

Supporting Information

Distance dependence of the energy transfer rate from a single semiconductor nanostructure to graphene

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Synthesis of CdSe/ CdS nanocrystals

Chemicals: 1-Octadecene (ODE, 90 %, Aldrich), oleylamine (OLA, 70 %, Fluka), oleic acid (OA, 90 %, Aldrich), sodium myristate (99 %, Fluka), cadmium oxide (99.99 %, Aldrich), selenium powder 100 mesh (99.99 %, Aldrich), sulfur (99.998 %, Aldrich), trioctylphosphine (TOP, 90 %, Cytec) and tetradecylphosphonic acid (TDPA, 97 %, PCI synthesis) were used as received.

Precursors preparation: Cadmium myristate was prepared according to ref.¹ The solution of cadmium oleate 0.5 M in oleic acid was synthesized by heating 6.42 g of CdO in 100 mL of oleic acid at 160 °C under argon until it turned colorless. The solution was then degassed under vacuum at 100 °C for 1 hour. Sulfur stock solution in ODE (S-ODE 0.1 M) was prepared by heating 480 mg of sulfur in 150 mL of degassed ODE at 120 °C until complete dissolution. TOP-Se 1 M in TOP was prepared by dissolving 15.8 g of Se powder in 200 mL TOP under magnetic stirring overnight in a glove box.

Synthesis of CdSe cores: CdSe nanocrystals (NCs) were prepared by a procedure slightly modified adapted by Mahler *et al.*² from Mohamed *et al.*³ A mixture of 2 mL of Cd(oleate)₂ (0.5 M) and 3 mL of ODE was degassed under vacuum at 70 °C during 30 min and heated under argon flow up to 240 °C. A mixture of 1.5 mL of TOP-Se 1 M, 1.5 mL of oleylamine and 1 g of TDPA was heated until complete dissolution then injected and the solution was annealed for 30 seconds at 190 °C, and then immediately cooled down to room temperature. The solution was washed up with 40 mL of ethanol. The solution was centrifuged at 5500 RPM in order to precipitate the TDPA. The nanocrystals were suspended in 20 mL of toluene, washed again in 20 mL of ethanol, and dispersed in 10 mL of hexane. The nanocrystals obtained with this protocol were around 2 nm diameter, and their approximate concentration was 80 μ M.

Synthesis of CdS shell on the CdSe cores: For the CdS shell growth on the CdSe cores, a mixture of 3.1 mL of solution of cores dispersed in hexane, 5 mL ODE and 50 mg Cd(myristate)₂ was degassed under vacuum, at 70 °C for 30 minutes, and then put under argon flow. The temperature set value was then increased to 300 °C, and when the temperature reached 100 °C, 1 mL of OLA was injected, followed by a mixture of 8 mL SODE (0.1 M), 1.6 mL Cd(OA)₂ (0.5 M) and 1 mL OLA at an injection rate of first 2 mL/h for 2 mL, then 16 mL/h for the rest of the syringe. Once the injection was finished, a mixture of 0.5 mL OLA and 0.5 mL Cd(OA)₂ 0.1 M diluted in OA was added, and the solution was annealed for 10 minutes at 300 °C. The solution was then cooled down to room temperature and the nanocrystals were washed with ethanol, centrifuged and redispersed in 10 mL hexane.

NC characterization: The ensemble absorption spectrum was measured on a Cary 5E UV-visible spectrometer. The ensemble photoluminescence (PL) spectrum was acquired with an Edinburgh Instruments FCS900 spectrometer. Transmission electron microscopy (TEM) images were taken using a TEM JEOL 2010 with field emission electron gun. The results for CdSe/CdS NCs are shown in Figure S1. The NCs show strong PL at 2.14 eV, with a full width at half maximum (FWHM) of 140 meV. From the analysis of the TEM images, we find an statistically averaged diameter of (9.5 ± 1.5) nm.

