}}{C_{SY}}\right) \tag{4}$$

Where,  $Q_i$  and  $C_i$  (i = SY or MB) are equilibrium adsorbed amounts for SY and MB, and equilibrium concentration in bulk-liquid phases, respectively.

## 3. Results and discussion

## 3.1. Textural characterization

**Fig. 1** shows the SEM images of the parent UiO-66, UiO-66-V, UiO-66-T and UiO-66-Y. Parent UiO-66 (**Fig. 1a**) exhibited integral crystal structure having octahedral morphology (average particle size of 150 nm) as well as good stress-homogeneous and optical quality. Its average particle size of the UiO-66 increased to 150~250 nm after modification with three AAs, while morphology was transformed to irregular cubical shape. Moreover, UiO-66-V, UiO-66-T

and UiO-66-Y crystals exhibited unclear edges and corners, which can be attributed to the presence and role of V, T and Y on the crystalline growth of MOF crystal.

PXRD data of pristine and AA doped UiO-66s in **Fig. 2** revealed similar structural and crystalline morphology as reported earlier [6, 37], which having high degree of crystallinity and well-arranged structure. Both the pristine as well as modified samples realized minimal variation in the intensity of diffraction peaks. The results suggest that the crystallographic structure and morphology of the samples have sustained, lucid and compact. Compared to original UiO-66, the intensity of diffraction peaks slightly decreased for the AA doped UiO-66s owing to the association of different acidic and basic groups, accumulation of free spaces and inducing different charges on the crystal lattice. However, the overall crystal structure of the defected UiO-66s remained compact and integrated as that of parent UiO-66, with stronger peak intensity than many reported of UiO-66 composites [38, 39].

Though pristine UiO-66 is strongly recommended as adsorbent owing to its remarkable surface area [40], it still faces the problem of the presence of large number of micropores. Therefore, the determination of surface porosity and pore size distribution of the parent and AA modified UiO-66s are of significant importance. **Fig. 3** explicating the surface parameters measured via N<sub>2</sub> adsorption isotherm at 77 K. It is obvious that parent UiO-66 lucidly exhibited Type-I isotherm confirming the predominance of micropores [6] with pore width < 2 nm in the whole pore size distribution. While a kind of hybrid Type I/IV isotherm with a sharp uptake of N<sub>2</sub> was obtained for UiO-66-V, UiO-66-T, and UiO-66-Y with a visible hysteresis at high pressures. The high uptake of N<sub>2</sub> at 0.9 relative pressures (P/P<sub>0</sub>) for the AA modified UiO-66 species suggested the appearance of mesopores [10, 25]. The structural parameters listed in **Table 1** revealed that UiO-66 possessed a relatively high surface area (1217 m<sup>2</sup>/g) with higher

ratio of micropores (82 %). After being modified with AAs, some mesopores appeared in UiO-66 pore structure to a certain extent, inferring the generation of defects with larger pores than that of parent UiO-66 following a decreasing order of: UiO-66-V > UiO-66-Y > UiO-66-T. As shown in **Fig. 3a**, UiO-66-V possesses dominant micropores at 9~11 and 16 Å. UiO-66-T and UiO-66-Y possess similar microporous distribution to parent UiO-66 and UiO-66-V. Also, many mesopores appeared in their pore size distribution at 20~23 Å. Also, **Table 1** further suggests that total volume of the modulated UiO-66s was increased due to the generation of mesopores in their textural structure with a subsequent increase in meso-/micropores volume ratio following the sequence as: UiO-66-Y > UiO-66-T > UiO-66-V. Thus, it can be concluded that Tyr (Y) having the largest 3-dimentional size and robust benzene groups created more mesopores in UiO-66 compared to aliphatic Val (V) and Thr (T), inferring that higher content of Tyr (Y) was doped into UiO-66.

