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# Journal of Materials Chemistry C

Materials for optical, magnetic and electronic devices

### Accepted Manuscript

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Received 00th January 20xx, Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

# Catalyst + Chemodosimeter → Chemosensor: Incorporation of a catalytic functionality in an indicator displacement assay to realize reversible chemosensing detection

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A new bimetallic complex,  $(CN)_3Fe^{II}(tpp2)Cu^{IICI}(tppz = 2,3,5,6-tetra(2'-pyridyI)pyrazine) including a Fe(II)-diimine indicator$ and a dual functional Cu(II) receptor/catalyst, was synthesized to demonstrate the concept of indicator/catalystdisplacement assay for the simultaneous detection and detoxification of cyanide. The catalytic degradation property in theassay was necessary for making the detecting system reversible, which the traditional indicator displacement assays couldnever achieve. After the realization of this new property, the silica-gel-based solid-supporting complex**1**was fabricated forapplication in a device, which was demonstrated for its use in the naked-eye detection and degradation of cyanide in tap,river, and underground water samples in a repeatable and real-time manner, even in the presence of interfering anions(CH<sub>3</sub>COO<sup>-</sup>, N<sub>3</sub><sup>-</sup>, HCO<sub>3</sub><sup>-</sup>, Cl<sup>-</sup>, NO<sub>3</sub><sup>-</sup>, HPO<sub>4</sub><sup>2-</sup>, SO<sub>4</sub><sup>2-</sup>, SCN<sup>-</sup>, and OCN<sup>-</sup>). Within 300 min, cyanide was quantitatively oxidized into theless toxic cyanate by**1**in the presence of H<sub>2</sub>O<sub>2</sub>. The detection limit of**1**for cyanide was found to be 1.16 × 10<sup>-4</sup> M (3.02mg/L).

#### Introduction

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Reversible detection of analytes allows real-time medical, industrial, and environmental applications.<sup>1</sup> Reversibility is an important characteristic of supramolecular chemistry, involving association, dissociation, and exchange of molecules.<sup>2</sup> Recent research attention has been focused on the development of displacement assays as one of the emerging tools for in-situ monitoring of xenobiotics<sup>3a</sup>, *in-vivo* determination of bio-analytes<sup>3b-</sup> <sup>d</sup>, drug and prodrug discovery<sup>3e-f</sup>, and latent catalysis<sup>3g</sup> because of its simple design, good analyte selectivity, and/or high detection sensitivity. The working principle of indicator displacement assays (IDAs) involves (i) initial binding of an indicator to a receptor, forming an "indicator-receptor ensemble"; (ii) introduction of a competitive analyte into the system, causing the dissociation of the ensemble, followed by release of the indicator and hence, triggering an action such as a colorimetric and/or fluorometric signal; and (iii) a new formation of "receptor-analyte ensemble". In principle, molecular device based on the displacement assay is a one-off mechanism because the thermodynamically more stable "receptoranalyte ensemble" formed does not allow the system to revert to its original form, i.e., the less stable "indicator-receptor ensemble".4 These irreversible and non-repeatable properties of the displacement assay always limit its application.

To realize the reversible functionality in the displacement assay, incorporation of a catalytic unit is a possible solution. In

this study, a bimetallic donor-acceptor ensemble (BmDAE)<sup>5</sup> has been synthesized as the first displacement-based device for reversible monitoring of pollutants by destroying the pollutants. To this end, the BmDAE includes a metallic indicator with a metallic receptor. Most importantly, the receptor is also formulated as a catalyst for degrading the analyte to be tested. In the presence of a toxic analyte, the indicator displacement design allows the BmDAE to dissociate into its signal indicator via the formation of the "receptoranalyte ensemble". Therefore, the analyte is quantitatively monitored. Furthermore, since the receptor also acts as a catalyst, the pollutant can be catalytically degraded into harmless components simultaneously. Due to the degradation of the pollutants, the "receptor-analyte ensemble" is destroyed, reforming the "indicator-receptor ensemble" and thus, providing the reversibility. Instead of using indicator displacement assay for irreversible and cumulative detection, use of this new indicator/catalyst displacement assay could open a new direction for real-time analyte detection.

