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## COMMUNICATION

## Nanostructured charge transfer complex of CuTCNQF<sub>4</sub> for efficient photo-removal of hexavalent chromium†

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High toxicity of hexavalent chromium warrants development of efficient catalysts that could reduce chromium into a relatively non-toxic trivalent chromium species. Pristine charge transfer complexes of MTCNQ family (M = Cu or Ag; TCNQ = 7,7,8,8-tetracyanoquinodimethane) have previously failed to catalyse reduction of Cr<sup>6+</sup> to Cr<sup>3+</sup>. We demonstrate that due to the outstanding electron transfer properties of one of the fluorinated derivatives of MTCNQ, i.e., 7,7,8,8-tetracyano-2,3,5,6-tetrafluoroquinodimethane (CuTCNQF<sub>4</sub>), it is able to catalyse the reduction of hexavalent chromium in aqueous solution at room temperature. We further demonstrate that the semiconducting nature of these organic charge transfer complexes allows CuTCNQF<sub>4</sub> to act as an outstanding material for reductive photo-removal of hexavalent chromium under UV photoexcitation conditions. Such materials are likely to play an important role in photoactive electron transfer reactions.

### Introduction

Metal-organic semiconducting materials of MTCNQ family (M = Cu or Ag; TCNQ = 7,7,8,8-tetracyanoquinodimethane) have attracted considerable attention over the last decade due to their potential applications in data and energy storage,<sup>1, 2</sup> sensors,<sup>3, 4</sup> electric devices,<sup>3-5</sup> catalyst surfaces,<sup>6-9</sup> and antibacterial.<sup>10</sup> Fluorinated analogues of TCNQ, such as 7,7,8,8-tetracyano-2,3,5,6-tetrafluoroquinodimethane (TCNQF<sub>4</sub>) have shown significant improvement in the stability of the anion and dianion radicals in acetonitrile, while further improving its electron accepting properties, thereby enhancing the potential applicability of TCNQF<sub>4</sub>-based semiconducting materials.<sup>6, 11, 12</sup> Synthesis and structural characterization of MTCNQF<sub>4</sub> crystals have shown outstanding optical, electrical, and magnetic properties<sup>13-20</sup> compared to their non-fluorinated analogues. However, it is of surprise that the applications of TCNQF<sub>4</sub>-based semiconducting materials have remained limited.<sup>11, 12</sup> Recently, the potential of CuTCNQF<sub>4</sub> and AgTCNQF<sub>4</sub> for electron transfer reactions between ferrocyanide and thiosulfate was investigated, which revealed that the balance between the injection of charge to the catalyst surface and the ejection of charge from the surface to the solution is an important factor in promoting this reaction.<sup>6</sup>

Similarly, CuTCNQF<sub>4</sub> and AgTCNQF<sub>4</sub> have also been used to fabricate field emission<sup>17</sup> and switching devices.<sup>21</sup>

Hexavalent chromium, a carcinogen and mutagen, is a serious pollutant found in many industrial effluents, including metal plating, wood processing, pigment manufacturing and leather tanning.<sup>22, 23</sup> Chromium usually exists in two oxidation states *viz.* trivalent (Cr<sup>+3</sup>) and hexavalent (Cr<sup>6+</sup>) in aqueous solutions. While Cr<sup>+3</sup> is minimally toxic to the environment and humans (it is even known as an essential nutrient for humans),<sup>24</sup> Cr<sup>6+</sup> remains extremely toxic to humans.<sup>25</sup> It is also well-known that in comparison to Cr<sup>6+</sup> that can easily migrate through groundwater and soil, Cr<sup>+3</sup> can be readily precipitated down in the form of Cr(OH)<sub>3</sub> in aqueous solutions at neutral pH.<sup>26</sup> This further negates the toxic effect of trivalent chromium in the environment. Therefore, it is of utmost importance to find effective ways to remove Cr<sup>6+</sup> from aqueous solutions.

