Electrical control of near-field energy transfer between quantum dots and 2D semiconductors

Supporting Information

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S1. Supplementary discussion: FRET between 0D and a 2D system

In general, the rate of Forster Resonant Energy Transfer ($k_{\text{FRET}}$) between two quantum dots follows from the Fermi’s golden rule and is well-known (Reference 1 of the main manuscript):

$$k_{\text{FRET}(0D-0D)} \sim |\vec{E}|^2 \int_0^\infty \varepsilon_A(\lambda) f(\lambda) \lambda^4 d\lambda.$$  

Here $|\vec{E}|^2$ is the square of electric field created by a QD dipole at the position of the other QD, $f(\lambda)$ is the normalized emission spectrum of the donor QD as a function of wavelength $\lambda$, and $\varepsilon_A(\lambda)$ is the acceptor molar extinction coefficient. Since dipole field decays with distance as $r^{-3}$, $|\vec{E}|^2$ is proportional to $r^{-6}$. Therefore, $k_{\text{FRET}(0D-0D)}$ has the same distance dependence.

For the case of FRET between a 0D and a 2D system, we can formally split a 2D material into a 2D array of point-like absorbers and then integrate $k_{\text{FRET}(0D-0D)}$ over 2D material area. If the 2D material is located in oXY plane and a QD is elevated above that plane by distance $d$, the distance $r$ between QD and the point on the plane can be written as $r = \sqrt{d^2 + x^2 + y^2}$. Then integration over area yields:

$$k_{\text{FRET}(0D-2D)} \sim \int_{\text{Area}} d(\text{Area}) k_{\text{FRET}(0D-0D)} \sim \int_{\text{Area}} \frac{\int_0^\infty \varepsilon_A(\lambda) f(\lambda) \lambda^4 d\lambda}{\sqrt{d^2 + x^2 + y^2}}.$$  

Replacing absorptivity $\varepsilon_A(\lambda)$ by 2D absorption coefficient $\alpha(\lambda)$ and performing simple integration over area we obtain the expression used in the main text:

$$k_{\text{FRET}} \sim \frac{1}{d^4} \int_0^\infty \alpha(\lambda) f(\lambda) \lambda^4 d\lambda.$$  

S2. MoS$_2$ – Spacer – QD Device

Supplementary Figure S2 (a) Device schematic for MoS$_2$/spacer/QD device. (b) Raman spectra of MoS$_2$ before (black) and after (red) SiO$_2$ spacer deposition. (c) QD quenching factor vs. spacer thickness. Inset: PL spectra of QD and QD/MoS$_2$ for 15nm spacer device.
S3. hBN – QD Device

**Supplementary Figure S3** Photoluminescence spectra for QDs covered by hBN (blue and green curves) and QDs away from hBN (black and red curves). Inset: schematic of a hBN/QD device.

S4. Solid electrolyte characterization

**Supplementary Figure S4** (a) The efficiency of the solid electrolyte gating approach was estimated using a separate graphene Hall-bar device covered by the same electrolyte used in QD/MoS\(_2\) devices. Carrier density \(n\) vs. gate voltage \(V_g\) in that device was determined via Hall measurements. From a fit (red line) to the acquired \(n(V_g)\) data (black symbols), we extract an estimate for the capacitance of the polymer electrolyte, \(C=8.8fF/\mu m^2\). (b) PL modulation of a representative gated MoS\(_2\) device without the QD layer. Schematic of the device is shown in the inset.
S5. Confocal transmission microscopy

The absorption spectrum of MoS$_2$ could not be obtained directly from standard differential reflectivity measurements for our electrolyte gated MoS$_2$ samples. This is due to the non-uniformity of the solid electrolyte layer. Instead, we used confocal transmission microscopy to determine transmittance modulation of gated MoS$_2$ devices on transparent glass substrates (Fig. S5). Transmittance modulation is defined as $M = \frac{I(\hbar\omega, V_g) - I(\hbar\omega, 0V)}{I(\hbar\omega, 0V) - I_0(\hbar\omega)}$, where $I(\hbar\omega, V_g)$ is the intensity of light transmitted through MoS$_2$ at photon energy $\hbar\omega$ and gate voltage $V_g$. Transmittance modulation is closely related to absorption modulation. We can rewrite the definition of $M$ as

$$M = \frac{I(\hbar\omega, V_g) - I(\hbar\omega, 0V)}{I_0(\hbar\omega)}.$$

Here $I_0(\hbar\omega)$ is the intensity of the incident light. Since $I(\hbar\omega, V_g)/I_0(\hbar\omega) = 1 - \alpha(\hbar\omega, V_g)$, we get:

$$M = \frac{\alpha(\hbar\omega, 0V) - \alpha(\hbar\omega, V_g)}{1 - \alpha(\hbar\omega, 0V)}.$$

Since MoS$_2$ absorption is small (~5%) in our wavelength region, $M \approx \alpha(\hbar\omega, 0V) - \alpha(\hbar\omega, V_g)$ or $\alpha(\hbar\omega, V_g) = \alpha(\hbar\omega, V_g = 0V) - M(\hbar\omega, V_g)$. Therefore, we can estimate $\alpha(\hbar\omega, V_g)$ from measured $M$ and $\alpha(\hbar\omega, V_g = 0V)$~5% obtained from an unbiased MoS$_2$ flake before deposition of solid electrolyte.