Herein we report a new BmDAE, complex 1 (CN)<sub>3</sub>Fe<sup>II</sup>(tppz)Cu<sup>II</sup>Cl (tppz = 2,3,5,6-tetra(2'-pyridyl)pyrazine), and its silica-gel-based solid-supporting material for monitoring and detoxifying cyanide in real water samples (tap, river, and underground water). Through the indicator/catalyst displacement assay (ICDA), the advantages of the system will be reported in terms of "SSDRRA", i.e., selectivity, sensitivity. detoxification, reversibility, repeatability. and applicability. Cyanide is chosen as the analyte because of its high toxicity, broad industrial applications, and because it has reportedly caused widespread concern.<sup>6</sup> Furthermore, such chemosensing and chemodosimetric systems for cyanide detection can be used in rare molecular devices to synergically detect and remediate the pollutant in a one-step process.6a,6c,7

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<sup>\*</sup>Experimental Procedures and UV-vis spectroscopic titrations can be found in the Electronic supplementary information (ESI): [details of any supplementary information available should be included here]. See DOI: 10.1039/x0xx00000x

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**Scheme 1** Proposed ICDA mechanism of complex **1** for the simultaneous detection and degradation of cyanide.

#### **Experimental section**

#### Synthetic procedures of (CN)<sub>3</sub>Fe"(tppz)Cu<sup>II</sup>Cl (1).

A mixture of  $[BTPPC][Fe^{II}(tppz)(CN)_3]$  (BTPPC = benzyltriphenylphosphonium bromide; 437.5 mg, 0.5 mmol) and CuCl<sub>2</sub> (66.5 mg, 0.5 mmol) was stirred at 298 K in ethanol (100 mL) for overnight. The blue solids precipitated out were collected, washed with ethanol, and air-dried at room temperature. (215.0 mg, 67.3%) IR (KBr):  $v_{C=N} = 2092 \text{ cm}^{-1}$ . High-resolution ESI-MS (positive mode): m/z 642.9438 {(Na)(CN)<sub>3</sub>Fe<sup>II</sup>(tppz)Cu<sup>II</sup>Cl}<sup>+</sup> (calculated mass: 642.9760 amu); Anal. calcd. for C<sub>27</sub>ClCuFeH<sub>16</sub>N<sub>9</sub>·4.5H<sub>2</sub>O·CH<sub>3</sub>CH<sub>2</sub>OH: C, 46.54; H, 4.17; N, 16.84. Found C, 46.56; H, 4.13; N, 17.20.

#### Chemosensing Selectivity of Complex 1 Toward Various Anions.

Various anions, including CN<sup>-</sup>, SO<sub>4</sub><sup>2-</sup>, HCO<sub>3</sub><sup>-</sup>, HPO<sub>4</sub><sup>2-</sup>, N<sub>3</sub><sup>-</sup>, CH<sub>3</sub>COO<sup>-</sup>, NCS<sup>-</sup>, NO<sub>3</sub><sup>-</sup>, NCO<sup>-</sup>, and Cl<sup>-</sup> (0–2.0 × 10<sup>-3</sup> M) were titrated with complex **1** solution (1.0 × 10<sup>-4</sup> M). The titrations were carried out in phosphate buffer (pH 7, 0.02 M) at 298 K. The spectroscopic changes of resulting mixtures at 597 nm were plotted as a function of the analyte mole ratio. The colorimetric responses of **1** by the analytes were also obtained by digital photography. The binding constants<sup>8</sup> and method detection limits<sup>9</sup> were evaluated from the spectroscopic changes.