A facile approach for removal of hexavalent chromium may involve reduction of Cr<sup>6+</sup> to Cr<sup>+3</sup> followed by its precipitation to Cr(OH)<sub>3</sub> in combination with other separation methods.<sup>27</sup> Several strategies have been developed to reduce Cr<sup>6+</sup> to Cr<sup>+3</sup> in aqueous solution, including, treatment with sulphur compounds or iron salts<sup>28, 29</sup> under acidic conditions followed by its precipitation with an alkali, electrochemical reduction,<sup>30</sup> photocatalytic reduction using semiconducting materials either by directly using the semiconductor for reduction or using the semiconductor as an adsorbent material followed by the catalytic conversion in the presence of light illumination conditions<sup>31, 32</sup> and more recently bacteria<sup>33, 34</sup> and marine planktons.<sup>35</sup> Among these strategies, the use of photocatalytic processes, wherein a semiconducting material is employed in combination with additional electron donors such as organic

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acids, is finding particular attention due to improved efficiencies.<sup>9, 11, 27, 36</sup> Although use of inorganic semiconductors as photocatalysts is well-established,<sup>27, 36</sup> recent investigations have started to reveal that organic semiconductors decorated with noble metals can also effectively reduce  $\text{Cr}^{6+}$  to  $\text{Cr}^{3+}$ .<sup>9</sup> However, those studies found that pristine organic semiconductors without noble metals do not have enough driving force to catalyse this reaction. This is challenging, as noble metals typically add significant costs to the catalytic processes, which make their use impractical for environmental remediation.

In the current study, we report for the first time, the ability of a pristine organic semiconductor based on  $\text{CuTCNQF}_4$  in promoting the catalytic reduction of toxic  $\text{Cr}^{6+}$  to its non-toxic  $\text{Cr}^{3+}$  counterpart. The influence of reaction conditions including solution pH, electron donors, temperature, and UV light irradiation on the reduction efficiency is evaluated.

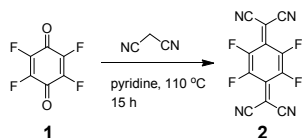
## Materials and Methods

### Materials

Copper foil (99.99 % purity) was procured from Chem Supply. Acetonitrile, concentrated sulphuric acid, nitric acid, methanol, acetic acid, and sodium dichromate ( $\text{Na}_2\text{Cr}_2\text{O}_7$ ) were purchased from Ajax Finechem. Tetrafluoro-1,4-benzoquinone was purchased from Sigma-Aldrich. All chemicals were used as received.  $\text{TCNQF}_4$  was synthesised in house. Copper foil was treated with dilute nitric acid, thoroughly rinsed with deionized water (MilliQ) and dried with a flow of  $\text{N}_2$  gas prior to use.

### Synthesis of $\text{TCNQF}_4$

$\text{TCNQF}_4$  synthesis was performed using a protocol reported previously.<sup>37</sup> A suspension containing 5 mM of compound **1** in 150 mL of pyridine was added to 10 mM of  $\text{TiCl}_4$  (**Scheme 1**). This reaction mixture was slowly heated under nitrogen atmosphere. To this heated mixture, 100 mM of malononitrile in 20 mL of dry pyridine was added and the reaction was refluxed for 15 h. The reaction mixture at the end of 15 h was concentrated to the half of its volume. The solid product obtained after cooling was filtered, washed and dried in vacuum oven. The product containing  $\text{TCNQF}_4$  was purified by recrystallization (methanol and acetonitrile) yielding a brown solid ( $\text{TCNQF}_4$ ) with 87% yield. Elemental analysis for  $\text{C}_{12}\text{F}_4\text{N}_4$ : Calculated: C – 52.19, N – 20.29; Actual: C – 52.20, N – 20.29; FTIR using KBr disc,  $\nu$  3012  $\text{cm}^{-1}$  (C-H aromatic), 2226  $\text{cm}^{-1}$  ( $\text{C}\equiv\text{N}$ ), 1665  $\text{cm}^{-1}$  (C=C ring) and 1460  $\text{cm}^{-1}$  (C–N stretching); MALDI-TOF (m/z):  $[\text{M}^+]$  calculated for  $\text{C}_{12}\text{F}_4\text{N}_4$ : 276.0059, actual: 276.0057.



Scheme 1. Synthesis of  $\text{TCNQF}_4$ .

### Synthesis of $\text{CuTCNQF}_4$

Copper foil ( $2 \times 0.5 \text{ cm}^2$ ) was immersed in 6 mL of 2 mM  $\text{TCNQF}_4$  solution at 45 °C for 3 h. The surface of the copper foil turned purple in colour indicating the formation of  $\text{CuTCNQF}_4$ . The sample was rinsed several times with deionized water and dried in a stream of  $\text{N}_2$  gas prior to characterization.