Moreover, **Fig. 3b** interprets the behavior and distribution of micro-/mesopores in the pristine and AA modified samples using density functional theory (DFT). Highly intense characteristics peaks of UiO-66 were found at 9.2 and 11.7 Å, while sharp peaks at 16.5-23 Å in UiO-66-V, UiO-66-T, and UiO-66-Y depicted the prominence of mesopores resulted from the incorporation of AA onto pristine UiO-66 and strong coordination with Zr species. The generated pore size of the modulated UiO-66s was in the order of: UiO-66-Y > UiO-66-T > UiO-66-V, which is similar to their corresponding volume ratio of meso-/micropores.

**Fig. S1** exhibits the full survey XPS spectra of the pristine and AA doped UiO-66 samples, and the elemental distributions of C, O, Zr and N are shown in **Table S2**. The results confirmed the successful doping of N element into UiO-66 structure. The order of N-interaction increased

in a sequence of: UiO-66-V (3.4 N wt.%) < UiO-66-T (3.7 N wt.%) < UiO-66-Y (4.1 N wt.%), with slight changes in the distribution of all other elements.

**Fig. 4a** explicates the C 1s core level interactions of the parent and AA doped UiO-66s. The parent UiO-66 exhibited two peaks located at 284.6 and 288.6 eV, which respectively belonged to the C=C/C-C and O-C-O species [41, 42]. After doping AA, C-N peak located at 286.2 eV appeared in the XPS spectra of C 1s [43, 44], indicating the successful incorporation of AA on the surface of UiO-66-V, UiO-66-T and UiO-66-Y. Moreover, the area (%) of C and O reduced in the AA doped UiO-66s due to the substitution of N. Among these UiO-66s, UiO-66-Y possesses the highest content of C-N, while UiO-66-V has the lowest without changes in its binding energy. This once again verified the doping amount with an order of: UiO-66-Y (8.0 %) > UiO-66-T (7.4 %) > UiO-66-V (3.5 %). It was attributed to the greatly similar chemical structure of Tyr (Y) to BDC ligand facilitating easier replacement of the latter by the former in UiO-66 structure than Thr (T) and Val (V).

**Fig. 4b** compiles the O 1s core level spectra of the pristine and AA doped UiO-66s, which were divided into three peaks corresponding to Zr-O, C=O and O-C-O [45]. Position of the Zr-O peak shows a negative shift, indicating a decrease in binding energy between O and Zr due to asymmetric coordination of  $-COO^{-}$  of AA bridging to Zr compared to H<sub>2</sub>BDC [46]. Moreover, Zr-O and C=O contents decreased in AA doped UiO-66s, and further decreased with a sequence of: UiO-66-V > UiO-66-T > UiO-66-Y. On the contrary, C-O contents increased after doping AA into UiO-66, showing an opposite trend to that of Zr-O and C=O peaks. Based on the experimental facts, it can be seen that the carboxylic coordination with central metal ions showed a declining trend in AA doped UiO-66s compared to the perfect crystal. The lack of ligands on original position with Zr would weaken the binding force between O and Zr [6, 47], thus leading

to the shifting of binding energy to lower value. Deficient coordination induced negative charge and hence enhanced the electron density on the surface of UiO-66s that will further strengthen the electrostatic interactions among the pores. Additionally, we can make an inference that the induced negative charges may strongly attract dyes compound possessing cationic functionalities, thereby enhancing the effective adsorption and selectivity separation of selected dye from the mixture of dyes.

The N 1s XPS spectra of AA doped UiO-66s are given in **Fig. S2**, showing only one N 1s peak at 400.2 eV for the samples arising from  $-NH_2$  groups in these compounds. It is worth mentioning that no Zr-N bond was detected in the N 1s spectra, indicating the Zr sites coordinated with carboxylic groups rather than amino groups of AA. **Fig. S2** further shows that UiO-66-Y possesses highest intensity of  $-NH_2$  groups, which in turn verifies the successful doping large amount of Tyr (Y) onto the parent UiO-66 surface.