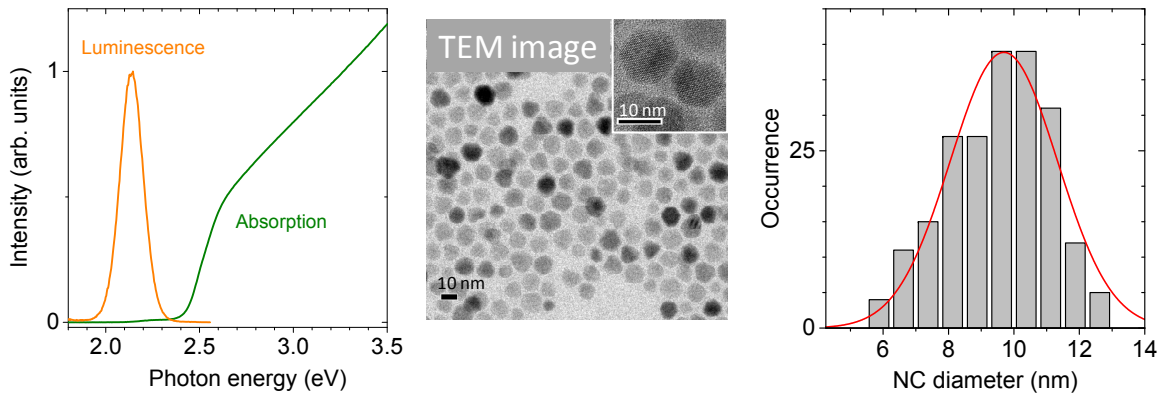


Figure S1: (left) Ensemble absorption and photoluminescence spectra of the CdSe/CdS nanocrystals used in our measurements. (center) Transmission electron microscope image of the CdSe/CdS nanocrystals. (right) Histogram of the NC diameters.

Synthesis of CdSe/CdSeS/ZnS nanoplatelets

Preparation of CdSe nanoplatelets CdSe nanoplatelets (NPs) with an atomically controlled thickness of 4 monolayers were prepared as described in ref.⁴ In a 100 mL three neck flask 170 mg (0.3 mmol) of cadmium myristate were introduced along with 12 mg (0.15 mmol) of Se powder and 15 mL of octadecene. The solution was degassed under vacuum for 30 min at room temperature. Under Ar flow, the temperature was set at 240 °C. When the temperature reached 200 °C (the solution is yellow orange at this step), 40 mg (0.15 mmol) of cadmium acetate were quickly added to the solution. Finally the reaction was left for 12 min at 240 °C. Oleic acid (2 mL) were then injected to quench the reaction, and the flask was cooled down to room temperature. The nanoplatelets were precipitated by adding 15 mL of hexane and 15 mL of EtOH. After centrifugation at 6000 rpm for 10 min, the clear supernatant was discarded, and the solid precipitate was re-dissolved in fresh hexane (8 mL). The cleaning procedure was repeated a second time.

Preparation of CdSe/(CdS)₃/(ZnS)₂ nanoplatelets CdSe NPs (500 μ L of the solution previously obtained were charged in a 3 mL vial with 0.5 mL of N-methylformamide (NMF) obtaining a biphasic mixture. Then 20 μ L from a freshly solution of Na₂S 0.3 M in NMF were added to the biphasic system stirring at room temperature for few minutes. The NPs were thus transferred in the polar NMF bottom phase that turned into orange. The hexane phase was discarded and NPs in NMF were washed twice with hexane to remove residual organic ligand. Then, a mixture of toluene: acetonitrile in a ratio 3:1 is added and NPs were precipitated using centrifugation. The NPs were re-dissolved in 0.5 mL of NMF and 30 μ L of Cd(OAc)₂ 0.1 M in NMF were added to complete the first CdS monolayer shell deposition. After stirring of few minutes a room temperature, the NPs were precipitated as described above and re-dissolved in 0.5 mL of NMF. The procedure was repeated two more times for a total of 3 CdS layer deposition. To deposit the two final ZnS shell layers, 20 μ L of Na₂S 0.3 M in NMF were added to NPs in NMF and NPs were precipitated

using toluene:acetonitrile in a ratio 3:1. After redispersion on NPs in 0.5 mL of NMF, 30 μL of $\text{Zn}(\text{OAc})_2$ 0.1 M in NMF were added and the mixture stirred for few minutes at room temperature. Then, it was precipitated as described above and the procedure was repeated once to complete the shell. The final NPs core/shell were precipitated with toluene and redispersed in 1 mL of hexane adding 100 μL of oleic acid and 50 μL of oleylamine. The excess of organic ligands was washed away by precipitation with EtOH and finally NPs were dissolved in hexane or toluene to be analyzed by transmission electron microscopy (TEM).

