“Continuous Wave Infrared Optical Gain and Amplified Spontaneous Emission at Ultralow Threshold by Colloidal HgTe Quantum Dots”

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1 Low Temperature Photoluminescence

Supplementary Figure 1 shows the temperature dependence of the spontaneous photoluminescence (PL). An increase of the gap-state emission is observed upon cooling.

Supplementary Figure 1: Temperature dependent photoluminescence of dropcast HgTe nanocomposite (0.01 vol% in PMMA) after excitation with CW 400 nm light. A sub-gap component is revealed more clearly at lower temperatures, yet is also present at room temperature (ca. 2.5% of the total emission intensity).

2 Tight Binding Calculations

We studied the electronic structure and the optical properties of HgTe QDs using semi-empirical tight-binding calculations following closely the methodology described by Delerue et al.\textsuperscript{1}. In a first step, the single-electron states are computed using a tight-binding model of HgTe (see Supplementary Fig. 2a). In a second step, the excitonic states $\Psi^\text{exc}$ are obtained using a Configuration Interaction (CI) method, \textit{i.e.} they are expanded in a basis of Slater determinants built using the single-particle states obtained in tight-binding. The optical cross section (see Supplementary Fig. 2b) of a single nanocrystal of dielectric constant $\varepsilon_{\text{in}}$ embedded in a solvent of dielectric constant $\varepsilon_{\text{out}}$ is then calculated as:

$$\sigma(\hbar\omega) = \frac{4\pi^2e^2|f_{\text{IF}}|^2}{cn} \sum_i \omega_i |\langle0|\sum_n \mathbf{e} \cdot \mathbf{r}_n |\Psi^\text{exc}\rangle|^2 L(\hbar\omega - \hbar\omega_i)$$

Here $\hbar\omega$ is the photon energy, $\hbar\omega_i$ is the energy of the excitonic state $\Psi^\text{exc}$, $\mathbf{e}$ is the polarization vector, $n = \sqrt{\varepsilon_{\text{out}}}$, $f_{\text{IF}} = 3\varepsilon_{\text{out}}/(\varepsilon_{\text{in}} + 2\varepsilon_{\text{out}})$ is the local-field factor. $|\langle0|\sum_n \mathbf{e} \cdot \mathbf{r}_n |\Psi^\text{exc}\rangle|$ is the dipolar matrix element in which $\mathbf{r}_n$ is the position of the electron $n$. The function $L$ is a Gaussian which describes the homogeneous/inhomogeneous broadening (here 35 meV) of the optical transitions. The radiative lifetime $\tau$ is calculated using:

$$\frac{1}{\tau} = \frac{4e^2|f_{\text{IF}}|^2n \sum_i p_i \omega_i^3 |\langle0|\sum_n \mathbf{e} \cdot \mathbf{r}_n |\Psi^\text{exc}\rangle|^2}{3c^3\hbar}$$

Here, $p_i$ is the thermal population of the excitonic state $\Psi^\text{exc}$ at 300 K. The effective dielectric constant is calculated in tight-binding as described in earlier work\textsuperscript{2}. Basically, we calculate the screened electrostatic potential in a nanocrystal on which we apply a uniform (static) electric field. By fitting this potential using the expression derived from...
classical electrostatic theory, we deduce a value of \( \varepsilon_{\text{in}} = 6.8 \) for a spherical nanocrystal of diameter 3.5 nm. We assume that the resulting local-field factor is the same in tetrahedral QDs as in spherical QDs with the same volume. A value of 480 ns is found for 3.5 nm HgTe QDs.

Supplementary Figure 2: Tight binding calculations on HgTe QDs – (a) The level structure in the valence band where two 4-fold hole states (VB1/2) are separated by 54 meV is clearly different from the conduction band where the lowest level (CB1) is 2-fold degenerate. The excitonic transitions \( X_1 \) and \( X_2 \) are also indicated. (b) Calculated absorption spectra of (full black line) an empty 3.5 nm QD, (dashed black line) a 3.5 nm QD charged with one additional hole and (dashed grey line) and with one additional electron.