**Fig. 5** explicates the differential thermogravimetric (DTG) analysis of the parent and AA doped UiO-66s. Thermal decomposition temperature for the parent UiO-66 was occurred around 561 °C, while that of AA doped UiO-66s slightly decreased. It was attributed to the missing of partial ligands in UiO-66 structure. AA partially onto UiO-66s can still maintain their good thermal stability. In addition, the residual percentage of the AA doped UiO-66s remained higher (51-48 wt.%) than the parent UiO-66 (47 wt.%) owing to more residual AA ligands than BDC ligands [48]. This illustrated that the doped AA formed a strong interaction with the metal cluster in UiO-66.

## **3.2.** Investigating Zeta potential for AA doped UiO-66s

In order to understand the variation in surface chemistry, zeta potential at pH=6 for original UiO-66, UiO-66-V, UiO-66-T, and UiO-66-Y are displayed in **Fig. 6a**. As shown, zeta potential

was gradually increased for three AA doped samples. UiO-66-Y showed the maximum positive value of 34.6 mV. From the XPS spectra, carboxylic group in AA was proved to be coordinated with metal sites in UiO-66. Thus, the exposure of -NH<sub>2</sub> group resulted in an increase in zeta potential in UiO-66 surface [49]. This increased zeta potential can correspondingly illustrated the increased positive charge on the surface of the defected UiO-66, which can facilitate the selective adsorption of anionic organic compounds [50-52].

The zeta potential of UiO-66 and UiO-66-Y was detected in a pH range of 2-10 as shown in **Fig. 6b**, indicating an initial decrease in zeta potential with the increasing pH values. As shown, zeta potential of these UiO-66s gradually decreased with pH value from 2 to 6, and then sharply dropped from positive to negative value from 6 to 10. For the original UiO-66, the reversal value from positive to negative occurred at pH 6.9-7.0. While for the UiO-66-Y, the reversal phenomenon appeared at pH 8.5-8.6. These variations noted in the surface property associated with pH through the reversible transformation of  $(-NH_2 \stackrel{H^+}{\approx} -NH_3^+)$  will affect their adsorption  $OH^-$ 

performance and selectivity for organic dyes having anionic/cationic groups.

## 3.3. Evaluation of adsorption performance of various dyes on different UiO-66s

The adsorption performance of various UiO-66s samples was tested for AO, SY, MB, and RhB dyes having great difference in chemical properties as listed in **Table S3**. **Fig. 7a** suggests that the adsorption uptakes of parent UiO-66 for anionic dyes (AO and SY) were lower than those of AA doped UiO-66 samples. On the contrary, the parent UiO-66 exhibited higher adsorption uptake for cationic dyes (MB and RhB) than those of the AA doped samples. These variations are mainly endorsed to the surface modification by AA rather than the reason of higher surface area of the parent UiO-66. **Table 1** shows that the specific surface area of the AA doped UiO-66 samples (except UiO-66-V) was lower than that of the parent UiO-66. However,

surface chemical properties of UiO-66 changed greatly after grafting AA. As shown in **Fig. 6a**, the zeta potential of the AA doped samples was increased to higher positive value, indicating a favorable surface for the process of adsorbing anionic dyes (with negative charges). This was also evidenced by the enhanced adsorption capacity for anionic dyes in **Fig. 7a**. Compared to AO, SY has one more sulfonic group and hence bears higher anionic properties. As a result, three AA doped UiO-66s exhibited a higher adsorbed uptake for SY than that for AO. Moreover, the introduction of AA also fabricated some defects with expanded pore size in UiO-66s, and it was favorable the adsorption of dyes with relatively large molecular size [53]. UiO-66-Y exhibited an uptake of 352.8 mg/g (0.78 mmol/g) for SY, about 1.86 times higher than that of parent UiO-66, while its adsorption update for cationic MB and RhB was only 31.9 and 36.2 mg/g (0.10 and 0.08 mmol/g) respectively, about one-tenth of that for SY. This suggested highly selective uptake by AA doped UiO-66 for certain anionic and cationic dyes having similar molecular dimensions, and hence can be of great potential applications on industrial level for the separation of specific dyes from complex mixtures.