#### Catalytic Degradation of Cyanide by Complex 1.

A 15.00 mL test solution (pH 7 phosphate buffer) containing 1, CN<sup>-</sup>, and H<sub>2</sub>O<sub>2</sub> (1.0 × 10<sup>-4</sup>, 1.0 × 10<sup>-3</sup>, and 2.0 × 10<sup>-3</sup> M, respectively) was stirred for 180 min at 298 K. The test solution was measured at regular intervals using a Thermo Scientific<sup>™</sup> Orion<sup>™</sup> analyzer and ion chromatography<sup>10</sup> to evaluate the levels of CN<sup>-</sup> and NCO<sup>-</sup>, respectively. All the samples were immediately analyzed to avoid errors due to subsequent reactions.

## Solid-supported Complex 1 and its Repeatability of Chemosensing and Catalytic degradation toward Cyanide.

The solid-supported complex **1** was fabricated by adding SiO<sub>2</sub> (40–63 µm, 2.5 g) to complex **1** solution ( $1.0 \times 10^{-4}$  M, 50 mL, pH 7 phosphate buffer). The moist green powders obtained were collected by filtration, washed with deionized water, and air-dried at 298 K. IR (KBr):  $v_{C=N} = 2145$  cm<sup>-1</sup>. The green solid-supported complex **1** material (2.5 g) was suspended in 50 mL phosphate buffer. Initially, CN<sup>-</sup> ( $1.0 \times 10^{-3}$  M) was added to activate the chemosensing activity of the solid-supported complex **1**. H<sub>2</sub>O<sub>2</sub> ( $1.0 \times 10^{-2}$  M) was then added to initiate its

catalytic activity. The spectroscopic changes warefeet the supernatant solution at 532 nm and the Pernoval efficiency of CN<sup>-</sup> were analyzed as functions of time. The above operations were performed four times by the reversible addition of CN<sup>-</sup> ( $1.0 \times 10^{-3}$  M) and H<sub>2</sub>O<sub>2</sub> ( $1.0 \times 10^{-2}$  M) to test the repeatability of the material.

#### **Results and discussion**

#### Synthesis and Characterization of Complex 1.

In this study, [BTPPC][Fe<sup>II</sup>(tppz)(CN)<sub>3</sub>] was used as a building block to construct a multifunctional chemosensor/catalyst material because of its advantages: (i) strong and low-energy UV-Vis absorption, which is an ideal property for the signal-transducing counterpart; (ii) the free N^N^N tridentate site, which is believed to be a good coordination position for the reversible association and dissociation of a metallic receptor/catalyst; and (iii) free C=N ligands, which can be exploited for adsorption on solid-supporting materials.

Bimetallic complex **1** was synthesized by simply stirring equivalent molar amounts of  $[BTPPC][Fe^{II}(tppz)(CN)_3]$  to CuCl<sub>2</sub> in ethanol at 298 K and isolated as an air-stable compound with high solubility in aqueous medium. The results of high-resolution ESI-MS and elemental analysis confirmed the proposed bimetallic structure of complex **1**, where the tppz ligand is believed to act as a bridge connecting the Fe(II) and Cu(II) metal ions (Scheme 1).

The UV-Vis absorption spectrum of [BTPPC][Fe<sup>II</sup>(tppz)(CN)<sub>3</sub>] featured a broad and low-energy band at 425–650 nm. According to the literature, this low-energy absorption band originates from the  $Fe(d\pi) \rightarrow tppz(\pi^*)$  metal-to-ligand charge transfer (MLCT) absorption.<sup>11</sup> [BTPPC][Fe<sup>II</sup>(tppz)(CN)<sub>3</sub>] appears purple in color when dissolved in aqueous pH 7 phosphate buffer. Upon coordination of a Cu(II) ion, the MLCT transition of Fe(II)-diimine chromophore in complex 1 shows a red-shift from  $\lambda_{max}$  at 532 to 597 nm, due to the electron-withdrawing effect of Cu(II) in destabilizing the *d*-orbitals of the Fe(II)-diimine chromophore (S.Figure 1a). The color of complex 1 is blue in aqueous pH 7 phosphate buffer. The results of the UV-Vis spectroscopic titration of [BTPPC][Fe<sup>II</sup>(tppz)(CN)<sub>3</sub>] by CuCl<sub>2</sub> fitted the 1:1 Benesi–Hildebrand equation with a good linear relationship ( $R^2$ =0.999) for the plot of  $A_0/(A-A_0)$  at 597 nm versus 1/[CuCl<sub>2</sub>] (S.Figure. 1b). This further suggests that the free N^N^N tridentate site in [Fe<sup>II</sup>(tppz)(CN)<sub>3</sub>]<sup>-</sup> is associated with one Cu(II) metallic counterpart to form the bimetallic complex. The overall binding constant, log K, for this formation is estimated as 2.86  $M^{-1}$ .

