Supporting Information

Directed Energy Transfer from Monolayer WS2 to near Infrared Emitting PbS-CdS Quantum Dots

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Section 1: Photoluminescence excitation (PLE) data scaling

**SI Figure 1 a-b:** a) Unscaled heterostructure (red) and PbS-CdS (black) PLE data. b) Heterostructure and PbS-CdS PLE normalised to mean PLE values off-resonant to underlying WS$_2$ donor (670-700 nm).
Section 2: Photoluminescence contribution (PL<sub>ctr</sub>) derivation

The photoluminescence contribution (PL<sub>ctr</sub>) by the transition metal dichalcogenide (TMD) monolayer to the quantum dot (QD) emitter is derived. Vavilov’s rule, which states that PLQE is independent of excitation wavelength, forms the key assumption in this derivation. Given the range of wavelengths presented in PLE measurements (560 nm – 680 nm) this assumption is regarded as reasonable. We consider the photoluminescence excitation (PLE) of the QD at excitation resonant and non-resonant to the underlying WS<sub>2</sub> monolayer i.e. PLE<sub>λ<sup>*</sup></sub> and PLE<sub>λ</sub> respectively. In each case the PLE from the QD emission detection is given by equations 1 and 2:

\[ PLE_{\lambda} = \frac{P_L}{n_{\lambda}} = Abs_{\lambda} \times PLQE \]  
(1)

\[ PLE_{\lambda} = \frac{P_L}{n_{\lambda}} = Abs_{\lambda} \times PLQE \]  
(2)

Where \( n \) and \( Abs \) are the number of photons per second injected and absorption of the QDs. By dividing equation 1 by equation 2 we obtain:

\[ \frac{PLE_{\lambda}}{PLE_{\lambda}} = \left(\frac{n_{\lambda}}{n_{\lambda}}\right) \frac{P_L}{P_L} = \left(\frac{Abs_{\lambda}}{Abs_{\lambda}}\right) \]  
(3)

Hence the absorption ratio is equivalent to the ratio of WS<sub>2</sub> resonant PLE to non-resonant PLE. This is ratio is given by \( R \):

\[ R = \frac{PLE_{\lambda}}{PLE_{\lambda}} = \left(\frac{n_{\lambda}}{n_{\lambda}}\right) \frac{P_L}{P_L} = \left(\frac{Abs_{\lambda}}{Abs_{\lambda}}\right) \]  
(4)

By comparing the \( R \) values on the heterostructure and the QD control, we can identify an additional contribution to the QD absorption i.e. \( \Delta R \) from the underlying WS<sub>2</sub>.

\[ \Delta R = R_{Het} - R_{QD} \]  
(5)

Expressing equation (6) as a proportion of the heterostructure \( R \) value (\( R_{Het} \)), we obtain the contribution of PL by the WS<sub>2</sub> to the QDs.

\[ PL_{ctr} = \left(\frac{R_{Het} - R_{QD}}{R_{Het}}\right) = \left(\frac{\Delta R}{R_{Het}}\right) \]  
(6)
Section 3: Corroborating Förster resonance energy transfer (FRET)

Section 3.1: PLE study on heterostructures with alternative quantum dot to two dimensional material (QD-2D) surface attachment ligands of increasing length

SI figure 2 shows the wide field PLE spectra of tungsten disulphide/ lead sulphide-cadmium sulphide (WS₂/PbS-CdS) heterostructures with varying QD-2D surface attachment thiol ligands. Table 1 lists the ligands used and their corresponding lengths. The difference in prominence of the WS₂ resonant peak is due to the variation in size of the WS₂ monolayers used. The 1,3 Benzene dithiol (BDT) sample has the largest monolayer and hence the most prominent WS₂ ‘A’ exciton signal with less contribution of the QD emission shoulder blue of the WS₂ peak as seen in other samples. All signals were obtained by scanning about WS₂ ‘A’ exciton and detecting and PbS-CdS emission (~ 900 nm). All signals show the WS₂ ‘A’ exciton peak in the expected spectral region (614 – 620 nm).