Fig. 7b shows the adsorption performance of various UiO-66s for four typical dyes with different molecular dimensions. In general, the adsorption uptake gradually declined with increasing molecular dimension. The adsorption uptake of parent UiO-66 for SY (11.9×8.2×2.4 Å) was up to 0.42 mmol/g, while sharply decreased to 0.15 and 0.04 mmol/g for CR ( $26.2\times8.1\times5.0$  Å) and CBB ( $27.3\times17.0\times9.1$  Å). From N<sub>2</sub> adsorption isotherm, the pore size of parent UiO-66 was mainly concentrated in the range of 8-10 Å. Considering the slight swelling of its skeleton, only few CR and CBB molecules could enter into parent UiO-66 pores, resulting in a savage reduction in their adsorption performance for the two dyes. Similar phenomenon occurred in the adsorption of the two dyes on AA doped UiO-66s. However, the sharp drop in

adsorption uptake was observed for CBB dye rather than for CR dye, which could be attributed to larger dynamic diameter of CBB molecule than that of CR molecule. From the adsorption measurement, it could be found that the dimensional limitation of UiO-66-V, UiO-66-T and UiO-66-Y is about in the range of ~17-27 Å, and this is highly consistent with their pore size distribution calculated from DFT model in **Fig. 3b**.

## 3.4. Equilibrium and kinetics performance of SY/MB on UiO-66 and UiO-66-Y

In order to get deeper insight about adsorption behaviors of anionic SY and cationic MB, the adsorption equilibrium and kinetic curves of SY and MB on UiO-66 and UiO-66-Y were measured and shown in **Fig. 8a-b**. The adsorption capacity of anionic SY on UiO-66-Y sharply increased with increasing dye concentration as compared to that on original UiO-66, indicating an enhanced adsorption affinity of SY towards UiO-66-Y continuously. On the contrary, the equilibrium uptake of cationic MB on UiO-66-Y decreased greatly as compared to that on original UiO-66, indicating their weaker mutual affinity.

In addition, the adsorption isotherms were fitted using Langmuir-Freundlich (L-F) model (Eq. (5)), and the resulting linear plots are shown as red dashed line while the correlation parameters are listed in **Table S4**. All of the correlation coefficients were higher than 0.99, indicating the best fitting of the adsorption behavior of SY and MB on UiO-66s with the L-F model. For the original UiO-66, the  $b_{L-F}$  of anionic SY was very close to that of cationic MB, inferring that original UiO-66 has similar adsorption property for them. However, for the UiO-66-Y, the  $b_{L-F}$  of anionic SY was much higher than that of cationic MB, verifying the high discrepancy in their adsorption behaviors on UiO-66-Y.

$$Q_e = \frac{Q_{max}b_{L-F}C^{n_{L-F}}}{(1+b_{L-F}C^{n_{L-F}})}$$
(5)

Where  $Q_e$  and  $Q_{max}$  (mmol/g) are the equilibrium and maximum uptakes, respectively;  $b_{L-F}$  and  $n_{L-F}$  are the constants of L-F model representing the sorption capacity and adsorption intensity of the adsorbent, respectively [54-57].

Similarly, their kinetic curves on original UiO-66 and UiO-66-Y samples were also simulated using the pseudo-first-order kinetic model (**Eq. (6**)). In **Fig. 8b**, it showed very similar trend in the equilibrium adsorption of two molecules on UiO-66 and UiO-66-Y. From **Table S4**, the calculated rate constants (k) of UiO-66 were 28.4×10<sup>-3</sup> min<sup>-1</sup> and 23.3×10<sup>-3</sup> min<sup>-1</sup> for SY and MB respectively, indicating a very comparable kinetic property of the parent UiO-66 towards two dyes having variable charges. After being doped by Tyr (Y), the kinetic properties towards anionic SY and cationic MB changed dramatically and the k value over UiO-66-Y for SY was increased from 28.4 to  $168 \times 10^{-3}$  min<sup>-1</sup> corresponded to about 5.9 times as that of the parent UiO-66, while its k of MB was decreased from 23.3 to  $9.1 \times 10^{-3}$  min<sup>-1</sup>.