According to these calculations,\(^1\) 3.5 nm HgTe QDs feature a twofold degenerate lowest conduction-band level (CB1) and two closely spaced 4-fold degenerate upper valence-band levels (VB1 and VB2), see inset of Supplementary Fig. 2. Combining these single particle states into exciton states yields the various optical transitions around the band gap. Supplementary Fig. 2b shows the thus calculated absorption spectrum for both neutral (no holes or electrons) and singly charged (1 electron or 1 hole) QDs. The 2- and 4-fold degeneracy of the CB1 and VB1 states lead to an 8-fold degenerate lowest energy exciton – denoted by \( X_1 \). The combination of CB1 and VB2 states lead to a second exciton, \( X_2 \), with a similar 8-fold degeneracy, separated from \( X_1 \) by 54 meV in this calculation. This energy difference exceeds the typical phonon energies in HgTe (17 meV)\(^3\), possibly rendering relaxation between these states slow. Importantly, the \( X_2 \) transition has an oscillator strength about 10 times larger than \( X_1 \) (see Supplementary Fig. 1b), making that \( X_2 \) dominates the absorption spectrum. We can hence interpret the large apparent Stokes shift between the absorption and emission maxima as originating mainly from this \( X_2X_1 \)- splitting. In the charged cases, especially the holes show additional intraband absorption at longer wavelengths. Tetrahedral QDs exhibit qualitatively similar energy levels (not shown), which indicates that this is an appropriate level structure to interpret experimental results on an ensemble of possibly differently shaped HgTe QDs.

3 Slow hole cooling

Fig. 1d (main text) shows a 2D TA map, obtained after a 700 nm pump pulse that leads to an average exciton density per QD \( \langle N \rangle \) of 0.1 (see Methods). The bleach of the first exciton transition, clearly visible around 1200 nm, narrows down and loses intensity in the first nanoseconds after the pump pulse. By comparing the difference between spectral cuts at 5 ps, when carrier cooling is complete, and 2.5 ns, it follows that especially the bleach at the blue side of the first exciton transition is reduced (dotted green line, Supplementary Fig. 3a). In view of the tight binding calculations (see
Supplementary Information S2), we attribute this change to the depletion of the higher energy, higher oscillator strength $X_2$ manifold in favour of the lower energy, lower oscillator strength $X_1$. A detailed decomposition of the spectra points towards an $X_1$-$X_2$ splitting of 76 meV similar to the 54 meV splitting predicted by tight binding calculations. The $X_2$-$X_1$ relaxation happens on a 700 ps time-scale (see Supplementary Fig. 3b), a decay component also found in the time resolved photoluminescence traces (see Supplementary Fig. 3c). We thus conclude that the slow dynamics of the first exciton bleach reflect hole relaxation between the VB2 and VB1 state manifold.

**Supplementary Figure 3:** (a) Decomposition of early-time bleach spectrum in $X_1$ and $X_2$ contributions (see main text and section 2). The $X_1$-$X_2$ splitting is determined from this fit to be 76 meV which compares well to the calculated 54 meV (see Supplementary Fig. 2). (b) Kinetics at 1340 nm and 1071 nm where the latter is subject to hole cooling in the VB1/2 manifold, whereas the former is not. (c) Zoom of photoluminescence decay at blue and red side of emission spectrum (inset) (PL) under 700 nm excitation. PL decay at 1050 nm (blue line) and 1350 nm (red line). A bi-exponential fit yields a fast component lifetime of 1.1 ns, similar to the 0.7 ns component observed in the TA experiments.

### 4 Larger size QDs

Supplementary Fig. 4 shows the analysis of slight larger HgTe QDs, similar to the analysis in the main text. A red-shifted PL, absorption (a) and gain spectrum (c) is observed with an equally low threshold for net amplification (see c).

**Supplementary Figure 4:** Analysis of larger size HgTe QDs providing gain from 1410 nm to beyond 1620 nm (detection limited by the setup) under similar conditions as the particles described in the main article (a) Linear absorption and photoluminescence (b) Non-linear absorbance $A$ for increasing pump fluence taken 2.5 ns after photo-excitation with 700 nm and (c) wavelength dependent threshold derived from (b).