### Characterization of $\text{CuTCNQF}_4$

The crystal structures and elemental composition of  $\text{CuTCNQF}_4$  grown on copper foil was studied by scanning electron microscopy (SEM) and energy dispersive X-ray (EDX) using an EDX-equipped Phillips XL30 SEM instrument. Fourier transform infrared (FTIR) was performed on a PerkinElmer D100 spectrometer in attenuated total reflectance mode, while Raman spectroscopy was performed using a PerkinElmer Raman Station 200F. The Raman spectra was background corrected using a smoothing free algorithm developed in house.<sup>38</sup> X-ray photoelectron measurements (XPS) were carried out using a K-Alpha XPS instrument using monochromatic Al as the X-Ray source. The C 1s, Cu 2p, N 1s and F 1s core level spectra were recorded with an overall resolution of 0.1 eV. The core level spectra were background corrected using Shirley algorithm and chemically distinct species were resolved using a nonlinear least squares fitting procedure. UV-Vis reflectance measurements were carried out using a CRAIC Technologies microspectrophotometer with a 15X objective. The measurements were obtained from a  $50 \mu\text{m} \times 50 \mu\text{m}$  area.

### Reduction of $\text{Cr}^{6+}$

The catalysis experiments were carried out by placing  $\text{CuTCNQF}_4$  at the bottom of a 50 mL beaker containing a total of 20 mL reaction volume with 10 mM of  $\text{Cr}^{6+}$  and 1 mL of electron donor (either dried methanol or acetic acid). The pH of the mixture was adjusted using 1 M  $\text{H}_2\text{SO}_4$  before the reaction.  $\text{CuTCNQF}_4$  grown on  $1 \times 0.5 \text{ cm}^2$  foil was used for electron donor and pH-depending catalytic experiments. For dark and UV irradiation (200  $\text{mW}/\text{cm}^2$  UV with a  $\lambda_{\text{max}}$  of 254 nm obtained from Edmund Optics) experiments, the Cu foil size on which  $\text{CuTCNQF}_4$  was grown, was increased to  $2 \times 0.5 \text{ cm}^2$  to increase the surface for light absorption. The sample was placed 2 cm away from the light source. The reaction mixture was continuously stirred at 250 rpm during the experiment. Samples were collected at different time points and examined using a Cary 50 UV-Vis spectrophotometer to determine the reduction of  $\text{Cr}^{6+}$  to  $\text{Cr}^{3+}$  by measuring the absorbance changes between 300 and 500 nm (characteristic absorption maxima  $\lambda_{\text{max}} = 352 \text{ nm}$ ). For reusability experiments, the  $\text{CuTCNQF}_4$  catalyst grown on Cu foil was removed from the reaction vessel after completion of the reaction, followed by washing the catalyst surface three times with deionized water, before being used for the subsequent cycle for up to 10 cycles.

## Results and Discussion

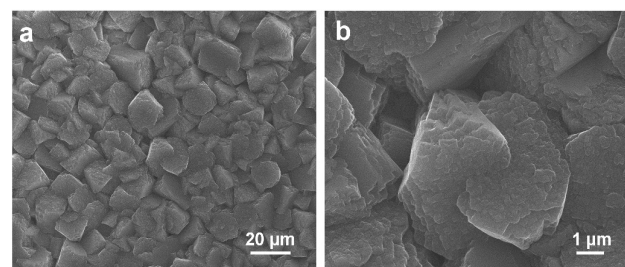


Fig. 1 SEM image of pristine CuTCNQF<sub>4</sub> crystals synthesised on Cu foil in acetonitrile.

The synthesis of TCNQF<sub>4</sub> derivative [2] from precursor tetrafluoro-1,4-benzoquinone [1] was performed using a previously described protocol (Scheme S1).<sup>37</sup> Briefly, the quinones present in [1] were reacted with malononitrile to form TCNQF<sub>4</sub> [2], which was purified by precipitation and recrystallization from methanol and acetonitrile, and obtained as a crystalline high-melting solid with 87% yield. The structure of TCNQF<sub>4</sub> derivative [2] was confirmed by mass spectroscopy, elemental analysis (see Materials and Methods) and FTIR.