$$\log (Q_e - Q_t) = \log Q_e - \frac{k}{2.303}t$$
 (6)

Where  $Q_t \pmod{g}$  is the amount of dye adsorbed at time *t* and *k* (min<sup>-1</sup>) is the pseudo-first-order reaction rate constant.

Based on the above equilibrium and kinetic data of dyes adsorption, we estimated the selectivity of UiO-66 and UiO-66-Y for SY and MB having similar molecular dimension and the results are compiled in **Fig. 8c**. The red column representing to UiO-66-Y exhibited a significantly higher selectivity in both equilibrium (k = 8.4) and kinetic state (k = 18.5) than that of pristine UiO-66.

More interestingly, the Tyr (Y) doped UiO-66-Y showed a special pH-responsiveness with good recycling performance for dye adsorption. As shown in **Fig. 8d**, the adsorption uptake of SY on UiO-66-Y exhibited a significant decline with solution pH increased from 6 to 10. After

recycling six times, its adsorption uptake for SY recovered from high (in acidic medium) to low (in basic medium) as that on the fresh UiO-66-Y. Thus, basic solution can be used to desorb SY from UiO-66-Y due to great variation in surface functionalities under different pH conditions. This process plays key role in its recycling performance minimizing process cost to considerable extent. In conclusions, these findings successfully verified that UiO-66-Y possessed excellent pH-responsive properties with easy regeneration and good recycling performance. Hence, UiO-66-Y can be envisioned of great promise for practical applications regarding selective separation of various dyes from industrial wastewater.

## 3.5. pH-responsive selective performance of SY/MB on UiO-66 and UiO-66-Y

Attributed to the excellent pH-responsive adsorption of the Tyr (Y) modified UiO-66-Y for anionic SY, its pH-responsive selective performance in the mixture of SY/MB was further investigated by varying the concentration ratio of SY/MB and solution pH. The results of separation factor ( $\alpha_{SY/MB}$ ) are shown in **Fig. 9a**. UiO-66-Y exhibited much higher  $\alpha_{SY/MB}$  than that of parent UiO-66 at pH 6. Furthermore, the value of  $\alpha_{SY/MB}$  sharply increased (from 31.9 to 398) by decreasing SY/MB ratio (from SY: MB = 9:1 to 1:9). This is because comparatively less anionic SY molecules have the absolute advantage to occupy more adsorption sites on UiO-66-Y surface compared to cationic MB molecules. Thus, UiO-66-Y exhibited the selective absorption for anionic SY molecules rather than cationic MB molecules. As a result, before achieving the saturation adsorption, UiO-66-Y can capture all the SY molecules in binary dyes mixture, and thus facilitate the increase in separation factor ( $\alpha_{SY/MB}$ ) of SY against MB [58].

For comparison, **Table 4** enlists the adsorption selectivity of binary anionic/cationic dyes mixture system on recently reported novel porous materials. Results indicated that low adsorption selectivity (< 50) by the un-modified MOFs for binary anionic/cationic dyes, while

some porous polymers showed relatively higher adsorption selectivity. For example, microcrystalline cellulose coated with PDA showed a selectivity of 90 for MB against RhB under the concentration of 25 mg/L. By comparison, the Tyr (Y) defected UiO-66-Y exhibited remarkably higher adsorption selectivity of 398 for SY/MB under a considerable lever of concentration (33 mg/L). In this work, it is 12.4 times higher than that of UiO-66 and far exceeds than other state-of-the-art porous hybrid materials reported in **Table 4**.