NP characterization: Optical and TEM characterizations of CdSe/CdS/ZnS NPs used in our measurements were performed using the same instruments as for the CdSe/CdS nanocrystals. Figure S2 shows the absorption and PL spectra, as well as a typical TEM image. These NPs show strong emission at 1.925 eV, with a FWHM of 60 meV. From the analysis of the TEM images, we find an average lateral dimensions of $(9 \pm 1.5) \text{ nm} \times (22 \pm 2) \text{ nm}$. The average height of the NPs is estimated to be $(3.5 \pm 0.5) \text{ nm}$.

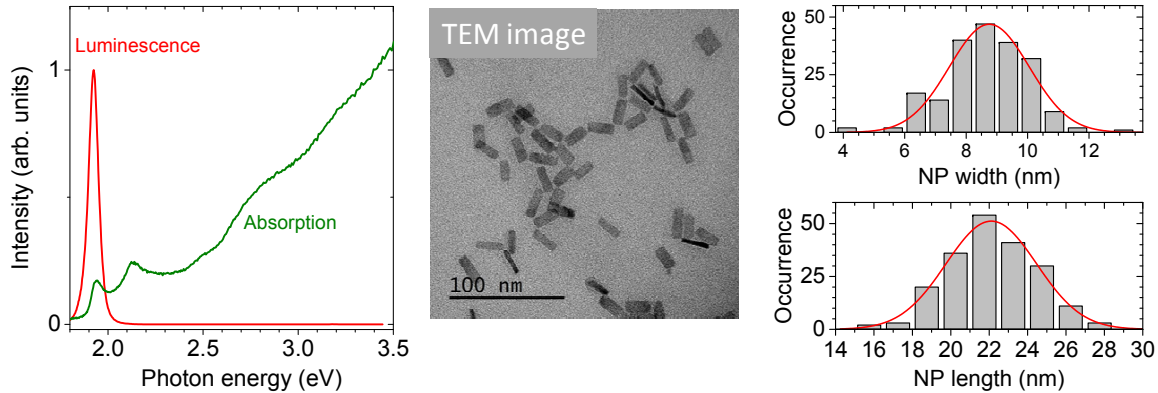


Figure S2: (left) Ensemble absorption and photoluminescence spectra of the CdSe/CdS/ZnS nanoplatelets used in our measurements. (center) Transmission electron microscope image of the CdSe/CdS/ZnS nanoplatelets. (right) Histogram of the NP widths and lengths.

Graphene grown by chemical vapor deposition

To investigate the distance scaling of the energy transfer rate we made use of graphene grown by low-pressure chemical vapor deposition (LPCVD) on a Cu foil (Alfa Aesar, Item No. 46986, 99.8 %, cut into 6 x 6 cm strips) in a hot wall furnace consisting of a 4 inch fused silica tube.⁵ Prior to CVD, the foils were cleaned using a Ni etchant for 5 min and then thoroughly rinsed with DI water. A typical growth process flow is as follows: (1) load the Cu foil, evacuate, heat to 1000 °C, and anneal for 20 min under a 100 sccm H₂ flow (at a pressure of about 70 – 80 mTorr); (2) introduce 30 sccm CH₄ and 30 sccm H₂ for 40 min(60 mTorr); (3) final exposure to CH₄ for 40 min, followed by a cool down of furnace to room temperature in vacuum. A poly(methyl methacrylate) (PMMA) solution (950 K, 4% by volume dissolved in chlorobenzene) was spin-coated onto the top side of the sample followed by baking at 60 °C for 5 min. The Cu under the graphene film was etched using a copper etchant solution and washed with DI water 3 times. The resulting PMMA/grapheme film is transferred onto a fused quartz substrate and the PMMA film is dissolved using acetone. In order to remove resist residues and other chemical contaminants from the graphene surface, the samples were heated at 250 °C for 4 hours in a tube furnace in a Ar/H₂ (90/10 % mixture composition) atmosphere.

Sample characterization by Raman spectroscopy

Micro-Raman measurements were performed using a home-built setup, with a laser photon energy of 2.33 eV (532 nm) and a power of a few hundred μ W focused onto a diffraction limited spot of $\sim 0.6 \mu\text{m}$ diameter. Figure S3a shows Raman spectra of a mechanically exfoliated graphene monolayer before and after deposition of a thin MgO layer by means of molecular beam epitaxy.⁶ The narrow and quasi symmetric lineshape of the 2D mode feature (frequency $\omega_{2D} = 2670 \text{ cm}^{-1}$, FWHM $\Gamma_{2D} = 28 \text{ cm}^{-1}$) is a fingerprint of a graphene monolayer.⁷ The bare graphene monolayer exhibits a G-mode frequency (FWHM) of 1586 cm^{-1}