The fabrication of CuTCNQF<sub>4</sub> on copper foil proceeds through a one electron transfer reaction between copper metal and TCNQF<sub>4</sub> in acetonitrile solution. During this process, a simple reduction of TCNQF<sub>4</sub><sup>0</sup> dissolved in acetonitrile by Cu<sup>0</sup> as electron donor results in the formation of Cu<sup>+</sup>TCNQF<sub>4</sub><sup>-</sup> crystals on the surface of Cu foil. This is similar to that observed in the case of CuTCNQ crystal formed on a copper foil.<sup>5-9, 15</sup> Illustrated in Fig. 1 are the SEM images of CuTCNQF<sub>4</sub> crystals synthesised on both sides of a copper foil through a spontaneous crystallisation process in acetonitrile. These crystals show cuboidal morphology with the edge length of approximately 3 μm. Reaction time was optimised to obtain a uniform coating of the crystals throughout the surface of the copper foil, wherein reaction time of 3 h yielded complete coverage of copper foil with CuTCNQF<sub>4</sub> crystals, while using 2 mM TCNQF<sub>4</sub> at 45 °C.

EDX spectrum (Fig. 2a) obtained from CuTCNQF<sub>4</sub> crystals show characteristic C Kα, N Kα, F Kα energy lines at 0.277, 0.392 and 0.677 keV, respectively, which are attributed to TCNQF<sub>4</sub> in the sample. Additional characteristic energy line for Cu Lα at 0.930 keV suggests the formation of CuTCNQF<sub>4</sub> crystals. The calculated atomic ratios of C:F:N:Cu from EDX measurements were 12:4:4:1, which is consistent with the expected stoichiometric ratio of the CuTCNQF<sub>4</sub> elemental composition.<sup>17</sup> Raman spectroscopy is an ideal technique to distinguish between neutral (TCNQF<sub>4</sub><sup>0</sup>) and reduced TCNQF<sub>4</sub> (TCNQF<sub>4</sub><sup>-</sup>). Illustrated in Fig. 2b is background-corrected Raman spectra<sup>38</sup> obtained from pristine TCNQF<sub>4</sub> powder and CuTCNQF<sub>4</sub>. The pristine TCNQF<sub>4</sub> powder shows characteristic signatures at 2226 cm<sup>-1</sup> (C≡N), 1665 cm<sup>-1</sup> (C=C ring) and 1460 cm<sup>-1</sup> (C-CN stretching), confirming its neutral state (TCNQF<sub>4</sub><sup>0</sup>).<sup>6, 15, 17</sup> Following the reaction of TCNQF<sub>4</sub> with Cu, the C≡N (2200 cm<sup>-1</sup>) and C=C (1640 cm<sup>-1</sup>) bands shift to lower wavenumbers, confirming that the neutral TCNQF<sub>4</sub> has converted to its reduced state (TCNQF<sub>4</sub><sup>-</sup>), signifying CuTCNQF<sub>4</sub> formation.<sup>6, 15, 17</sup> Further, an important signature suggesting the formation of TCNQF<sub>4</sub><sup>-</sup> radical is the splitting of the C≡N stretch, which

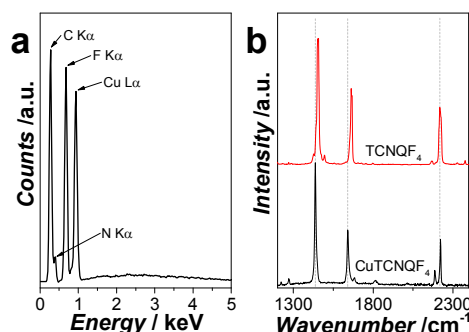
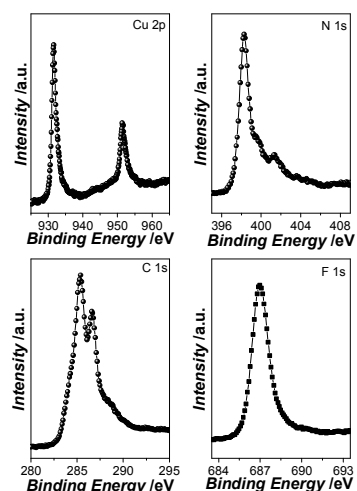


Fig. 2 a) EDX spectra of CuTCNQF<sub>4</sub> crystals; b) Raman spectra of pristine TCNQF<sub>4</sub> and CuTCNQF<sub>4</sub> crystals.

