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Journal:	<i>ChemComm</i>
Manuscript ID	CC-COM-08-2019-006163.R1
Article Type:	Communication

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## COMMUNICATION

## Correlation at Two-Dimensional Charge-Transfer FeSe Interface

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

DOI: 10.1039/x0xx00000x

**The charge transfer and spin coupling effects are explored at the interface of two-dimensional (2D) superconducting FeSe nanosheets and molecular photochromic potassium-7,7,8,8-tetracyanoquinodimethane (KTCNQ). Light-induced conductivity in 2D FeSe nanosheets is enhanced by the electron doping from KTCNQ by the destabilized spin-Peierls phase through their interface. Furthermore, the spin coupling at the interface of FeSe and KTCNQ shifts the dimerization transition temperature of KTCNQ. Our results suggest 2D exfoliated FeSe nanosheet as a versatile strongly correlated platform for the study of interfacial electron doping and spin coupling.**

Two-dimensional (2D) superconducting FeSe is crystallized in tetragonal layered structure with the space group of P4/nmm by stacking the edge-shared tetrahedral FeSe<sub>4</sub> layers. The bulk FeSe compound has a superconducting transition temperature  $T_c$  of 8 K,<sup>[1]</sup> which can be largely improved by pressure,<sup>[2]</sup> chemical doping,<sup>[3]</sup> intercalation<sup>[4,5]</sup> and electro-gating methods.<sup>[6]</sup> The electron interactions in 2D FeSe layers are believed to play an important role in the strongly correlated phenomena discovered in Fe-based superconductors, such as spin fluctuation,<sup>[7]</sup> nematic order,<sup>[8,9]</sup> interfacial effect,<sup>[10]</sup> spin density wave<sup>[11]</sup> and orbital-selective correlation.<sup>[12]</sup> Despite the intensive experimental and theoretical studies, the mechanism of electron doping and spin coupling effects in 2D FeSe sheets is still lacking.<sup>[13]</sup> In this context, molecular charge-transfer complexes (MCTs) provide an efficient method to tune the electron concentration in FeSe layers. To validate the electron-doping and spin coupling between FeSe layer and MCTs, it is crucial to have direct and clear evidence for the charge-transfer interaction across the interface, particularly light-responsive MCTs.

To investigate the strongly correlated phenomena through the interfacial effect between 2D FeSe and light-responsive MCT systems for the coupling interactions of charge, spin, orbital and lattice, we select photochromic potassium-7,7,8,8-tetracyanoquinodimethane<sup>[14]</sup> (KTCNQ) as a prototypical MCT model system which is a classical quasi-one-dimensional (1D) spin-Peierls system,<sup>[15]</sup> presenting 1D antiferromagnetic spin order and anion dimerization driven by spin-lattice (*s-l*) interaction. Therefore, spin coupling and electron doping could appear at the interface between 2D FeSe layer and KTCNQ. Generally, KTCNQ is a Mott insulator over the broad temperature range above and below the dimerization temperature  $T_d$  of 395 K.<sup>[16]</sup> At the critical temperature  $T_d$ , two adjacent TCNQ- radicals dimerize in the chains and form a spin-singlet state that are caused by the *s-l* coupling. A sharp decrease of magnetic susceptibility occurs as the temperature below  $T_d$  at which a spin gap forms. Here, we report the photo-induced charge transfer and spin coupling at the interface between KTCNQ and 2D exfoliated FeSe layer. The conductivity in 2D FeSe nanosheets can be significantly enhanced by electron doping from KTCNQ under light illumination, while the dimerization temperature in KTCNQ is improved from 389 K to 395 K through the interaction with 2D FeSe nanosheets.