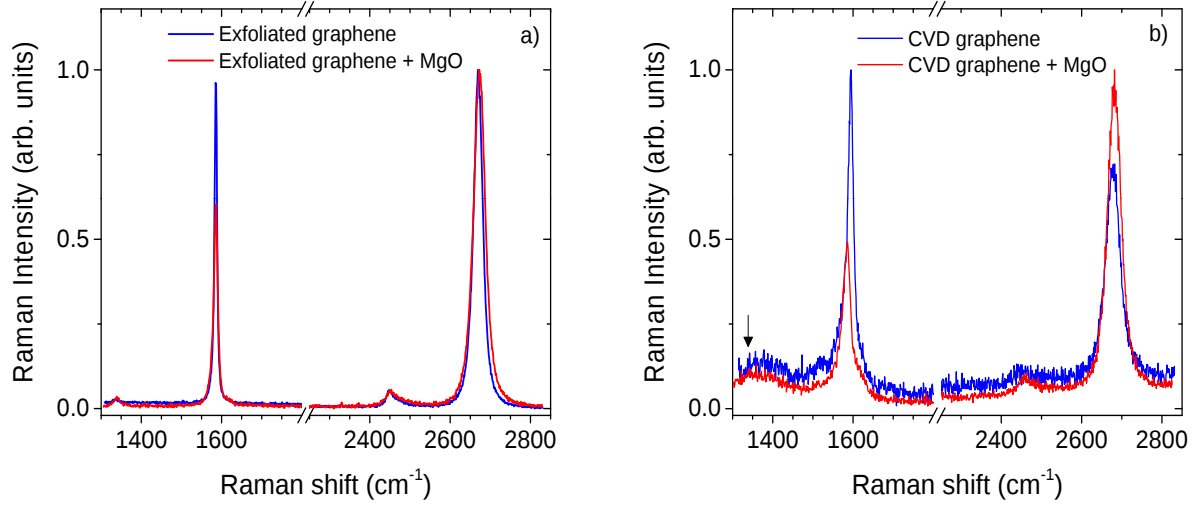


Figure S3: Raman spectra of (a) exfoliated graphene and (b) graphene grown by chemical vapor deposition before and after deposition of a thin MgO film. The arrow in b) indicates the expected position of the D mode feature, which is presumably drawn into the Raman background in these measurements.

(7 cm^{-1}) that are indicative of a slight unintentional doping, on the order of 10^{12} cm^{-2} . This translates into a shift of the Fermi level of less than 200 meV relative to the Dirac point.⁸

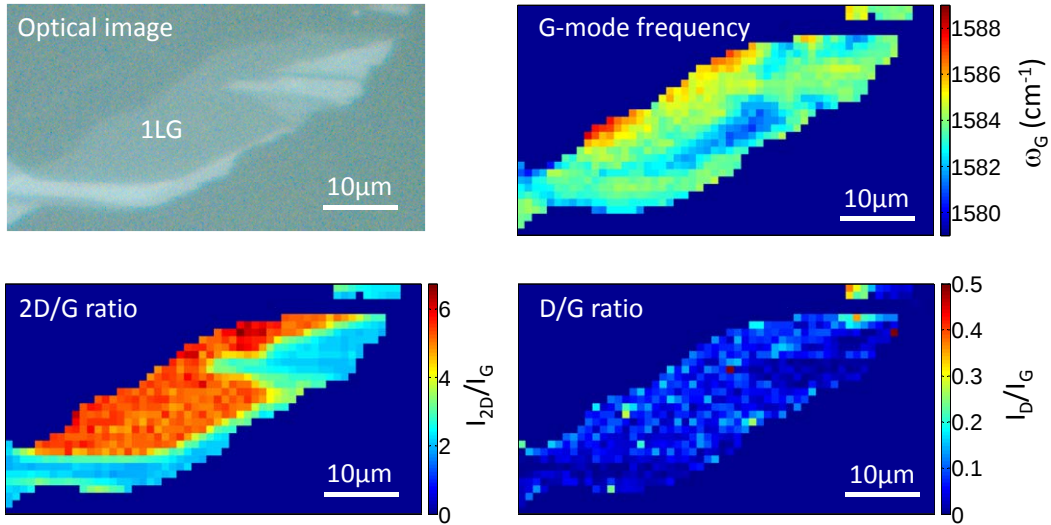


Figure S4: Optical image and spatially resolved Raman study of a mechanically exfoliated graphene sample after deposition of a 2.2 nm thick MgO film.