#### Chemosensing Property of Complex 1 Toward Cyanide.

The formation of complex 1 through the binding of the indicator,  $[Fe^{II}(tppz)(CN)_3]^-$ , to the Cu(II) receptor enables us to use this bimetallic "indicator-receptor ensemble" to detect cyanide. Figure 1a shows the UV-Vis spectroscopic titration of 1 by the addition of an increasing amount of cyanide in aqueous pH 7 buffer. Three clear isosbestic points at 346, 471, and 558 nm were obtained during the titrations, with a blue-shift of both  $\pi$ -  $\pi^*$  and MLCT absorptions from  $\lambda_{max}$  at 393 to 333 nm and from 597 to 532 nm, respectively. Figure 1b shows the mole ratio plot between 1 and cyanide, revealing that the maximum UV-Vis spectroscopic response occurs at a ratio of 1:4. The overall binding constant, log *K*, and the method detection limit (MDL) calculated from the titrations of 1 by cyanide ions were estimated as  $12.27 \pm 0.01$  M<sup>-4</sup>

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**Fig. 1** (a) UV-Vis spectroscopic titrations of complex **1** ( $1 \times 10^{-4}$  M) with CN<sup>-</sup> (0–1 ×10<sup>-3</sup> M), (b) mole ratio plot between **1** ( $3 \times 10^{-4}$  M) and cyanide (0–3 ×10<sup>-3</sup> M) at 532 nm, (c) the slope and y-intercept of the best-fitted plot of A<sub>0</sub>/(A-A<sub>0</sub>) at 532 nm versus 1/[cyanide]<sup>4</sup> as 4.48 × 10<sup>-13</sup> M<sup>4</sup> and 0.83, respectively, log *K* = 12.27, and (d) Photographs of the colorimetric responses of complex **1** ( $1 \times 10^{-4}$  M) in the presence of increasing concentration of CN<sup>-</sup> (0–1 × 10<sup>-3</sup> M). All the experiments were carried out in pH 7 phosphate buffer (0.02 M) at 298 K.

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and 1.16 × 10<sup>-4</sup> M (3.02 mg/L), respectively (Figure 1c). The lethal dose (LD<sub>50</sub>) of cyanide is 0.5–3.5 mgkg<sup>-1</sup> to body weight <sup>23</sup> Figure 1d shows that the colorimetric responses from blue to purple of **1** with increasing amounts of cyanide can be detected by naked eyes. Upon the recognition of 10 different anions, CN<sup>-</sup>, CH<sub>3</sub>COO<sup>-</sup>, N<sub>3</sub><sup>-</sup>, HCO<sub>3</sub><sup>-</sup>, Cl<sup>-</sup>, NO<sub>3</sub><sup>-</sup>, HPO<sub>4</sub><sup>2-</sup>, SO<sub>4</sub><sup>2-</sup>, SCN<sup>-</sup>, and OCN<sup>-</sup> by complex **1**, only cyanide could trigger UV-Vis spectroscopic changes (Figure 2a), producing a sharp naked-eye colorimetric response from blue to purple (Figure 2b).