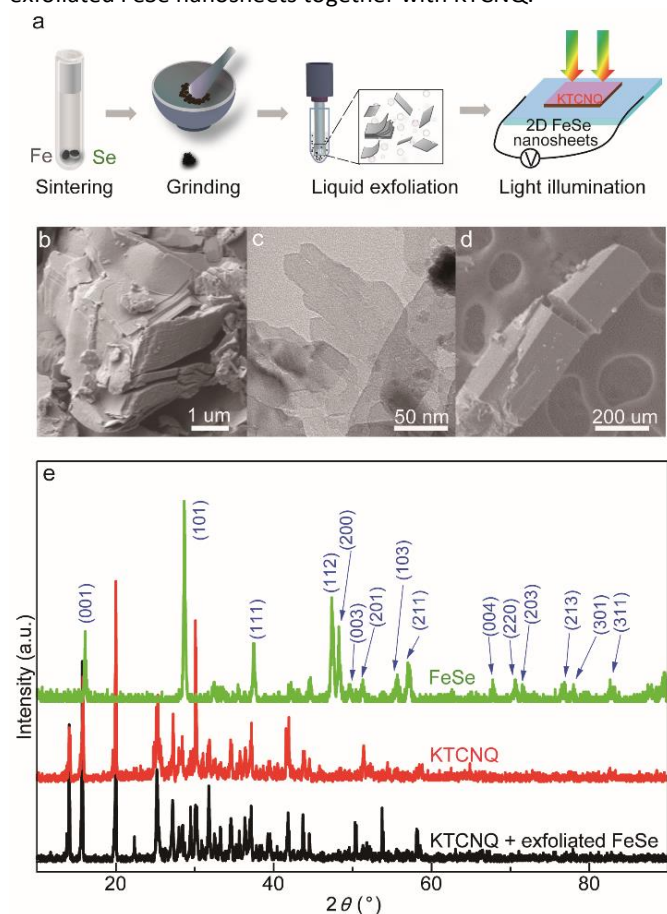
Superconducting FeSe bulk is synthesized by solid state sintering at a relatively lower temperature than that of the previous reports.<sup>[1,17]</sup> As shown in Fig. 1a, the FeSe solids are grinded and loaded into the acetonitrile solvent for liquid exfoliation to obtain 2D FeSe nanosheets. The interfacial FeSe-KTCNQ heterostructure is prepared by depositing a KTCNQ layer on 2D FeSe nanosheets. The synthesized FeSe solid appears in a two-dimensional layered structure as shown in the scanning electron microscopy (SEM) image (Fig. 1b). The 2D layered FeSe sheets stack together through Van der Waals force. These structural features facilitate the liquid exfoliation to obtain 2D FeSe nanosheets, where liquid exfoliation can efficiently produce large-scale FeSe nanosheets from its bulk layered solid.<sup>[18]</sup> Submicron-scale 2D FeSe nanosheets shown in the transmission electron microscopy image (TEM, Fig. 1c) are

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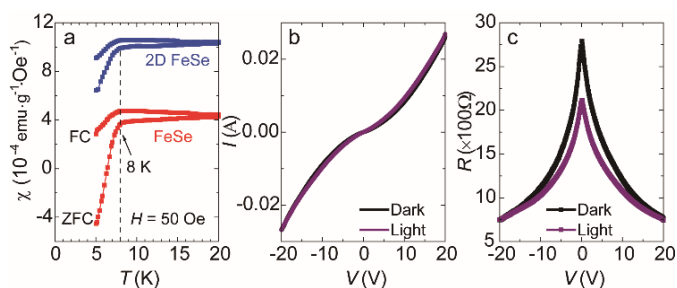
Electronic Supplementary Information (ESI) available: [details of any supplementary information available should be included here]. See DOI: 10.1039/x0xx00000x

exfoliated from FeSe in the acetonitrile solvent. A large specific surface area of 2D FeSe nanosheets facilitates the interface coupling with the molecular photochromic KTCNQ layer (Fig. 1d). X-ray diffraction (XRD) (Fig. 1e) confirms the existence of  $\beta$ -FeSe phase, while the KTCNQ phase is resolved in XRD of the exfoliated FeSe nanosheets together with KTCNQ.



**Figure 1.** (a) Schematic diagrams of the processes of FeSe powder synthesis and liquid exfoliation of 2D FeSe nanosheets; (b) SEM image of FeSe powder; (c) the TEM image of exfoliated 2D FeSe nanosheets; (d) SEM image of KTCNQ crystal; (e) X-ray diffraction patterns of FeSe powder, KTCNQ and KTCNQ mixed with FeSe nanosheets with a molar ratio of  $n(\text{FeSe}) : n(\text{KTCNQ}) = 0.0096$ .

The 2D exfoliated FeSe nanosheets maintain its superconducting diamagnetism feature as shown in the bulk solid. Figure 2a shows the superconducting transition temperature of 8 K in pristine bulk FeSe powder and the exfoliated 2D FeSe nanosheets. The zero-field-cooling (ZFC) and field-cooling (FC) susceptibility curves are measured for pristine and 2D exfoliated FeSe from 20 K to 5 K under an external magnetic field  $H = 50$  Oe. For 2D exfoliated FeSe nanosheets, a strong positive magnetic background leads to a non-negative diamagnetic signal at 5 K. In addition, the current versus voltage ( $I$ - $V$ ) curves of 2D exfoliated FeSe nanosheets under dark and light illumination suggest its semiconducting and weak photoresponsive behavior at room temperature (Fig. 2b). Derived from the  $I$ - $V$  curves, the resistance versus voltage curves (shown in Fig. 2c) of 2D FeSe nanosheets show the resistivity at 1 V decreases by 20.8% from dark to illumination.