![SI Fig 2](image)

**Table 1**: Dithiol ligands and corresponding lengths. (*) indicates value estimated using calculated dithiol ligand lengths from the open literature (Mispelon *et al.*, 2 Table 1, p. 18566) and the known bond angle of a hexagonal planar benzene ring.

| Ligand               | Length | Reference |
|----------------------|--------|-----------|
| 1,3 Benzene dithiol (BDT) | 0.47 nm | *         |
| 1,4 Butane dithiol (BuDT) | 0.68 nm | ^3        |
| 1,6 Hexane dithiol (HDT)  | 0.95 nm | ^3        |

While charge orbital overlap between donor and acceptor species is a possibility at these separation distances, the high oscillator strengths of the TMD donor and QD acceptor still render ET via dipole interaction (*i.e.* FRET) highly favourable, and more significant than proximity dependent Dexter energy transfer (DET).

The Förster radius, $R_0$, is defined as the distance between donor and acceptor through which there is a 50% probability excitation transfer. We therefore estimate the theoretical Förster radius to quantify the likelihood of FRET being the dominant ET mechanism from 2D $\rightarrow$ QD in the heterostructures measured.
Section 3.2: Theoretical FRET radius estimation

Considering the 2D TMD as an array of point-like emitters and the QD film as an array of point-like absorbers, the FRET radius, $R_0$, is defined in equation 7. This system is also well approximated by a 2D quantum well donor and nanoparticle acceptors, which follows a $d^6$ distance dependence for non-radiative energy transfer:

$$R_0 = \frac{9 \ln 10}{128 \pi^2 N_A n^3} \kappa^2 \text{PLQE}_D J$$

(7)

$N_A$ is Avogadro’s number, $n$ is the refractive index of the medium surrounding the FRET pair, PLQE$_D$ is the donor’s intrinsic photoluminescence quantum efficiency and $\kappa^2$ is the dipole orientation factor, which is equal to 2/3 for randomly oriented dipoles. $J$ is the overlap integral between the area normalised emission spectrum, $F_D$ and acceptor absorption spectrum given by the acceptor molar extinction coefficient, $\varepsilon_A$.

$$J = \int_0^\infty F_D(\lambda)\varepsilon_A(\lambda)\lambda^4 d\lambda$$

(8)

It must be noted that $J$ is evaluated with the wavelength in [nm] and $\varepsilon_A$ in [M cm$^{-1}$]. To compute $R_0$, we must calculate the overlap integral $J$ from measured $\varepsilon_A(\lambda)$ and $F_D(\lambda)$ data. The molar extinction coefficient is obtained via Beer Lambert’s law (equation 9) for absorbance, $A$ of a 0.1 mg ml$^{-1}$ suspension of QDs in toluene of molar concentration $c$, measured with a 1 cm path length, $l$, cuvette.

$$A(\lambda) = \varepsilon_A(\lambda)cl$$

(9)

However, to obtain the molar extinction coefficient, the molar concentration, $c$ of QDs in [M] is needed. The first step in calculating $c$ involves estimating the QD size by solving equation 10 provided by Moreels et al. for PbS QDs of diameter $D$ using their band gap energy, $E_0$. Since the QDs used consist mainly of a PbS core as per the modified preparation method originally developed by Neo et al., the use of equation 10 is considered reasonable. For the QDs used, where $E_0 \sim 1.76$ eV, we get $D \sim 2.4$ nm.

$$E_0 = 0.41 + \frac{1}{0.0252D^2 + 0.283D}$$

(10)

We then calculate the QD volume assuming a spherical shape. This is followed by multiplying the volume by the density of PbS (7.6 g cm$^{-3}$) to obtain the mass of a single QD. Multiplying the mass of a single QD by the Avogadro number yields an estimate for the QD molar mass, $Mr \sim 33128$ g mol$^{-1}$. Dividing the known QD concentration of 0.1 g L$^{-1}$ (ie 0.1 mg mL$^{-1}$) by the estimated QD molar mass $Mr$, yields $c \sim 3.02 \times 10^6$ M. We rearrange equation 8 for molar extinction coefficient in [M$^{-1}$ cm$^{-1}$], which is shown in SI figure 3 along with area normalised donor emission, $F_D$. 