indicates that the coordination between Cu<sup>+</sup> and TCNQF<sub>4</sub><sup>-</sup> is through CN group.<sup>6, 15, 17</sup> Additional peak shifts in the C-CN, C-C, and C-F stretching provides evidence on the presence of TCNQF<sub>4</sub><sup>-</sup> radical.<sup>6, 15, 17</sup> The formation of CuTCNQF<sub>4</sub> was also confirmed through the presence of characteristic FTIR bands at 2215, 1497 and 1223 cm<sup>-1</sup> (Fig. S1, ESI).<sup>6, 15</sup> The presence of 1497 cm<sup>-1</sup> peak corresponding to the C=C ring stretch, which is found at higher energy for TCNQF<sub>4</sub>, clearly suggests that the TCNQF<sub>4</sub> units in CuTCNQF<sub>4</sub> is present in its reduced form. In addition, the shift in the C-F out of plane bending at 1206 cm<sup>-1</sup> also confirms the formation of CuTCNQF<sub>4</sub>.<sup>15, 39</sup>

Further evidence for the formation of CuTCNQF<sub>4</sub> is evident from XPS measurements, wherein Cu 2p core level XPS spectrum shows two characteristic 2p<sub>3/2</sub> and 2p<sub>1/2</sub> splitting components at 931.6 eV and 951.5 eV, respectively (Fig. 3). The absence of signatures corresponding to shake-up satellites suggests that the Cu species in CuTCNQF<sub>4</sub> is present as Cu<sup>+</sup>, which corroborates well with values reported in the literature.<sup>17, 40, 41</sup> The N 1s core level XPS spectrum provides information about the involvement of CN functional group during the formation of CuTCNQF<sub>4</sub>.<sup>5, 7-9</sup> In comparison to pristine TCNQF<sub>4</sub> (Fig. S2, ESI), the N 1s core level spectrum of CuTCNQF<sub>4</sub> shifts to a lower binding energy (BE) of 398.2 eV with an additional shake-up peak at higher BE of 401.6 eV.<sup>18</sup> This additional higher BE feature is due to the π-π conjugated system, a feature commonly observed in TCNQ and its derivatives.<sup>42</sup> The BEs of C 1s and F 1s core level XPS spectra are also consistent with the reported values of TCNQF<sub>4</sub>.<sup>6, 15, 17</sup>

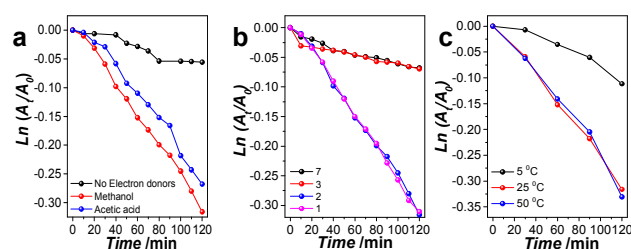
It is well-known that there is a considerable activation energy barrier during the reduction of Cr<sup>6+</sup>, even when a large driving potential is available during the reaction between Cr<sup>6+</sup> and an electron donor. For instance, the reduction potentials (versus the standard hydrogen electrode) of the two-half equations i.e. Cr<sup>6+</sup> reduction and methanol oxidation are 1.36 V and 0.02 V, respectively (E<sup>0</sup> values).<sup>43</sup> Therefore, even with a large driving potential of 1.34 V, the reaction does not proceed spontaneously and requires an efficient catalyst and/or high temperatures. This is probably the reason why non-fluorinated CuTCNQ could not catalyse Cr<sup>6+</sup> reduction, even at high temperatures.<sup>9</sup> However, when CuTCNQ was converted to CuTCNQ-metal hybrids, although Cr<sup>6+</sup> could be reduced at ambient temperature, elevated temperatures assisted in Cr<sup>6+</sup> reduction.<sup>9</sup> Given that the fluorinated analogues of TCNQ have



**Fig. 3** XPS spectra showing Cu 2p, N 1s, C 1s and F 1s core levels obtained from CuTCNQ<sub>4</sub> crystals grown on a copper foil.