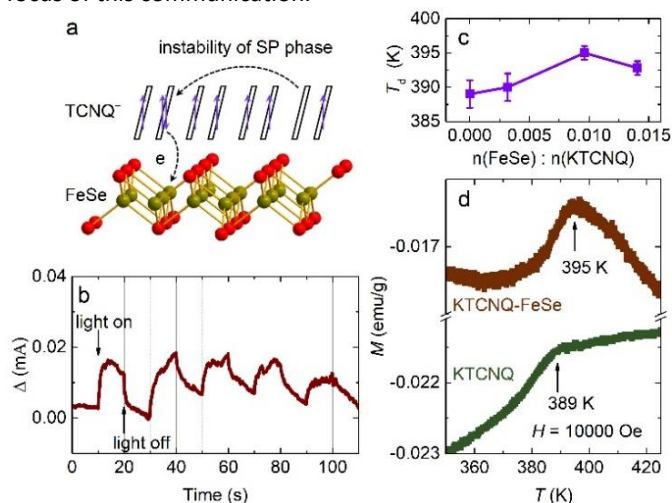


**Figure 2.** Magnetic properties of FeSe and  $I$ - $V$  curves of exfoliated FeSe nanosheets under dark and light illumination. (a) Diamagnetic transition of FeSe superconductor and exfoliated FeSe nanosheets show the same superconducting transition temperature of 8 K under an external magnetic field of 50 Oe. (b) Current versus voltage curves of exfoliated FeSe nanosheets show few differences under dark and light illumination. (c) Resistance versus voltage curves of exfoliated FeSe nanosheets derived from (b) show the decrease of resistance under light illumination.

The light-induced charge transfer from photochromic KTCNQ and the subsequent electron doping into FeSe nanosheets can result in the coupling behavior at the interface between FeSe layer and KTCNQ. Figure 3a illustrates the charge transfer and electron doping between FeSe layer and KTCNQ under light illumination. The light-induced current density in 2D FeSe layer with KTCNQ deposition is largely improved compared to that of the FeSe only structures. The charge transfer enhanced current density is plotted in Fig. 3b, which is the difference in current densities of FeSe nanosheets before and after KTCNQ coating. The current density enhancement in FeSe nanosheets can be explained by charge transfer at the interface between KTCNQ and 2D FeSe layer (Fig. 3a) under light illumination, and photoinduced destabilization of spin-Peierls (SP) phase in KTCNQ.<sup>[19]</sup> Under light illumination, electron transferred from K to TCNQ moves to the adjacent TCNQ<sup>-</sup> site, forming the localized electron and hole carriers that destabilize the SP phase. The melting of dimerization is basically stimulated by near-infrared photons with energy around 1 eV,<sup>[19]</sup> leading to charge transfer,  $(\text{TCNQ}^-, \text{TCNQ}^-) \rightarrow (\text{TCNQ}^0, \text{TCNQ}^{2-})$ . As an active radical, TCNQ<sup>2-</sup> can transfer one electron through the interface to 2D FeSe nanosheets, leading to the enhanced conductivity in FeSe layer. The charge transfer is also indirectly verified by the contrast experiment where KTCNQ is physically put on the top of FeSe nanosheets without forming an interface (Fig. S3). Due to the interfacial charge transfer of KTCNQ-FeSe under light illumination, the photoinduced current density in FeSe layer indeed follows the on-off cycle of light illumination as shown in Fig. 3b. Under the dark condition, TCNQ<sup>2-</sup> recovers back to TCNQ<sup>-</sup> by extracting one electron from 2D FeSe layer to reduce the carrier concentration in FeSe layer, while the TCNQ stacks return back to SP phase. The possibility of TCNQ<sup>2-</sup> radical donating one electron back to K<sup>+</sup> for the formation of a neutral potassium can be ruled out due to the stability and recyclability of the FeSe-KTCNQ device.