### 5 Gain Dynamics

The gain in HgTe is due to singly excited QDs as it persists on timescales beyond the reach of multi-$X$. This is clearly evidenced by the kinetic traces at low fluence where
gain is reached, yet no dynamics are observed in the 2.5 ns window of the measurement. 
Note that this implies that for these low fluence traces, the only loss mechanism is the (non-) radiative recombination, see Fig. 1c. When we increase the pump fluence, a faster decay component appears on a timescale of ca. 50 ps. Its occurrence corresponds to the onset of bi-exciton formation due to the pump pulse in HgTe QDs and as such we attribute it to bi-exciton Auger recombination, a conclusion quantitatively supported by other literature reports. 
Increasing the fluence further, we see, apart from the constant background of single excitons and the ca. 50 ps Auger decay of bi-excitons, a second component appear on a ca. 10 ps timescale. Previous reports attributed this component to unbalanced charge states (such as multiple holes combined with a single electron, …). It is worth to stress that these higher order dynamics do not remove the gain and are, as such, not relevant for the ultra-low threshold gain we observe. 
Supplementary Fig. 5 shows a zoom of a high fluence \((N) = 0.3\) kinetic trace at 1340 nm where a bi-exponential fit of the decay after 2 ps gives the mentioned 50 ps and 10 ps lifetime components. Before 2 ps, an initial hot carrier Stark shift and/or hot carrier intraband absorption induces a short lived positive feature which is overtaken by state-filling induced bleach as the carriers cool down on a 1.5 ps timescale.

**Supplementary Figure 5:** Decay kinetic close-ups showing the initial spectral shift (Stark Shift), for \((N) = 0.3\), leading to photo-induced absorption, followed by carrier cooling (1.5 ps time-constant) and (right) multi-X decay (Auger recombination time constant is 51 ps). A biexponential fit is needed to include the fast 10 ps higher order recombination (see discussion in Supporting Information 3).

### 6 Intrinsic gain coefficient

We can calculate the intrinsic gain based on the intrinsic absorption coefficient \(\mu_i\) at high energies starting from bulk values for the (complex) dielectric function \((\varepsilon = \varepsilon_R + i\varepsilon_I)\):

\[
\mu_{i,400} = \frac{2\pi}{\lambda_{400}} |f_{LE}|^2 \varepsilon_I = 4.84 \cdot 10^5 \text{ cm}^{-1}
\]

This theoretical value corresponds very well to the experimental value obtained by Lhuillier et al. \(^3\), \(\frac{\mu_{i,400,Ref}}{\mu_{i,400,Theory}} = 0.87\). By measuring the linear absorption \(A_{0,400}\) at 400 nm and knowing the path length \(L\) of the cuvette, we can determine the volume fraction \(f\) of QDs in solution, since:
\[
\mu_{i,400} (= 4.84 \cdot 10^5 \text{cm}^{-1}) = \frac{\ln(10) A_{0,400}}{f L}
\]  

From this, we calculate the intrinsic gain \(g_i\) by plugging in the obtained volume fraction \(f\), the non-linear absorption \(A\) (note that \(A < 0\) in case of stimulated emission) and the exciton density \(\langle N \rangle\):

\[
g_i = -\frac{\ln(10) A}{f L \langle N \rangle}
\]

The intrinsic gain is the gain provided by a fictitious material of 100% HgTe with the equivalent oscillator strength of a HgTe nanocrystal with \(\langle N \rangle = 1\).

7 HgTe PMMA films

7.1 Transient absorption on thin films

**Supplementary Figure 6:** Film fabrication. HgTe QDs are mixed with PMMA to obtain 0.1-1 vol% solutions which are dropcasted on a glass substrate and left to dry under controlled atmosphere. The dried films have a \(\sim 100\ \mu\text{m}\) thickness, can be delaminated from the support and are flexible (see inset). These freestanding films are then placed on a support structure. The resulting air/composite/air slab is then pumped using a cylindrical lens and the emission from the side is collected and sent to a spectrometer with a PMT detector for analysis.

As explained in the Methods section and Supplementary Fig. 6, thin films of PMMA:HgTe were fabricated with different volume fractions and spincoated/dropcasted on glass substrates. The inset of Supplementary Fig. 7 shows two of such films with 0.1 and 1 vol% of HgTe relative to PMMA. Supplementary Fig. 7 shows the non-linear absorbance \(A\) for photo-excitation at 700 nm for different fluences of a thick PMMA:HgTe QD film (on quartz glass) with 1 vol% QDs for a fluence of \(\langle N \rangle\sim 0.1\) and 0.005. We can observe stimulated emission beyond 1290 nm which implies that the results obtained in solution are indeed transferrable to the thin films used here.
Supplementary Figure 7: Transient absorption on thin films: non-linear absorbance $A$ for photo-excitation at 700 nm for different fluences of a spincoated 100 nm thick PMMA:HgTe QD film (on quartz glass) with 1 vol% QDs for a fluence of $N \sim 0.1$ and 0.005. We can observe net stimulated emission beyond 1290 nm. Inset shows the 0.1 and 1 vol% PMMA:HgTe composites on glass used for this purpose.