superior electron accepting properties over TCNQ, in the current study, we assessed the performance of CuTCNQ<sub>4</sub> as a potential catalyst for the reduction of hexavalent chromium in aqueous solutions at room temperature. In a typical reaction, the catalyst was immersed in an aqueous solution containing Cr<sup>6+</sup> ions in the presence of acetic acid and methanol as electron donors, and held at a stable temperature of 25 °C. The UV-Vis spectra of the dichromate ions in the presence and absence of electron donors were measured as a function of time. It is apparent that while reaction proceeds only in the presence of electron donors (**Fig. 4a**) due to ligand-to-metal charge transfer of dichromate ions;<sup>9, 44</sup> it is very interesting that pristine CuTCNQ<sub>4</sub> could in fact catalyse Cr<sup>6+</sup> reduction even at the 25 °C. This is a significant advantage over non-fluorinated CuTCNQ, which remained inactive even at high temperatures for this particular reaction.<sup>9</sup> Assuming that the reaction follows a pseudo-first-order kinetic model (the reaction proceeds in the presence of excess donor concentration), plotting the  $\ln(A_t/A_0)$  versus time (where  $A_t$  is the absorbance at time  $t$  and  $A_0$  is the absorbance at time zero) allows determination of rate constants. The relative rate constants for the reduction of Cr<sup>6+</sup> at pH 2.0 in the presence of two electron donors, *viz.* methanol and acetic acid, were  $2.5 \times 10^{-3} \text{ min}^{-1}$  and  $2.0 \times 10^{-3} \text{ min}^{-1}$ , respectively (**Table S1, ESI**). This suggests that methanol has higher driving force over acetic acid in the presence of the catalyst and was therefore the choice of electron donor for subsequent studies. It is noteworthy that the reaction rates largely depend on the reaction conditions; therefore these rates are calculated for comparative purposes under similar reaction conditions.<sup>6, 9, 11</sup>

Other reaction conditions such as the pH and temperature may also have significant impact on the reaction rates. Hence, the catalytic conversion of Cr<sup>6+</sup> was also performed at different pH in the presence of methanol as an electron donor. **Fig. 4b** shows that at 25 °C, the reaction proceeds only under acidic pH conditions; such that while the reaction rates do not



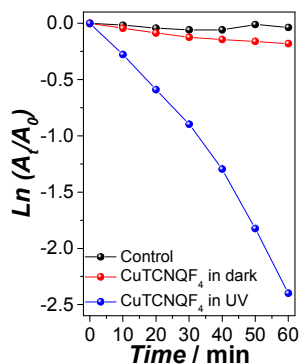
**Fig. 4** Plot of  $\ln(A_t/A_0)$  versus time for CuTCNQ<sub>4</sub> mediated reduction of Cr<sup>6+</sup> (a) in the presence of different electron donors at pH 2.0 and 25 °C; (b) at different pH in the presence of methanol at 25 °C and (c) at different temperatures in the presence of methanol and at pH 2.0.

improve at pH lower than 2.0, they dramatically drop at and above pH 3.0. Therefore, subsequent experiments were carried out at pH 2 in the presence of methanol. The role of pH in improving the reduction reaction is due to either increase in oxidising ability of Cr<sup>6+</sup> and/or availability of more catalytically active sites through reduction in the amount of Cr(OH)<sub>3</sub> deposited on the catalyst surface.<sup>11, 27</sup> **Fig. 4c** shows the influence of temperature on the catalytic reduction of Cr<sup>6+</sup>, wherein while CuTCNQ<sub>4</sub> was catalytically active at ambient temperature, an increase in temperature from 25 to 50 °C did not significantly improve the reaction rates. This suggests that outstanding electron transport properties of CuTCNQ<sub>4</sub> may allow it to act as an efficient catalyst even for room-temperature reduction of hexavalent chromium.

The photocatalytic activity of traditional inorganic semiconductors such as TiO<sub>2</sub>, SnO<sub>2</sub> and ZnO are well-known.<sup>45, 46</sup> Given that CuTCNQ<sub>4</sub> also possess semiconducting properties, we explored the possibility of improving the rate of Cr<sup>6+</sup> reduction through photo-excitation. The absorption characteristics of CuTCNQ<sub>4</sub> and pristine TCNQ<sub>4</sub> suggested that while similar to traditional oxides,<sup>45</sup> these molecules primarily absorbs in the UV region, they also have absorbance across the visible region of the electromagnetic spectrum (**Fig. S3, ESI**).