Experimentally, a broad (~1mm) light beam from a fiber-coupled halogen light source was used to illuminate our sample. Light passed through the sample was collected through a 40X objective and was further magnified ~10 times and focused on a screen with a ~0.5mm diameter pinhole. A magnified image of the device was projected on the screen. The pinhole was adjusted to block the light from the rest of the sample while transmitting light that passes through MoS$_2$. The spectrum of the transmitted light as a function of gate voltage was recorded using Shamrock 303i spectrometer.
Supplementary Figure S5 Schematic of measurement set up for transmission microscopy.

S6. Supplementary Discussion: Detailed description of $Q(\alpha)$ measurement

The data in the $Q(\alpha)$ parametric plot (Fig. 4d, main text) were obtained as follows. A QD/MoS$_2$ device was used for measurements of the quenching factor $Q$ vs. $V_g$. However, absorption of the MoS$_2$ layer, $\alpha_{MoS_2}$, could not be determined in the same device due to the strong background absorption of the QDs. For that reason, a separate MoS$_2$-only device without QDs was used for $\alpha_{MoS_2}$ vs. $V_g$ measurements (Fig. 4c of the main text, Supporting information S5). However, interpretation of $Q(\alpha)$ data is complicated by the difference of the intrinsic doping levels of MoS$_2$ between QD/MoS$_2$ and MoS$_2$-only devices.

At $V_g=0$ we observed reduced PL due to MoS$_2$ (peak at ~1.9eV) in QD/MoS$_2$ as compared to MoS$_2$-only devices (Fig. S4b). Since PL of MoS$_2$ can be used as a proxy for free carrier density (Fig. 1b, Fig. S4b, Fig.S6a), this observation suggests that the intrinsic doping level of MoS$_2$ in MoS$_2$-only devices is lower than that of MoS$_2$ in QD/MoS$_2$ devices. Moreover, the observation of near-absent absorption modulation for MoS$_2$ in MoS$_2$-only devices for $V_g<0$ (as compared to strong absorption modulation for $V_g>0$) suggests that the density of free carriers in that device approaches ~0 at $V_g=0$ (Fig. 4c). In contrast, robust changes of MoS$_2$ and QD photoluminescence in QD/MoS$_2$ devices (Fig. 4b, main text) hint that the density of free carriers is changing throughout our gating range and the Fermi level always stays within the conduction band. In Fig.S6b, we illustrated the proposed Fermi level positioning between MoS$_2$ and QD/MoS$_2$ devices due to difference in intrinsic doping levels.

Because of the difference in the intrinsic doping levels, we have to be careful in relating the experimentally measured $\alpha_{MoS_2}$ to the analysis of QD/MoS$_2$ devices. For $V_g>0$, the Fermi level of MoS$_2$ in both MoS$_2$-only and QD/MoS$_2$ devices is in the conduction band and the absorption of MoS$_2$ in both devices changes similarly. On the other hand, when $V_g<0$, the Fermi level of MoS$_2$ in MoS$_2$-only devices is shifted below the conduction band edge. In that case, the density of free carriers and hence $\alpha_{MoS_2}$ are nearly $V_g$-independent (Fig. S6b). At the same time, the absorption of MoS$_2$ in QD/MoS$_2$ devices strongly
changes with \( V_g \). This means \( \alpha_{\text{MoS}_2} \) in QD/MoS\(_2\) and MoS\(_2\)-only devices are only close when \( V_g > 0 \). Because of that, the data in Fig. 4c of the main text are only plotted in that range.

For completeness, we show \( Q(\alpha) \) for the entire range from -2V to 2V in the Figure S6c. The discussion above shows that the deviation from linear dependence for \( V_g < 0 \) is caused by inaccuracy in measured MoS\(_2\) absorption in that voltage range.

**Supplementary Figure S6** (a) Photoluminescence spectra of two different MoS\(_2\)-only devices without QDs, and of two different QD/MoS\(_2\) devices. (b) Proposed Fermi level (\( E_F \)) positioning of MoS\(_2\) in MoS\(_2\)-only and QD/MoS\(_2\) devices. (c) \( Q(\alpha) \) plot including the data for \( V_g < 0 \).

**S7. Off-peak QD/MoS\(_2\) and QD/Graphene Devices**

**Supplementary Figure S7** To check possible contribution of charge transfer to QD PL modulation in QD/MoS\(_2\), two additional types of devices were fabricated. In the first type of device (a) we used CdSSe QD with the emission peak at ~2.2eV (away from the excitonic absorption peak of MoS\(_2\)) to make hybrid QD/MoS\(_2\) devices. In the second type of device (b), same QDs as in the rest of the manuscript (emission peak at 2.02eV) were used, but MoS\(_2\) was substituted by monolayer graphene. In both devices, optical absorption of the 2D material was constant at relevant QD emission energies. PL spectra were recorded while varying the gate voltage \( V_g \) for both (a) QD/MoS\(_2\) and (b) QD/graphene devices. In both cases, we observed no changes in the PL at the emission wavelength of the QDs (2.2 eV in (a) and 2.02eV in (b)). This indicates that electrical modulation of the PL for the QDs used in the manuscript is due to changes in excitonic absorption of MoS\(_2\) and not just due to changes in its carrier density.
S8. Spectrally selective tuning of QDs using WS$_2$ and MoS$_2$

**Supplementary Figure S8.** (a) QD/WS$_2$ devices with QDs emitting at ~2.4eV (green color). The emission peak of these QDs is in resonance with excitonic absorption peak of WS$_2$. (b) QD/MoS$_2$ devices with QDs emitting at ~2.4eV (green color). The emission peak of these QDs is not in resonance with MoS$_2$ excitonic absorption peak. (c) QD/MoS$_2$ devices with QDs emitting at ~2.02eV (red color). The emission peak of these QDs is in resonance with MoS$_2$ excitonic absorption.