7.2. ASE in thin films under pulsed excitation

To increase the guiding in the hybrid polymer/QD films, we aimed at obtaining air/polymer/air films. Dropcasted films can be delaminated from the glass support to obtain flexible films (see Supplementary Fig. 6 & 7). These films are put on a support structure that enables side-collection using a lens and/or high NA (=0.22) multimode fiber. When pumping these films with pulsed laser focused onto a stripe, we observe (see Supplementary Fig. 8) a supralinear increase in the total light intensity for the gain region (> 1300 nm). As put forward in the main text, we decompose the emission spectrum in a band edge component and a ‘gap’ component, which is shown in Supplementary Fig. 8b. The integrated counts in this ‘gap’ component are plotted in Figure 3 (a,c in main text). The inset of Supplementary Fig. 8b shows the narrowing of the extracted gap emission spectrum with increasing fluence, another indication of ASE. Supplementary Fig. 8c shows that for the 0.1% composites, no variations are observed on the spectra. This indicates the absence of spurious effects such as heating or charging that could be misinterpreted. Supplementary Fig. 8d shows the VSL experiments using pulsed excitation where the total light intensity increases supralinearly with increasing stripe length.
**Supplementary Figure 8:** (a) Pulsed excitation ASE (amplified spontaneous emission) experiment showing supralinear increase of long wavelength component with an onset of 6 \( \mu \text{J/cm}^2 \). (b) Decomposition of spectra into band edge and gap component. Inset shows narrowing gap spectra for increasing pump. (c) Similar ASE experiments on 0.1% film showing no supralinear increase indicating that the observed effect is 'collective', i.e. ASE and not spurious such as due to charging. (d) VSL (Variable Stripe Length) experiments on 1 vol% PMMA:HgTe composites, again showing a supralinear increase of the total intensity and the gap intensity.

### 7.2 ASE in thin films under CW excitation

Supplementary Fig. 9 shows the absence of spectral changes in the normalized spectra for the CW ASE experiments on a 0.1% film, again indicating that no spurious effects such as heating or charging contribute to the observed enhanced emission and supralinear increase of Fig. 3a,b in the main text.

**Supplementary Figure 9:** Amplified spontaneous emissions spectroscopy for CW excitation of a 0.1% volume fraction film showing no supralinear increase of the long wavelength component observed in Figure 3(b,c).
8 HgTe gain model

8.1 Basic model

Let us consider a 3 level system where a 1.08 eV band gap separates a single conduction band level (reasonable for small QDs) at \( E = E_c \) from a valence band at \( E = 0 \). A band of defect levels centered at \( E = E_d \) is introduced where both the band edges and the defect have a FWHM of \( \delta E = 100 \) meV. The density of states for the defect band is taken to be a normalized Gaussian:

\[
n_d(E) = \frac{1}{\sqrt{\pi} \Gamma_d} \exp\left(-\frac{(E - E_d)^2}{\Gamma_d^2}\right) \quad (6)
\]

Here, \( \Gamma_d = \frac{\delta E}{\sqrt{\ln(2)}} \).

If we call \( N \) the total number of QD and \( N_{0,1} \) the number of QDs with 0/1 electrons in \( E_c \), we can write the population in the '0' state as \( p_0 = \frac{N_0}{N} \). We assume that \( p_0 + p_1 = 1 \).

The absorption coefficient for a photon of energy \( \hbar \omega \), can be written as:

\[
A(\hbar \omega) = A_d n_d(x)(2p_0 f(x) + p_1 f(x) - p_1[1 - f(x)]) + A_b n_b(x)(2p_0 + p_1) \quad (7)
\]

The first two terms describe absorption, the third one stimulated emission in QDs with a defect. The last term the valence to conduction band absorption of defect-free QDs.