Illustrated in **Fig. 5** is the effect of UV light irradiation on the reduction of Cr<sup>6+</sup>. To assess the influence of UV light irradiation, the experiments were first carried out in dark in the presence and absence of the catalyst. Under dark conditions, although the reaction proceeds faster in the presence of the catalyst, the reaction rate is not remarkably improved. In contrast, when the same reaction is carried out during UV light irradiation, CuTCNQ<sub>4</sub>-mediated reduction of Cr<sup>6+</sup> becomes significantly faster, such that the reaction rate is increased over an order of magnitude from  $3.4 \times 10^{-3} \text{ min}^{-1}$  to  $3.6 \times 10^{-2} \text{ min}^{-1}$  in the presence of CuTCNQ<sub>4</sub> (Reaction rates for all reactions are outlined in **Table S1, ESI**). Notably, although the non-fluorinated analogue (CuTCNQ) was previously found unable to promote the reduction of Cr<sup>6+</sup>,<sup>9</sup> it is very interesting that the use of a fluorinated analogue (CuTCNQ<sub>4</sub>) in the current case could not only actively promote the catalytic reduction of Cr<sup>6+</sup> even at room temperature, but the reaction rates could also be significantly enhanced by UV-light irradiation.

The reusability of the CuTCNQ<sub>4</sub> catalyst was also evaluated by employing the same catalyst for 10 consecutive



**Fig. 5** Plot of  $\ln(A_t/A_0)$  versus time for CuTCNQF<sub>4</sub>-mediated photo-reduction of Cr<sup>6+</sup> at pH 2 and 25 °C in the presence of methanol as electron donor. catalytic reactions, wherein the surface of the catalyst was washed several times with deionised water in between two reactions. The efficiency of Cr<sup>6+</sup> reduction was maintained for at least 10 cycles with no loss of efficiency (Fig. S4, ESI). In addition, the stability of the catalyst was also ascertained using SEM and Raman spectroscopy. No structural change was observed to the catalyst surface as seen from the SEM images (Fig. S5, ESI). The Raman spectra obtained before and after the catalytic reaction showed no change in the chemical composition (Fig. S6, ESI) further demonstrating the high stability of CuTCNQF<sub>4</sub>.

## Conclusions

In summary, we have shown the fabrication of nanostructured CuTCNQF<sub>4</sub> organic charge transfer complex on a copper foil by employing a facile redox reaction in acetonitrile. While non-fluorinated CuTCNQ is known to be inactive towards reduction of hexavalent chromium; for the first time, its fluorinated derivative CuTCNQF<sub>4</sub> is demonstrated to catalytically promote this reaction in aqueous solutions at room temperature. Importantly, under UV photo-excitation conditions, CuTCNQF<sub>4</sub> could enhance the rate of this reaction by an order of magnitude over that in dark. Given the ability of CuTCNQF<sub>4</sub> in promoting catalytic reactions that are not successfully catalysed by its non-fluorinated analogues, the outcomes presented here open up a new avenue for employing fluorinated MTCNQ type organic semiconductors for reductive photocatalysis applications.

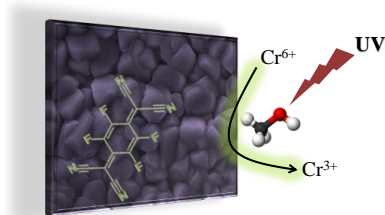
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High toxicity of hexavalent chromium warrants development of efficient catalysts that could reduce toxic chromium into a relatively non-toxic trivalent chromium species. Pristine charge transfer complexes of MTCNQ family (M = Cu or Ag; TCNQ = 7,7,8,8-tetracyanoquinodimethane) have previously failed to catalyse reduction of Cr<sup>6+</sup> to Cr<sup>3+</sup>. We demonstrate that due to the outstanding electron transfer properties of one of the fluorinated derivatives of MTCNQ, i.e., 7,7,8,8-tetracyano-2,3,5,6-tetrafluoroquinodimethane (CuTCNQF<sub>4</sub>), it is able to catalyse the reduction of hexavalent chromium in aqueous solution at room temperature. We further demonstrate that the semiconducting nature of these organic charge transfer complexes allows CuTCNQF<sub>4</sub> to act as an outstanding material for reusable reductive photo-removal of hexavalent chromium under UV photo-excitation conditions. Such materials are likely to play an important role in next-generation photoactive electron transfer reactions.