The sensing mechanism of complex 1 toward cyanide ions is proposed in Scheme 1. The clear isosbestic points obtained during the titration of 1 by cyanide and the close resemblance of the UV-Vis spectrum of the "complex 1 + cyanide mixture" to that of [BTPPC][Fe<sup>II</sup>(tppz)(CN)<sub>3</sub>] suggest that the N^N^N tridentate coordination between Cu<sup>2+</sup> and [Fe<sup>II</sup>(tppz)(CN)<sub>3</sub>]<sup>-</sup> is cleaved in the presence of cyanide ions. The results of UV-Vis spectroscopic titration between 1 and cyanide fitted the 1:4 Benesi–Hildebrand equation with a good linear relationship (R<sup>2</sup>=0.997; Figure 1c), further suggesting that four molecules of cyanide led to Cu(II) ion displacement. The dissociation of complex 1 into [Fe<sup>II</sup>(tppz)(CN)<sub>3</sub>]<sup>-</sup> and [Cu(CN)<sub>4</sub>]<sup>2-</sup>. The Gibbs free energy changes ( $\Delta$ G°) for complex 1 and [Cu(CN)<sub>4</sub>]<sup>2-</sup> are -16.3 (Fig. S1) and -125.5 kJ/mol<sup>13</sup>, respectively, further supporting our explanation.<sup>14</sup>



**Fig. 2** (a) Summary of UV-Vis spectroscopic titrations (A/A<sub>0</sub> at 597 nm) of complex **1** (1 × 10<sup>-4</sup> M) with ten different anions monitored as a function of their concentration (0–1 × 10<sup>-3</sup> M). (b) Photographs of the colorimetric responses of the above titration with anion concentration as 1 ×10<sup>-3</sup> M: from left to right is blank, CN<sup>-</sup>, CH<sub>3</sub>COO<sup>-</sup>, N<sub>3</sub><sup>-,</sup> HCO<sub>3</sub><sup>-</sup>, Cl<sup>-</sup>, NO<sub>3</sub><sup>-</sup>, HPO<sub>4</sub><sup>2-</sup>, SO<sub>4</sub><sup>2-</sup>, SCN<sup>-</sup>, and OCN<sup>-</sup>. All the experiments were carried out in pH 7 phosphate buffer (0.02 M) at 298 K.

Catalytic Activity of Complex 1 Toward Cyanide.

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The advantages of exploiting the bimetallic functionalities of complex 1 are not limited to the detection of cyanide but also to degrade pollutants into harmless substances. Cu(II) complexes have been studied as active metal catalysts to oxidize CN<sup>-</sup> to NCO<sup>-</sup> using  $H_2O_2$  as the oxidant.  $^{\rm 3g}$  In this study, we attempted to demonstrate the catalytic property of complex 1 in the presence of cyanide after the abovementioned displacement. For this investigation, the concentrations of CN<sup>-</sup> and NCO<sup>-</sup> in eight test solutions containing  $CN^{-}$ ,  $H_2O_2$ , and **1** in a molar ratio of 10:20:1 in deionized water were regularly measured at 30 min intervals.<sup>15</sup> As seen in Figure 3a, complex 1 catalyzes the oxidative degradation of cyanide quantitatively within 420 min. Control experiments conducted without the complex or with [BTPPC][Fe<sup>II</sup>(tppz)(CN)<sub>3</sub>] under the given conditions revealed that less than 25% of cyanide was oxidized during the experimental period. Even in the reaction using CuCl<sub>2</sub> instead of the bimetallic complex, cyanide was quantitatively oxidized within 420 min.10 The catalytic activity of complex 1 originated from the displacement of the Cu(II) complex by cyanide.  $[Cu(CN)_4]^{2-}$  was eventually formed as the active catalyst for this oxidation (Scheme 1). Interestingly, the subsequent observation of  $[Cu(OCN)(CN)_3]^{2-}$  (m/z 91.8; mass-to-charge ratio is 2) and  $[Cu(CN)_3]$  $(m/z \ 141.6)$  in the ESI-MS profile of the "complex **1**+CN-" mixture confirmed the degradation of not only the free cyanide but also the Cu-bound cyanide.