Another strongly correlated coupling phenomenon at the FeSe-KTCNQ interface is the tunable structural transition in KTCNQ through the interfacial interaction with 2D FeSe nanosheets. The temperature dependent susceptibility of KTCNQ and FeSe-KTCNQ show the structural transition temperature  $T_d$  increases from 389 K to 395 K by the incorporation of 2D FeSe nanosheets

(Fig. 3d). In comparison, magnetic susceptibility of KTCNQ decreases linearly from high temperature to structural transition temperature  $T_d$  that is manifested from the ZFC and FC curves (Fig. S5). As increasing the ratio of  $n(\text{FeSe}):n(\text{KTCNQ})$ , magnetic susceptibility is increased, as well as the structural transition temperature  $T_d$ , as shown in Fig. 3d and S7. The KTCNQ is a spin-Peierls system in which  $s$ - $I$  interaction determines the stability of SP phase by modulating the antiferromagnetic exchange coupling strength  $J$ . Thus, when temperature decreases to the structural transition temperature  $T_d$ , two adjacent TCNQ are dimerized to form a spin-singlet state with opposite spin orientations and a distorted lattice. The dimerization in KTCNQ can be controlled by the spin-spin interaction between KTCNQ and 2D FeSe nanosheets, due to the spin ordering contribution of FeSe nanosheets. Before the structural transition in KTCNQ, FeSe nanosheets could induce a ferromagnetic ordering at the interface of FeSe-KTCNQ as shown in Fig. S6 that could drive the spins of TNCQ into a singlet state, forming a dimerized phase. The spin coupling is also confirmed by the contrast experiment in which KTCNQ and FeSe powder are mixed mechanically, showing no change of  $T_d$  (Fig. S8). Therefore, the improved dimerization temperature  $T_d$  of KTCNQ could be understood by an interfacial spin coupling that enhances the spin-lattice interaction in KTCNQ due to the formation of KTCNQ-FeSe interface. In addition, the quantum size effects of FeSe layers (numbers and surface area) on prominent properties of FeSe-KTCNQ interface are significant topics and worth further investigation which lie beyond the focus of this communication.



**Figure 3.** (a) Schematic process of charge transfer at the interface of FeSe-KTCNQ. (b) Light-induced current enhancement in FeSe nanosheets layer. The calculation of  $\Delta$  is described in the supporting information and Fig. S2 (c) The dimerization temperature  $T_d$  is tuned by the quantities of FeSe nanosheets. (d) The high temperature magnetic susceptibility of KTCNQ and KTCNQ mixed with FeSe nanosheets of  $n(\text{FeSe}) : n(\text{KTCNQ}) = 0.0096$  show the varied  $T_d$  from 389 K to 395 K.

In conclusion, we design and synthesize 2D exfoliated superconducting FeSe layer which maintains the characteristics of its bulk counterpart. Molecular charge transfer complex KTCNQ can be incorporated into 2D FeSe layer for the studies of light induced charge transfer and electron doping. We demonstrate KTCNQ is a charge-transfer medium which injects

charge into 2D FeSe nanosheets through the interface under light illumination. The photoconductivity in 2D FeSe layer can be enhanced through the charge transfer from KTCNQ. The dimerization temperature  $T_d$  of KTCNQ can also be improved by the formation of FeSe-KTCNQ interface, where the spin coupling at the interface enhances the spin-lattice interaction in KTCNQ to suggest spin-Peierls mechanism of high-temperature structural transition in KTCNQ. Our results show 2D exfoliated FeSe nanosheets as a versatile strongly correlated platform to open up the electron doping studies in iron-based superconductors.

## Conflicts of interest

The authors declare no competing financial interests.

## Acknowledgment

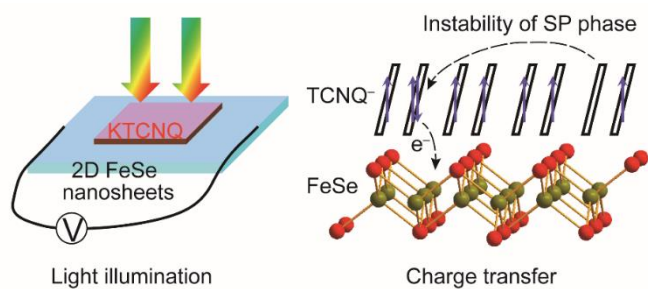
The U.S. Department of Energy, Office of Basic Energy Sciences, Division of Materials Sciences and Engineering supports S.R. under Award DE-SC0018631 (Organic conductors). Financial support was provided by the U.S. Army Research Office supports S. R. under Award W911NF-18-2-0202 (Materials-by-Design and Molecular Assembly).

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The 2D FeSe hybrid interface exhibits charge transfer triggered strongly correlated phenomena under light illumination.