In addition, pH-responsiveness of UiO-66-Y for the separation of SY/MB was also investigated under equimolar concentration of the two dyes. As shown in **Fig. 9b**,  $\alpha_{SY/MB}$  of UiO-66-Y and original UiO-66 gradually decreased with increasing solution pH from acidic to basic. Differently,  $\alpha_{SY/MB}$  showed a mild change for the pristine UiO-66 while a steeper change for UiO-66-Y within pH from 4 to 8. It can see that the  $\alpha_{SY/MB}$  of UiO-66-Y decreased from 157.21 to 1.78 sharply, while that of original UiO-66 only changed from 9.34 to 3.59. By further increasing pH to 10,  $\alpha_{SY/MB}$  showed a reversal separation performance from SY to MB, and the  $\alpha_{SY/MB}$  was lower than one. According to the adsorption performance of SY on UiO-66-Y, the adsorption uptake of SY sharply decreased at solution pH of 8 or above. This could be attributed to the fact that the negative surface of UiO-66-Y would not prefer further adsorption of SY, thus resulting in lower  $\alpha_{SY/MB}$  for the binary dyes mixture. This could be greatly useful for the selective adsorption of dyes with different charge characteristics, as it can be tuned the charge on the surface of adsorbents by varying solution pH.

## 3.6. Adsorption and separation mechanism

Many reports suggest that specific surface area is the key factor in determining the adsorption capacity as it facilitates greater chances of adsorbent-adsorbate or reactants' interaction [59-61]. As obvious from **Fig.3** and **Table 1**, a significant hysteresis loop along with high fraction of

micro/mesoporous area and pore volume can be found in the AA doped UiO-66s. It could be one reason for the remarkably higher adsorption selectivity performance of UiO-66-Y for SY/MB molecules than the pristine UiO-66. Zeta potential is another important factor to determine the adsorption efficiency and selectivity towards cationic and anionic dyes [62]. UiO-66-Y having higher positive zeta potential exhibited the higher adsorption ability for anionic dyes than pristine UiO-66 (**Fig. 6**) [63]. Moreover, the basicity of -NH<sub>2</sub> can be increased by capturing protons via electrostatic interaction, thus showing more positive zeta potential which can further facilitate the adsorption of anionic dyes [27]. These findings can be considered as key factors to induce the crystal defects with -NH<sub>2</sub> groups in UiO-66.

Moreover, dopant of AA in UiO-66 would generate defects in metal cluster position due to the asymmetric coordination of AA with Zr-O clusters [64]. As shown in the O 1s XPS spectra in **Fig.4b** and **Table 3**, the Zr-O cluster contents were proved to decrease in AA doped UiO-66s compared with pristine MOF, showing with a sequence of: UiO-66-V > UiO-66-T > UiO-66-Y. Based on hard and soft acid base theory, Zr-O clusters belong to a typical Lewis acid sites [32], which would like to attract alkaline MB rather than acidic SY. Thus, the decrease of Zr-O in AA doped UiO-66s weakened the adsorption capacity for MB, and facilitated the selective adsorption capacity of SY/MB molecules than the original UiO-66. As a result, AA modification endows parent UiO-66 with an excellent selective-adsorption for acidic dyes, which makes them of great industrial promise and application regarding the selective removal of dyes.

## 4. Conclusions

This study proposed amino acids (hydrophobic valine, hydrophilic threonine and aromatic tyrosine) doping strategy for engineering pH-switchable UiO-66. Asymmetric coordination of metal sites with carboxylic of AA generated larger pores with surface -NH<sub>2</sub> groups in UiO-66.