The band-to-band absorption is described as:

\[
n_b(x) = \frac{1}{\sqrt{\pi} \Gamma_c} \exp\left(-\frac{x^2}{\Gamma_c^2}\right) \quad (8)
\]

with \( \Gamma_c = \frac{\delta E}{\sqrt{\ln(2)}} \).

The functional \( f \) is the Fermi-Dirac distribution, with the (quasi-) Fermi level \( E_f \):

\[
f(E) = \frac{1}{\exp\left(\frac{E - E_f}{kT}\right) + 1} \quad (9)
\]

If we assume \( A_b/A_d = 5 \) and \( E_f = 0 \), we obtain a good correspondence with the experiments (see Figure 2b and Figure 4 in the main paper, Supplementary Fig. 10 below).

**Supplementary Figure 10:** Absorbance for different exciton densities (0-0.06-0.12-0.3) simulated based on the equations in section 9.1. The absorbance at the interband peak was rescaled to match the 0.1 absorbance of the experiment (see Fig. 2b).
8.2 Estimation of gain threshold under CW and pulsed conditions

The gain under continuous wave excitation occurs under remarkably low thresholds which we attribute to both the 'thresholdless' behaviour and the extraordinary long lifetime of the trapped hole. An estimate of the gain threshold $P_{th, ASE}$ under CW pumping follows from the following relation:

$$P_{th, ASE} = \frac{\langle N \rangle E_{ph}}{\tau_g \sigma_{abs}}$$

(10)

Here, $\langle N \rangle$ is the exciton density needed for gain, $\tau_g$ is the population inversion lifetime, $\sigma_{abs}$ is the absorption cross section ($\sigma_{abs} = \mu V$; with $V$ the volume of the QD) estimated as $10^{-14}$ cm$^2$ and $E_{ph}$ is the pump photon energy, which amounts to 2.77 eV at 447 nm. The measured CW gain coefficient is around 2.5 cm$^{-1}$, which concurs according to our results to 0.06 excitations per dot on average. Indeed, the intrinsic gain coefficient at $\langle N \rangle = 0.06$, see Figure 2, amounted to 250 cm$^{-1}$, a figure resulting in a gain coefficient of 2.5 cm$^{-1}$ in the case of a 1 vol% film. The excited state lifetime can be estimated from the average lifetime of the gap-state emission, which is close to 30 µs. Combining these numbers yields $P_{th, ASE} = 84$ mW/cm$^2$, fairly close to the pump rate of 100 mW/cm$^2$. Clearly, both the long lifetime of the gap state and the low threshold carrier density are crucial to obtain such low CW pump threshold.

To position the energy density under pulsed excitation, we consider the following. A gain threshold expressed in µJ/cm$^2$ provides the energy a single femtosecond pulse should deliver to create a state of population inversion that exhibits net optical gain. This threshold depends on the ratio between the excitation density $\langle N \rangle$ needed per QD and the cross section $\sigma$ of a QD. At the pump wavelengths typically used, $\sigma$ scales with the QD volume. This dependence forms the basis to represent ASE thresholds as a function of the QD volume, an example of which is shown in Supplementary Fig. 11 (figure taken from ref. 6). One sees that most systems included fall on a line with a slope of -1. This indicates that the threshold excitation density is roughly the same for all these systems. Hence, more voluminous systems have a lower threshold because the absorption cross section increases proportionally to the volume. In the case of the HgTe QDs used here, $\langle N \rangle$ is exceptionally low. However, since small HgTe QDs were used, also $\sigma$ is small and this counteracts the advantage of the small threshold density. This balance can be neatly illustrated by adding the threshold / volume pair for HgTe QDs as measured here to Supplementary Fig. 11. One sees that gain thresholds are obtained similar to those of nanocrystals that have a 100-fold larger volume or, conversely, that a 100-fold lower gain threshold is obtained as compared to nanocrystals with the same volume.
Supplementary Figure 11: Taken from the review by Pietyga et al. and adapted to show the position of this work. The observed ASE threshold energy density under femtosecond pulsed excitation is comparable to state-of-the-art, yet is achieved at a nanocrystal volume up to two orders of magnitude lower.