SI Fig 3: (Left axis) Molar extinction coefficient of $3.02 \times 10^{-6}$ M PbS-CdS QDs in toluene measured with 1 cm cuvette. (Right axis) Area normalized WS$_2$ emission spectrum, $F_D$ used to calculate overlap integral, $J$.

From the data shown in SI figure 3, the overlap integral is estimated via equation 8 as $J = 1.23 \times 10^{15}$ M$^{-1}$ cm$^{-1}$ nm$^4$. Using a simplified version of equation 7 below (equation 11) we estimate $R_0$ [nm] by assuming a vacuum between the emitter and absorber, i.e. $n = 1$ and orientation factor $\kappa^2 = 2/3$. For the ideal system, we assume the TMD donor to have unity PLQE. This approximation is however considered reasonable as we subsequently find that the energy transfer rate from WS$_2$ band edge to QD band edge outcompetes the intrinsic exciton quenching in WS$_2$, which is the known cause of low PLQE in newly prepared TMDs.

$$R_0 = 0.0211 \left( \frac{\kappa^2 \text{PLQE}_D J}{n^4} \right)^{\frac{1}{6}}$$

From equation 11, we obtain $R_0 \approx 6.5$ nm, which exceeds the ligand separation distances between donor TMD and acceptor QD listed in table 1. This highlights the significance of the oscillator strength of the constituent heterostructure materials over their physical separation distance. This strongly implies FRET as the dominant ET process observed.
Section 4: WS$_2$ PL map region for PL scatter data shown in Figure 5.a

WS$_2$ PL scatter data presented in Figure 5.a were measured from the 64 $\mu$m x 48 $\mu$m rectangular region (orange dashed lines) shown in the optical images of the monolayer below.

SI Fig 4: LHS image shows monolayer region outlined in red dashed lines and estimated region of PL map is outlined in orange dashed lines. Black dashed region in LHS corresponds zoomed optical image on RHS taken with the Invia microscope described in the experimental section of the manuscript. Orange dashed lined in RHS represents actual 64 $\mu$m x 48 $\mu$m PL map region taken with invia microscope (see experimental section). White mesh in RHS represents PL map resolution (2 $\mu$m x 2 $\mu$m) as described in experimental section.
**Section 5: Energy Transfer efficiency derivation**

![Energy level diagram](image)

**SI Fig 5**: Energy level diagram illustrating radiative exciton pathways in pristine WS$_2$ (LHS) and in heterostructure. Blue arrows represent initial excitation, orange arrows represent WS$_2$ excitons and red arrows represent down-shifted excitons that recombine at lower energy in the PbS-CdS QD.

**Table 2**: Fitted PL lifetimes of pristine and heterostructure samples and resulting estimates for ET efficiencies. Fast components of WS$_2$ PL decay in heterostructure $\tau'_1$ and transfer efficiencies $\eta_{ET}$ represent upper bound values due to limitations in instrument sensitivity.

| Intensity  | Pristine $\tau_1$ | Heterostructure $\tau'_1$ | Pristine $\tau_2$ | Heterostructure $\tau'_2$ |
|-----------|-------------------|--------------------------|-------------------|--------------------------|
| 0.21 W cm$^{-2}$ | 0.456 ns | 0.26 ns | 3.63 ns | 3.64 ns |
| 63.4 W cm$^{-2}$ | 0.62 ns | 0.26 ns | 2.95 ns | 2.9 ns |