These new intriguing properties awarded the defected UiO-66 crystal with high adsorption capacity, fast diffusivity, and greatly enhanced selectivity for anionic dyes. Moreover, the alteration in surface charge  $(-NH_2 \stackrel{H^+}{\approx} -NH_3^+)$  endorsed a great variation in the selectivity of AA doped UiO-66s to dyes when adjusting pH (4-8), showing an excellent pH on-off switchable property. Structural characterizations revealed that AA in UiO-66 effectively adjusted crystal morphology and fabricated the hierarchical structure with micro- and mesopores possessing high surface area (1072-1277 m<sup>2</sup>/g). The aromatic tyrosine with rigid molecular structure competitively coordinated with Zr-O clusters in UiO-66 compared to the other two AA, and resulted in the generation of more defects with larger pore size (16.5-23 Å) in UiO-66-Y. Dyes adsorption and selectivity experiments showed that the adsorption uptake and diffusion rate of UiO-66-Y were about 352.8 mg/g and 168×10<sup>-3</sup> min<sup>-1</sup> for SY, corresponded to 1.9 and 5.9 times as that on original UiO-66. Moreover, AA-doped UiO-66s exhibited a remarkable increase in selectivity (> 390) for anionic SY against cationic MB, which was about one order of magnitude higher than that of original UiO-66. Further, these defected UiO-66s realized a stable selfadsorption/desorption for 6 consecutive recycling via pH-switch. With these features, the pHswitchable defected UiO-66 realized highly efficiency adsorption and non-thermal separation/regeneration process for anionic dyes.

## Notes

The authors declare no competing financial interest.

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## Appendix A. Supplementary data

Supplementary material related to this article can be found, in the online version, at doi: https://doi.org/10.1016/j.apcatb.2018.03.061.

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26

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 Table 1 Surface area and porosity parameters of various UiO-66 samples.

Sample	$S_{BET}^{a}$	$S_{ m Micro}^{ m b}$	S <sub>Meso</sub> <sup>b</sup>	S <sub>Meso</sub>	<i>V</i> <sub>Total</sub> <sup>c</sup>	$V_{\rm Micro}^{\rm d}$	$V_{\rm Meso}$ <sup>d</sup>
Sampre	(m <sup>2</sup> g <sup>-1</sup> )	(m <sup>2</sup> g <sup>-1</sup> )	(m <sup>2</sup> g <sup>-1</sup> )	/S <sub>Micro</sub>	(cm <sup>3</sup> g <sup>-1</sup> )	(cm <sup>3</sup> g <sup>-1</sup> )	$/V_{ m Micro}$
UiO-66	1217	1030	187	0.18	0.62	0.50	0.24
UiO-66-V	1277	935	342	0.36	0.68	0.47	0.45
UiO-66-T	1072	651	421	0.65	0.71	0.37	0.92
UiO-66-Y	1108	548	560	1.02	0.79	0.33	1.39

<sup>a</sup>  $\overline{S_{BET}}$  is the surface area of BET;

<sup>b</sup> S<sub>Micro</sub> and S<sub>Meso</sub> is the surface area of microporous and mesoporous structure, respectively;

<sup>c</sup> V<sub>Total</sub> is the total volume;

<sup>d</sup> V<sub>Micro</sub> and V<sub>Meso</sub> is microporous and mesoporous volume, respectively.

**Table 2** C1s XPS peak position and elemental percentage in UiO-66, UiO-66-V, UiO-66-T andUiO-66-Y.

	C=C/C-C		C-N		<b>O-C-O</b>	
Sample	Binding	Area	Binding	Area	Binding	Area
	energy (eV)	(%)	energy (eV)	(%)	energy (eV)	(%)
UiO-66	284.6	81.6			288.6	18.4
UiO-66-V	284.6	79.7	286.2	3.5	288.6	16.7
UiO-66-T	284.6	76.5	286.2	7.4	288.6	16.1
UiO-66-Y	284.6	75.8	286.2	8.0	288.6	16.2

**Table 3** O1s XPS peak position and elemental percentage in UiO-66, UiO-66-V, UiO-66-T andUiO-66-Y.

	Zr-O	Zr-O			С-О	
Sample	Binding	Area	Binding	Area	Binding	Area
	energy (eV)	(%)	energy (eV)	(%)	energy (eV)	(%)
UiO-66	530.7	23.2	531.9	73.4	532.9	3.4
UiO-66-V	530.6	22.4	531.9	71.8	533.0	5.8
UiO-66-T	530.5	21.6	531.8	67.8	533.0	10.6
UiO-66-Y	530.4	20.3	531.7	67.0	533.0	12.7

 Table 4 Separation performance of UiO-66, UiO-66-Y and some recently reported porous materials for binary anionic/cationic dyes system.