8.3 Discussion of trion formation
A final complication in our model could arise from possible formation of trions in the particles with surface traps upon photo-excitation (see Supplementary Fig. 12). However, the probability for 2 holes to be present in the valence band level VB1 simultaneously is, assuming thermal equilibrium, given by: \( \exp\left(\frac{-2\Delta}{kT}\right) \), where \( \Delta \) is the energy difference between the Fermi level and VB1. This implies that the average rate for positive trion recombination is given by: \( k_{X^+} \times \exp\left(\frac{-2\Delta}{kT}\right) \), where \( k_{X^+} \) is the intrinsic interband trion recombination rate. The latter can be estimated from the Auger lifetime of a biexciton (ca. 50 ps, see Supplementary Fig. 3) as \( \tau_{X^+} = 4\tau_{XX} = 200 \) ps. The energy separation \( \Delta \) is estimated as 120 meV from the decomposition in Figure 1b, which results in: \( k_{X^+} \times \exp\left(\frac{-2\Delta}{kT}\right) \approx 3e5 \) s\(^{-1}\), or an effective lifetime of 3 \( \mu s \), much more compatible with the long timescales under CW excitation. Importantly, we also do not observe any trion recombination at low excitation densities (see Figure 2d, main text) confirming the ideas outlined above. If thermal excitation rates are slow (or even irreversible) compared to the overall timescales and/or when the presence of a hole blocks the addition of a second hole (e.g. through Coulomb repulsion), the above considerations will only tilt to longer lifetimes.

Supplementary Figure 12: Scheme explaining that the probability for 2 holes to be present in the valence band levels is very small giving rise to 'average' trion lifetimes in the order of several microseconds at least.
9 Estimation of Capture Rate

We assume that the capture of the hole from the valence band to the trap (T → G) is a multi-phonon process described by the configuration coordinate diagram of Supplementary Fig. 13. This is a reasonable assumption since we know from experiments that the ionization energy $E_i$ is about 100 meV, in average, to compare with the optical phonon energy of 17 meV in HgTe. An upper value of the relaxation energy $\Delta_r$ (Franck-Condon shift) can be estimated from the width of photoluminescence spectrum coming from the relaxation of the electron from the conduction band to the trap (blue arrow in Fig. 1). In absence of inhomogeneous broadening, the full width at half maximum (FWHM) at 300K is approximately given by $8\ln(2)\Delta_r kT$. From the experimental spectrum (that includes inhomogeneous broadening), we know that the FWHM must be smaller than ~100 meV, which gives an upper value for $\Delta_r$ of 35 meV. This is a surprisingly small value for a surface point defect. For example, in the case of the Si dangling bond, $\Delta_r$ is of the order of 300 meV. We take for example a value for $\Delta_r$ of 25 meV. In absence of energy barrier for the relaxation ($E_B = 0$) the capture cross of point defects is typically of the order of $10^{-14} - 10^{-15}$ cm$^2$. From that, we are able to calculate the capture lifetime as described by Delerue et al. Supplementary Fig. 13 (right) shows that, for $E_i$ of the order of 100 meV, the capture lifetime would be of in the range of 0.1-1 ns.

Supplementary Figure 13: Left: Configuration coordinate diagram for a HgTe quantum dot in its ground state (G), after band-to-band excitation (E), and after radiative relaxation of the electron on the trap state (T). Right: Capture (T→G) lifetime versus trap ionization energy $E_i$. The lifetime is calculated assuming a capture cross section $\sigma_{\text{cc}}$ of $10^{-15}$ cm$^2$ (solid red line) or $10^{-14}$ cm$^2$ (dashed blue line).

10 Surface Chemistry

Experimental Methods

Purification of HgTe QDs. HgTe QDs were purified by adding equal volumes of toluene and methanol as solvent and anti-solvent combination. We suspected that during washing steps, there is a loss of Hg-thiolates. To detect the presence of Hg-thiolates, XRF was used as a technique to do elemental analysis to confirm the presence of “Hg” in the supernatant. To rule out the possibility of detecting unreacted Hg, the analysis for Hg is carried out only from 3rd washing step. X-ray fluorescence (XRF) sample preparation. XRF measurements were performed on Rigaku NEX CG instrument. Samples for XRF analysis were prepared by concentrating the supernatant obtained during the purification of HgTe QDs. A few microliters of a given supernatant (3times washed, 4 times washed or 6 times washed) was drop casted
on a filter paper, it was allowed to dry for a while. Dried samples were analyzed with XRF.