After deposition of MgO, we find very similar G and 2D mode frequencies and a slight

broadening of the Raman features. The integrated intensity ratio of the defect-induced D mode and the G mode features increases moderately from $I_D/I_G \sim 1\%$ up to $I_D/I_G \sim 3\%$, but remains low (see also Figure S4). We conclude that the deposition of MgO has no major impact on the doping level and is not introducing significant strain as evidenced by the very slight changes in the frequencies. Similar conclusions are reached for a CVD graphene sample transferred on fused silica (see Figure S3b and Figure S5). We observe a slightly stronger background than for measurements on mechanically exfoliated graphene, presumably arising from PMMA residues. CVD graphene also exhibits broader Raman features, with slightly more scattered frequencies (compare Figure S4 and Figure S5) than for mechanically exfoliated graphene. This likely arises from increased disorder and residual charge inhomogeneity in CVD graphene. Nevertheless, the Raman features are not significantly affected by the deposition of MgO. These results justify the suitability of CVD graphene for our measurements.

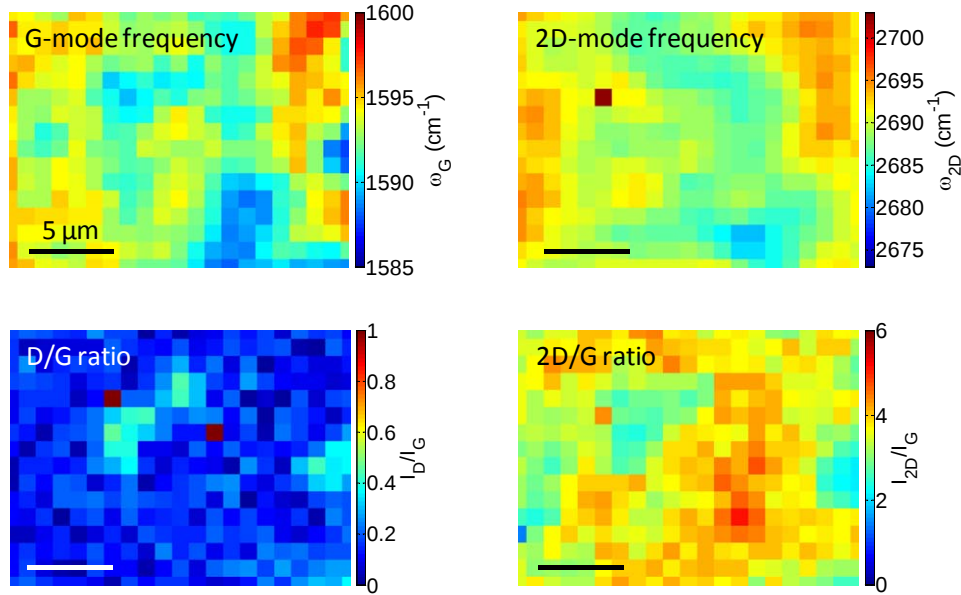


Figure S5: Spatially resolved Raman study of a CVD graphene sample after deposition of a 3.2 nm thick MgO film.

Determination of the decay rates

We define the *calculated* luminescence decay time τ_{calc} as the ratio between the area under the background corrected PL decay curve and its peak value. Applying the latter procedure to our instrument response function (IRF) (see Figures 2 and 3 in the main manuscript) yields a value of $\tau_{\text{calc}}^{\text{IRF}} = 176$ ps. Since the shortest τ_{calc} values measured for NPs on graphene are below 1 ns, the contribution of the IRF to the PL decay has to be taken into account. For this purpose, we have computed τ_{calc} for a set of mono-exponential decays (with a decay time τ_{real}) that have been convoluted with the IRF. The resulting τ_{calc} are plotted against τ_{real} in Figure S6).