#### Reversibility of Complex 1 Toward Cyanide.

As mentioned in the introduction, the formation of a more thermodynamically stable "receptor-analyte ensemble" with respect to the "indicator-receptor ensemble" makes IDAs irreversible.<sup>4</sup> However, the catalytic degradation property of complex **1** has been demonstrated to destroy this stable "receptor-analyte ensemble" to form a new "receptor-degradant ensemble"; hence, we believe that the reversibility of system should be changed. If a less stable "receptor-degradant ensemble" is formed during the degradation, the receptor from the "receptor-degradant ensemble" can be exchanged back to the free indicator, thus restoring the original "indicator-receptor ensemble."

Figure 3b shows the color changes in the test solution containing CN<sup>-</sup>, H<sub>2</sub>O<sub>2</sub>, and **1** (molar ratio of 10:20:1) with time. Unlike other traditional chemodosimeters and chemosensors, complex **1** regained its original color after a complete detection and degradation cycle. To investigate this reversibility, the cyanide and cyanate levels as well as the UV–Vis spectroscopic changes of the abovementioned test solution were regularly measured at 30 min intervals (Figures 3b and 3c). At 0 h, the  $\pi$ -  $\pi^*$  and MLCT absorptions of the Fe(II)-diimine chromophore, which existed as an intact bimetallic complex, were detected at  $\lambda_{max}$  383 and 597 nm, respectively. The color of test solution was blue, and the level of cyanide is full, indicating 100% cyanide concentration in the solution.

Stage 1 ("indicator-receptor ensemble" + analyte  $\rightarrow$  "receptoranalyte ensemble" + indicator): From 0 to 30 min, cyanide rapidly initiated the indicator displacement by dissociating complex 1 into [Fe<sup>III</sup>(tppz)(CN)<sub>3</sub>]<sup>-</sup> and [Cu(CN)<sub>4</sub>]<sup>2-</sup>. Thus, four equivalents of cyanide were found to be decreased, and 60% of cyanide was left in the test solution. The dissociation caused the original  $\pi$ - $\pi$ \* and MLCT absorptions in complex 1 to be gradually suppressed and blueshifted to 333 and 532 nm, respectively (S.Figure 2b); thus,  $\lambda_{max}$  at 383 nm was found to be decreased. At this stage, the color of the test solution changed from blue to purple. No cyanate was found in this stage.



**Fig. 3** (a) Catalytic degradation of CN<sup>-</sup> by complex 1 (  $\blacktriangle$ , 1 × 10<sup>-4</sup> M), CuCl<sub>2</sub> (  $\bigtriangledown$ , 1 × 10<sup>-4</sup> M) and [BTPPC][Fe(tppz)(CN)<sub>3</sub>] ( $\bigcirc$ , 1 × 10<sup>-4</sup> M) and control ( $\blacksquare$ ) in the presence of H<sub>2</sub>O<sub>2</sub> as the oxidant; for the degradation of CN<sup>-</sup> by complex 1: (b) photograph of its colorimetric responses; (c) absorbance changes (383 nm); and (d) cyanide and cyanate concentrations ( $c_0$  = initial concentration, c = concentration after a given time). All the experiments were carried out in DI water at 298 K with the concentrations of CN<sup>-</sup> and H<sub>2</sub>O<sub>2</sub> set as 1 × 10<sup>-3</sup> and 2 × 10<sup>-3</sup> M, respectively.

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Stage 2 (analyte  $\rightarrow$  degradant): During the next 4.5 h (30–300 min), [Cu(CN)<sub>4</sub>]<sup>2-</sup> formed served as the active catalytic center to initiate the oxidative degradation of CN<sup>-</sup> to OCN<sup>-</sup> in the presence of H<sub>2</sub>O<sub>2</sub>. During the catalytic oxidation, all the unbound cyanide anions were completely degraded, while the concentration of cyanate proportionally increased. Note that at this stage, the level of cyanate reached only 60% with respect to the original level of cyanide used, because 40% of the cyanide existed as [Cu(CN)<sub>4</sub>]<sup>2-</sup>. No UV-Vis spectroscopic changes for the test solution were found, and  $\lambda_{max}$  at 383 nm was unchanged throughout this period. The color of test solution remained purple. At the end of this stage, [Cu(CN)<sub>4</sub>]<sup>2-</sup>, NCO<sup>-</sup>, and [Fe<sup>III</sup>(tppz)(CN)<sub>3</sub>]<sup>-</sup> were formed and present in the test solution.

