Supporting Information for

# Tunable Photoluminescence of Monolayer MoS<sub>2</sub> via Chemical Doping

Shinichiro Mouri<sup>1</sup>, Yuhei Miyauchi<sup>1,2</sup>, and Kazunari Matsuda<sup>1</sup>

<sup>1</sup>Institute of Advanced Energy, Kyoto University, Uji, Kyoto 611-0011, Japan

<sup>2</sup>Japan Science and Technology Agency, PRESTO, 4-1-8 Honcho Kawaguchi, Saitama

332-0012, Japan

# 1. PL spectra of F<sub>4</sub>TCNQ-doped 2L-MoS<sub>2</sub>



Fig. S1 PL spectra of 2L-MoS<sub>2</sub> with and without F<sub>4</sub>TCNQ doping

We observed the PL spectrum of  $F_4TCNQ$  doped 2L-MoS<sub>2</sub> as shown in the Fig. S1. The PL intensity enhancement and blue shift of PL peak of A exciton, which is similar to those observed for 1L-MoS<sub>2</sub>, are observed. This result indicates that the extraction of electrons also occurred in the 2L-MoS<sub>2</sub> by  $F_4TCNQ$  doping.

#### 2. Series of data of decomposed results of PL spectra



Fig. S2 Series of decomposed PL spectra of F<sub>4</sub>TCNQ-doped 1L-MoS<sub>2</sub>

Figure S2 shows the decomposed PL spectra of  $F_4TCNQ$ -doped 1L-MoS<sub>2</sub> at each doping step. All spectra are normalized by the peak height. The PL spectra can be decomposed into three components: A exciton PL (X; ~1.88 eV; red line), A trion PL (X<sup>-</sup>; ~1.84 eV; blue line), and B exciton PL (B; 2.05 eV; green line), as described in the main text. Although the shape of the PL peak differs in each 1L-MoS<sub>2</sub>, reflecting the doped electron density, all PL spectra are well reproduced (orange lines) by the sum of three peak components.

### 3. PL spectral change of 1L-MoS<sub>2</sub> with *p*-type (TCNQ) and *n*-type (NADH) dopants

Figure S3 shows the decomposed PL spectra of  $1L-MoS_2$  before and after chemical doping with *p*-type (TCNQ) and *n*-type dopants (NADH). These PL spectra also can be decomposed into three components: A exciton PL (X; ~1.88 eV; red line), A trion PL (X<sup>-</sup>;

~1.84 eV; blue line), and B exciton PL (B; 2.05 eV; green line). The shape of the PL spectra of the as-prepared 1L-MoS<sub>2</sub> differs depending on the sample's initially doped electron density. We prepared less-electron-doped 1L-MoS<sub>2</sub> for the NADH doping experiment to confirm the electron injection effect.



Fig. S3 PL spectra of 1L-MoS<sub>2</sub> before and after chemical doping with p-type (TCNQ) and n-type dopants (NADH).

# 4. PLE spectra of 1L-MoS<sub>2</sub>

We measured excitation photon energy dependence of PL spectra of 1L-MoS<sub>2</sub> as shown in Fig. S4 (a). The spectral shape does not change with changing excitation energy. The peak A can be decomposed into the exciton (X; ~1.88 eV; red line) peak and the negative trion ( $X^-$ ; ~1.84 eV; blue line) peak. The PL excitation (PLE) spectra of 1L-MoS<sub>2</sub> of the exciton (X) and trion ( $X^-$ ) peak are obtained in the range between 1.9 and 2.4 eV as shown in Fig. S4 (b). The absorption spectrum of 1L-MoS<sub>2</sub> taken from Ref. S1 is also plotted for comparison. The PLE spectrum of trion shows the resonant excitation peak of B exciton observed in absorption spectrum which suggests that the trions are formed via excitons.



Fig. S4 (a) PL spectra of 1L-MoS<sub>2</sub> measured by various excitation photon energy. The very small peak at 1.92 eV in the bottom spectrum comes from the Raman peak. (b) The PLE spectra monitored at the excitons (X) and trions ( $X^-$ ) peak of 1L-MoS<sub>2</sub>. The absorption spectra of 1L-MoS<sub>2</sub> (black circles) is taken from the previous study by Mak et al.<sup>S1</sup>.

# 5. Analysis of PL intensity of excitons and trions in 1L-MoS<sub>2</sub> with chemical doping within the framework of a three-level model

The rate equations for the population of exciton  $N_x$  and trion  $N_x^-$  can be expressed as

$$\frac{dN_{\rm x}}{dt} = G - \{\Gamma_{\rm ex} + k_{\rm tr}(n)\}N_{\rm x}, \qquad (S1)$$

$$\frac{dN_{\mathrm{x}^{-}}}{dt} = k_{\mathrm{w}}(n)N_{\mathrm{x}} - \Gamma_{\mathrm{w}}N_{\mathrm{x}^{-}}, \qquad (S2)$$

where *n* is the number of doping steps,  $k_{tr}(n)$  is the formation rate of the trion from the exciton, and *G* is the optical generation rate of excitons. The populations of excitons and trions derived from the steady-state solutions of these equations are expressed as

$$N_{\rm x}(n) = \frac{G}{\Gamma_{\rm ex} + k_{\rm tr}(n)} , \qquad (S3)$$

$$N_{\rm x^{-}}(n) = \frac{k_{\rm w}(n)}{\Gamma_{\rm w}} \frac{G}{\Gamma_{\rm ex} + k_{\rm w}(n)},$$
 (S4)

where the decay rates of the exciton and trion are denoted as  $\Gamma'_{ex}$  and  $\Gamma_{tr}$ , respectively. The PL intensity of the exciton  $(I_x)$  and trion  $(I_x)$  can be expressed on the basis of the relationship where the PL intensity is proportional to the exciton (trion) populations as follows:

$$I_{\rm x}(n) = \frac{AG\gamma_{\rm ex}}{\Gamma_{\rm ex} + k_{\rm x}(n)},$$
(S5)

$$I_{x^{-}}(n) = \frac{k_{w}(n)}{\Gamma_{w}} \frac{AG\gamma_{w}}{\Gamma_{ex} + k_{w}(n)},$$
 (S6)

where  $\gamma_{ex}$  and  $\gamma_{tr}$  express the radiative decay rate of the exciton and trion, respectively. For simplicity, the change of these values with chemical doping is assumed to be small and neglected in the analysis. However, experimental determination of them is the important issue as a future work. With consideration of PL spectral shape, the PL spectra at 0 µg/ml (0.3 µg/ml) in our experiments correspond to those at applied gate voltage of 0 V (-70 V) in the FET gating experiments at room temperature.<sup>S2</sup> The absorption spectrum of exciton only slightly changes in this region. This suggests that the change of radiative decay rate in our experimental range is small. Therefore, we assume that the radiative decay rate of exciton is independent of carrier density in this region for simplicity. The coefficient *A* expresses the collection efficiency of luminescence. The parameters  $\Gamma'_{ex} = 0.002 \text{ ps}^{-1}$ ,  $\Gamma_{tr} =$  $0.02 \text{ ps}^{-1}$ , and  $k_{tr}(0) = 0.5 \text{ ps}^{-1}$  in this analysis were based on the previously reported values obtained from transient absorption measurements.<sup>S3</sup> The best-fit parameters of  $AG\gamma_{ex}$  and  $AG\gamma_{tr}$  to reproduce the experimental results shown in Fig. 2d are 10 and 1.5, respectively. In the condition studied here (i.e.,  $k_{tr} \gg \Gamma'_{ex}$ ), the PL intensity of the exciton ( $I_x$ ) and trion ( $I_x$ -) can be approximately expressed as

$$I_{\rm x}(n) \approx \frac{AG\gamma_{\rm ex}}{k_{\rm w}(n)},\tag{S7}$$

$$I_{\rm x}(n) \approx \frac{AG\gamma_{\rm w}}{\Gamma_{\rm w}},\tag{S8}$$

As shown in Fig. 2d, the experimental behavior of the exciton PL intensity  $I_x$  strongly depends on the extent of F<sub>4</sub>TCNQ doping, whereas the trion PL intensity  $I_x$ <sup>-</sup> is insensitive to the level F<sub>4</sub>TCNQ doping; these results can be explained by eqs. (S7) and (S8).

#### 6. Mass action model

The mass action law associated with the trions<sup>S4</sup> is used to evaluate the doped electron density in 1L-MoS<sub>2</sub>. In this scheme, the following relation is obtained:

$$\frac{N_{\rm x}n_{\rm el}}{N_{\rm x^{-}}} = \left(\frac{4m_{\rm x}m_{\rm e}}{\pi\hbar^2 m_{\rm x^{-}}}\right)k_{\rm B}T\exp\left(-\frac{E_{\rm b}}{k_{\rm B}T}\right) , \qquad (S9)$$

where *T* is the temperature,  $k_{\rm B}$  is the Boltzmann constant,  $E_{\rm b}$  is the trion binding energy (~20 meV),<sup>S2</sup> and  $m_{\rm e}$  (0.35 $m_0$ ) and  $m_{\rm h}$  (0.45 $m_0$ ) are the effective mass of electrons and holes,<sup>S5</sup> respectively, where  $m_0$  is the mass of a free electron. The effective masses of an exciton  $m_x$  and a trion  $m_x$ <sup>-</sup> can be calculated as  $0.8m_0$  and  $1.15m_0$ , respectively. Using these parameters, the trion PL intensity weight is expressed as

$$\frac{I_{\rm X^-}}{I_{\rm total}} = \frac{\frac{\gamma_{\rm tr}}{\gamma_{\rm ex}} \frac{N_{\rm X^-}}{N_{\rm X}}}{1 + \frac{\gamma_{\rm tr}}{\gamma_{\rm ex}} \frac{N_{\rm X^-}}{N_{\rm X}}} \approx \frac{4 \times 10^{-14} n_{\rm el}}{1 + 4 \times 10^{-14} n_{\rm el}} \,. \tag{S10}$$

The trion PL intensity weight calculated from eq. (S10) is shown in the inset of Fig. 4b.

## References

S1. Mak, K. F.; Lee, C.; Hone, J.; Shan, J.; Heinz, T. F., *Phys. Rev. Lett.* **2010**, *105* (13), 136805(1)-136805(4).

S2. Mak, K. F.; He, K. L.; Lee, C.; Lee, G. H.; Hone, J.; Heinz, T. F.; Shan, J., *Nat. Mater.* **2013**, *12* (3), 207-211.

S3. Shi, H.; Yan, R.; Bertolazzi, S.; Brivio, J.; Gao, B.; Kis, A.; Jena, D.; Xing, H. G.; Huang, L., *ACS Nano* **2013**, *7* (2), 1072-1080.

S4. Ross, J. S.; Wu, S.; Yu, H.; Ghimire, N. J.; Jones, A. M.; Aivazian, G.; Yan, J.;
Mandrus, D. G.; Xiao, D.; Yao, W.; Xu, X., *Nat. Commun.* 2013, *4*, 1474(1)-1474(6).

S5. Cheiwchanchamnangij, T.; Lambrecht, W. R. L., *Phys. Rev. B* 2012, *85* (20), 205302(1)-205302(4).