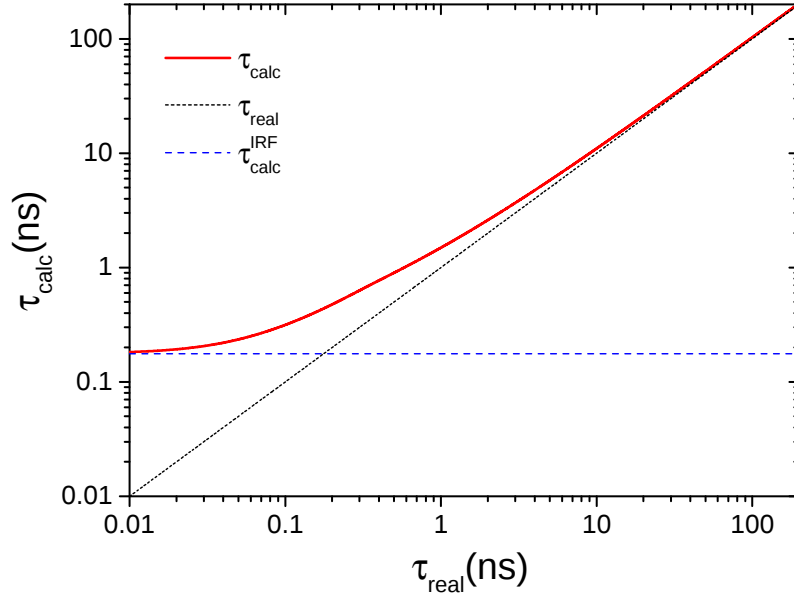


Figure S6: Decay time τ_{calc} numerically computed from the convolution of an exponential decay (decay time τ_{real}) and our instrument response function as a function of τ_{real} .

Then, for each measured PL decay, we calculate τ_{calc} and estimate a value of τ_{real} , by interpolating the calibration curve shown in Figure S6. Obviously, the obtained correction factor assumes a mono-exponential decay. In practice, since τ_{calc} is always significantly greater than $\tau_{\text{calc}}^{\text{IRF}}$, similar correction factors are obtained using other functional forms (bi-

exponential decays or stretched exponential decays). We therefore chose to use the procedure described above in order to obtain a general definition of τ_{real} .

In Figures 4 and 5 of the main manuscript, for each thickness of the MgO spacer, we have defined the average decay rate γ as the inverse of the average decay time τ_{real} . We have verified that our conclusions are independent of the method used to define the average PL decay rate.

Comparison of the distance dependent decay rates

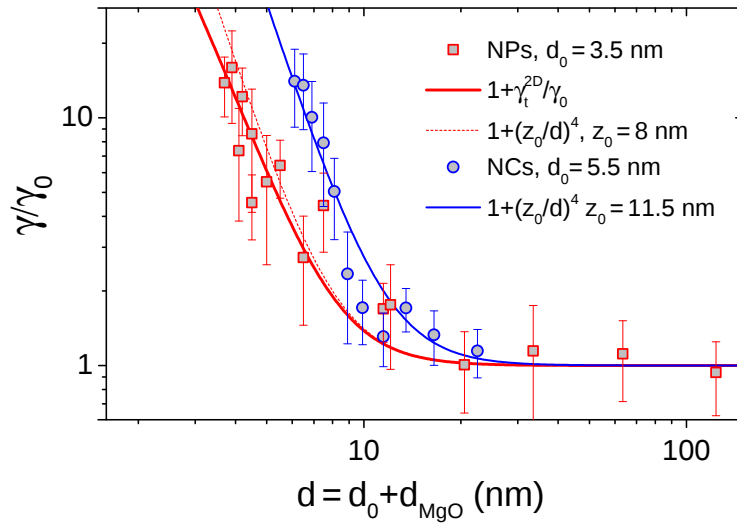


Figure S7: Normalized decay rates measured on individual CdSe/CdS NCs (circles) and CdSe/CdS/ZnS NPs (squares) as a function of the total distance $d = d_0 + d_{\text{MgO}}$ between the nanoemitters and graphene. The solid blue line is computed using Equation 1 in the main text, with $p = 4$ and $z_0 = 11.5$ nm. The solid red line is computed using Equation 3 of the main text, with $\Lambda = 7.5$ nm and a proportionality factor that best fits our results. The dashed red line is computed using Equation 1 in the main text, with $p = 4$ and $z_0 = 8.0$ nm.

Figure S7 compares the normalized distance decay rates γ/γ_0 measured for NCs and NPs (see Figures 4 and 5 of the main manuscript) as a function of the *total* distance $d = d_0 + d^{\text{MgO}}$ between the nanoemitters and graphene. Since the minimal distance d_0 (see main text) is smaller for NPs than for NCs, our results suggest that at a given *total* distance, the RET rate is larger in the case of a zero dimensional NC than for a two-dimensional NP.

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