Stage 3 ("receptor-analyte ensemble" + indicator  $\rightarrow$  "indicatorreceptor ensemble" + degradant): After complete degradation of the free cyanide, during the next 3 h (300-480 min), the cyanide ligands in [Cu(CN)<sub>4</sub>]<sup>2-</sup> were further degraded to cyanate. During this degradation, the concentration of cyanate gradually increased, and the quantitative amount of cyanate was reached at 19 h. The  $\pi$ - $\pi$ \* and MLCT absorptions gradually increased and red-shifted to their original wavelengths at 383 and 597 nm, respectively (S.Figure 2c). Figure 3c shows a steep change in  $\lambda_{\text{max}}$  at 383 nm from 300 to 360 min, with a steady change from 360-480 min. These UV-Vis spectroscopic changes could be explained by the re-formation of the [(CN)<sub>3</sub>Fe<sup>II</sup>(tppz)Cu<sup>II</sup>]<sup>+</sup> ensemble due to the exchange of Cu<sup>2+</sup> from the [Cu(OCN)<sub>4</sub>]<sup>2-</sup> intermediate<sup>16</sup>, the so-called "receptor-degradant ensemble", to [Fe<sup>II</sup>(tppz)(CN)<sub>3</sub>]<sup>-</sup>. The Gibbs free energy changes  $(\Delta G^{\circ})$  for complex 1 and  $[Cu(OCN)_4]^{2-}$  were -16.3 (S. Figure 1) and -14.1 kJ/mol,<sup>17</sup> respectively, which confirmed that the driving force for this exchange is due to the formation of the more stable [(CN)<sub>3</sub>Fe<sup>II</sup>(tppz)Cu<sup>II</sup>]<sup>+</sup> ensemble. Consequently, the system could be restored to its initial stage, where the color of test solution was also restored from purple to blue, indicating (i) the end of the detoxification and (ii) the time for restarting a new sensing and degradation cycle.

## Solid-supported Material 1: Fabrication, Reversibility, and Repeatability, and Detection/Oxidation of Cyanide in Real Water Samples.

To further apply and test the reversibility and repeatability of complex 1 toward cyanide, a solid-supported material 1 was fabricated by adsorbing complex 1 onto commercially available silica gel (SiO<sub>2</sub>, 0.040–0.063 mm) in 1:780 w/w ratio. The red-shift of the  $v_{C=N}$  stretching frequencies from 2077 to 2145 nm in the FTIR spectrum of solid-supported complex 1 with respect to the free complex 1 suggested that the C=N ligands in complex 1 acted as bridges for this adsorption.

Upon the addition of cyanide to the green solid-supported material **1** in pH 7 buffer, the color of supernatant solution changed from colorless to purple while the color of solid-supported material **1** changed from green to white (Figure 4a inset). Furthermore, cyanide was found to be quantitatively degraded within 60 min under the given conditions, in the presence of  $H_2O_2$  (Figure 4a). These results concurred with the ICDA mechanism, according to which the adsorbed complex **1** dissociated into  $[Cu(CN)_4]^{2-}$  and  $[Fe^{II}(tppz)(CN)_3]^-$ . The negatively charged Fe(II) and Cu(II) complexes caused the desorption and imparted color to the supernatant solution.