Sample	Mixed dye*	<i>C</i> <sub>0</sub> (mg/L)	Concentration ratio	Selectivity	Ref.
porous hybrid	AR/TH			13.6	
materials	AO/MG	20	1:1	11.6	65
microcrystalli	MB/ST			40.8	
ne cellulose		25	1:1		66
coated with	MB/RhB			90.3	
PDA					
Poly					
(allylamine)	CR/RhB	5	1:4	5.8	67
modified yeast					
Acetic acid-					
promoted	MO/MB	10	1:1	156.7	68
UiO-66					
MOF-545	MB/MO	10	1:1	1.7	69

		Journal Pr	e-proofs		
<b>UiO-66</b>	SV/MB	33	1.9	32	Present
010-00	51/1010	55	1.7	52	work
Ui <b>O-66-</b> Y	SY/MB	33	1:9	398	Present
			,	270	work

\*AR: Alizarin red; TH: Thionin acetate; AO: Acid orange II; MG: Malachite green; MB: Methylene blue; ST: Safranine T; RhB: Rhodamine B; CR: Congo red; MO: Methyl orange and SY: Sunset yellow FCF.



Fig. 1 SEM images of (a) UiO-66, (b) UiO-66-V, (c) UiO-66-T and (d) UiO-66-Y.



Fig. 2 PXRD patterns of UiO-66, UiO-66-V, UiO-66-T and UiO-66-Y.



Fig. 3 (a) Nitrogen adsorption isotherms and (b) pore distributions of UiO-66, UiO-66-V, UiO-66-T and UiO-66-Y.



Fig. 4 High-resolution XPS spectra of C1s core energy levels (a) and O1s core energy

levels (b) of UiO-66, UiO-66-V, UiO-66-T and UiO-66-Y.



Fig. 5 TGA and DTG curves of UiO-66, UiO-66-V, UiO-66-T and UiO-66-Y.





Fig. 6 (a) Zeta potential at pH=6.0 for UiO-66, UiO-66-V, UiO-66-T and UiO-66-Y,

(b) effect of pH value on zeta potential for UiO-66 and UiO-66-Y.



Fig. 7 (a) Adsorption capacity of different anionic and cationic dyes and (b) different size anion dyes on UiO-66, UiO-66-V, UiO-66-T and UiO-66-Y. (Conditions: T= 298 K, pH = 6.0, dye concentration: 0.1 mmol/L, V = 50 mL, adsorbate dosage: 10 mg)



Fig. 8 (a) Adsorption isotherms, (b) adsorption kinetics curves, (c) equilibrium and kinetic selectivities of SY and MB on UiO-66 and UiO-66-Y, and (d) pH response and cycling performance of SY on UiO-66-Y.



Fig. 9 (a) Selectivity of different molar ratio of SY/MB in binary solution and (b)

equimolar SY/MB on UiO-66 and UiO-66-Y under different pH. (Conditions: T=298 K, total dye concentration: 0.1 mmol/L, V=50 mL, adsorbate dosage: 10 mg)



The main attractive research highlights of this work are listed as follows:

- pH-switchable UiO-66s were fabricated via three amino acids
- Asymmetric carboxylic coordination expanded pore size with -NH<sub>2</sub> surface in UiO-66
- UiO-66-Y realized 1.9 times higher adsorption uptake for SY than pristine sample
- UiO-66-Y exhibited >10 times higher selectivity (> 390) for SY/MB than pristine one
- UiO-66-Y realizes self-ad/desorption for 6 consecutive recycling via pH-switch