Following the RHS of SI Figure 5. WS$_2$ donor PL kinetics in the heterostructure can be described via the following set of related ordinary differential equations (ODEs):

$$\frac{dD^*}{dt} = -(k_D + k_{TR} + k_{ET})D^*$$  \hspace{1cm} (12)

$$\frac{dTr}{dt} = k_{TR}D^* - k_2Tr$$ \hspace{1cm} (13)

Where $D^*$ and $Tr$ represent the WS$_2$ donor and trap state exciton populations respectively. The constants $k_0$, $k_{TR}$, $k_{ET}$ and $k_2$ represent the donor’s intrinsic recombination rate; intrinsic trapping rate; donor-acceptor energy transfer (ET) rate; and trap-ground state recombination rate respectively. By integration we arrive at the solutions to **equations 12 and 13**.

$$D^*(t) = D_0^* e^{-(k_D + k_{TR} + k_{ET})t}$$ \hspace{1cm} (14)
\[
Tr(t) = \frac{k_{TR}D_0^*}{[k_2 - (k_D + k_TR + k_{ET})]} \left( e^{-(k_D+k_{TR}+k_{ET})t} - e^{-k_2t} \right)
\]

(15)

Where \(D_0^*\) represents the initial donor population. As such, the PL dynamics in the heterostructure can be defined as the sum of donor and trap population decay terms given by equations 14 and 15:

\[
PL(t) = D^*(t) + Tr(t)
\]

(16)

\[i.e.
PL(t) = D_0^* e^{-(k_D+k_{TR}+k_{ET})t} + \left( \frac{k_{TR}D_0^*}{[k_2 - (k_D + k_TR + k_{ET})]} \left( e^{-(k_D+k_{TR}+k_{ET})t} - e^{-k_2t} \right) \right)
\]

(17)

In the absence of the QD acceptor the pristine WS\(_2\) kinetics can be modelled by setting the transfer term \(k_{ET} = 0\) so that:

\[
PL(t) = D_0^* e^{-(k_D+k_{TR})t} + \left( \frac{k_{TR}D_0^*}{[k_2 - (k_D + k_TR)]} \left( e^{-(k_D+k_{TR})t} - e^{-k_2t} \right) \right)
\]

(18)

The PL dynamics described by equations 17 and 18 consist of fast and slow decay components. In the pristine case (equation 18), at short time, \(i.e.\ t \rightarrow 0\), the fast decay time is given by:

\[
\tau_1 \sim \frac{1}{(k_D + k_{TR})}
\]

(19)

Similarly, in the heterostructure case (equation 17):

\[
\tau'_1 \sim \frac{1}{(k_D + k_{TR} + k_{ET})}
\]

(20)

At long time \(i.e.\ t \rightarrow \infty\), given that the slow decay component (\(\tau_2\)) remains unchanged for a given fluence (see Table 2), the slow decay time in both pristine and heterostructure cases is given as:

\[
\tau_2 \sim \tau'_2 \sim \frac{1}{(k_2)}
\]

(21)

From equations 19 and 20, we can deduce the ET rate, \(k_{ET}\), as:

\[
k_{ET} = (k_D + k_{TR} + k_E) - (k_D + k_{TR})
\]

(22)

The ET efficiency can then be determined in terms of rate constants. Using equations 19, 20 and 22, the ET can be simplified in terms of fast decay time constants as shown in equation 2 of the main text:
\[
\eta_{\text{ET}} = \frac{k_{\text{ET}}}{(k_D + k_{\text{TR}} + k_{\text{ET}})} = 1 - \frac{\tau_1'}{\tau_1}
\] (23)

**Section 6: QD PL image on TMD monolayer**

SI Fig 6: (LHS) Wide-field QD PL (900 nm) image of heterostructure at 620 nm excitation. (RHS) Optical image of monolayer used in heterostructure. QD PL clearly enhanced on TMD monolayer.

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