Most importantly, the reversible property of complex 1 resulted in repeatability to solid-supported material 1. One hour after the 1<sup>st</sup>





**Fig. 4** (a) Repeatability of the detection and degradation of cyanide by the solid-supported complex **1** material in the presence of H<sub>2</sub>O<sub>2</sub>. The black line represents the  $\lambda_{max}$  of the supernatant at 532 nm, while the blue line is the ratio of [cyanide] in the supernatant (c<sub>0</sub> = initial concentration, c = concentration after a given time). (inset) Photographic images of the solid and the supernatant solution. (b) The removal efficiency of CN<sup>-</sup> by the material in different types of water samples. All the experiments were carried at 298 K with the solid-supported complex **1** material (63.8 mg/L, complex **1** component: 1 × 10<sup>-4</sup> M), CN<sup>-</sup> (1 × 10<sup>-3</sup>M), and H<sub>2</sub>O<sub>2</sub> (1 × 10<sup>-2</sup> M).

cycle of ICDA, the purple supernatant solution became colorless, while the white-colored solid-supported material reverted to green (Figure 4a inset). This was because the  $[(CN)_3Fe^{II}(tppz)Cu^{II}]^+$  ensemble was re-formed as the mechanism stated above, and it readsorbed onto the blank SiO<sub>2</sub>. Experiments were performed on the material continuously for four cycles by the addition of a new portion of cyanide and  $H_2O_2$  after each round. Afterward, the sensing signals were fully recovered, and the degradation efficiency was >99%, thus indicating that the material showed repeatable ICDA performance (Figure 4a).

Finally, the application of solid-supported material **1** to detect and detoxify cyanide ions in real water samples such as tap water, river water, and underground water was investigated. The real water samples were spiked with a constant amount of cyanide ions at room temperature. The concentration of residual cyanide was regularly analyzed every 30 min.<sup>3f,10</sup> The complete oxidation (85% oxidation) of cyanide to cyanate ions required approximately 180 min for all the water samples (Figure 4b). These results indicated that the presence of organic and inorganic matter in the real water

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samples does not interfere with the operation of solid-supported material  ${\bf 1}.$ 

#### Conclusions

A new bimetallic complex,  $(CN)_3Fe^{II}(tppz)Cu^{II}CI$ , has been synthesized and used to demonstrate the concept of ICDA for the simultaneous detection and detoxification of cyanide. Two major components are incorporated in the bimetallic design, a Fe(II)diimine indicator and a dual functional Cu(II) receptor/catalyst, in order to achieve "SSDRRA": selectivity, sensitivity, detoxification, reversibility, repeatability, and applicability.

Complex **1** shows good selectivity and sensitivity by producing a naked-eye colorimetric response to cyanide but not to the other common anions. The log *K* and MDL values are  $12.27 \pm 0.01 \text{ M}^{-4}$  and  $1.16 \times 10^{-4} \text{ M}$  (3.02 mg/L), respectively. The complex also shows catalytic activity for the oxidation of cyanide. This detoxification is quantitative and can be achieved in 60–180 min. A silica gel-based solid-supporting complex **1** material is fabricated and demonstrated to be suitable for the detoxification of cyanide ions in real water bodies, such as tap water, river water, and underground water bodies, with 85% recovery.

The catalytic degradation is demonstrated as a necessary tool to make the ICDA system reversible and repeatable. Through the degradation of cyanide by complex **1** in the test solution, a free Cu(II) complex, NCO<sup>-</sup>, [Fe<sup>II</sup>(tppz)(CN)<sub>3</sub>]<sup>-</sup> is revealed to be formed. The stability of complex **1** ( $\Delta$ G° = -16.3 kJ/mol) over that of [Cu(NCO)<sub>4</sub>]<sup>2-</sup> ( $\Delta$ G° = -14.1 kJ/mol) is revealed and used to explain the reversibility and repeatability offered by the system.

#### **Conflicts of interest**

Published on 07 February 2020. Downloaded on 2/8/2020 2:58:40 AM

There are no conflicts to declare.

#### Acknowledgements

The work described in this paper was funded by a grant from the Education University of Hong Kong (Project No. R3444, R4175 and R4201), and grants from the Research Grants Council of Hong Kong SAR, China (GRF 18300415).

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