Results
To support the proposed surface-related gain mechanism, we analysed the surface chemistry and elemental composition of the HgTe QDs using a combination of NMR (nuclear magnetic resonance) and XRF (X-ray fluorescence) spectroscopy. Our goal is to demonstrate that HgTe QDs are stripped of as Z-type ligands, i.e. Hg-thiolates instead of thiols, upon washing, a prerequisite to the formation of mid-gap states through earlier work of Houtepen et al.\textsuperscript{11} (see also Supplementary Fig. 14). As the authors pointed out, the Z-type nature is important as it induces mid-gap states when multiple ligands are stripped due to the formation of 2-coordinated chalogenide atoms. Thus, we aim at showing that (a) we strip ligands upon washing (using NMR) and (b) we specifically displace metal-thiolates, not just thiolates (using XRF).

Supplementary Figure 14: Model of HgTe surface chemistry and the effect of consequent washing steps. where X=RS.

The use of NMR to study the surface (chemistry) of colloidally dispersed QDs is well established and a large toolbox is available to study ligand binding to QD facets.\textsuperscript{12} Our goal is to use quantitative 1D-NMR to measure the ligand density on the QD surface and study the effect of subsequent washing steps (see Supplementary Figs. 15,16). Table 1 shows the results for washing steps 4 and 6, the earlier steps are difficult to analyse as residual organics cloud the NMR analysis. A clear decrease of 20% in the ligand density is observed going from washing step 4 to 6 (see Table 1), which would amount to a removal of roughly 20 ligands on a 3 nm particle. This result is not entirely unexpected as exposure to strong protic non-solvents can lead to ligand stripping as was shown by Hassinen \textit{et al.}\textsuperscript{13} Assuming that the washing displaces Hg-dithiolates (see further), this would correspond to the removal of 10 Z-type metal-dithiolate units from the surface. Importantly, the ligand density of ca. 3 - 3.5 nm\textsuperscript{-2} corresponds quite well to the model of Houtepen \textit{et al}, where a similar critical ligand density was found for the formation of mid-gap states\textsuperscript{11} and the DFT modeling of this work (see section 11).
Supplementary Figure 15: Nuclear Magnetic resonance (NMR) measurements on HgTe QDs were performed in deuterated Toluene-d8. For the quantification of ligands on the surface of HgTe QDs, -CH₃ protons of 1-Dodecanethiol were analyzed. 1D-H NMR spectra showing decomposition of bound (dashed) and free (dotted) ligands for (a) 4 and (b) 6 times washed HgTe QDs. The assignments to bound and free are made based on the DOSY analysis shown in Supplementary Figure 15. The sharp peaks at lower ppm values are due to free contaminants, most likely residual OLAm.

Supplementary Table 1: NMR results showing the concentration used in the experiment, the total ligand density and the extracted bound density (in ligands/nm²).

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<th>HgTe sample</th>
<th>Concentration (µM)</th>
<th>Size of particles (nm)</th>
<th>Total density (lig/nm²)</th>
<th>Bound density (lig/nm²)</th>
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<tr>
<td>4 times washed</td>
<td>106.5</td>
<td>3.3</td>
<td>4.25</td>
<td>3.5</td>
</tr>
<tr>
<td>6 times washed</td>
<td>140.1</td>
<td>3.3</td>
<td>4.03</td>
<td>2.76</td>
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</table>

Supplementary Figure 16: DOSY analysis of DDT showing bound DDT and freely exchanging DDT together with free DDT. Note that the hydrodynamic diameter matches quite well with the 3 nm HgTe QDs used.
Supplementary Figure 17: XRF spectra measured using different sources (a) Mo for Hg and (b) Al for Te, showing strong presence of Hg, yet no clear sign of Te.

The loss of ligands does not necessarily imply that metal-ions are displaced, i.e. we still have to find evidence for displacing Hg-dithiolate (Z) instead of just thiolates (L). To do so, we analysed the supernatant of a number washing step using XRF (see Supplementary Fig. 16), where we look specifically for Hg and Te. As is pointed out in Table 2, we find a strong presence of Hg and no trace of any Te. S is also detected yet is difficult to separate from the Hg-signals.

Supplementary Table 2: XRF analysis results on different purification steps of HgTe QDs.

<table>
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<th>No. of purification steps</th>
<th>Total (mg/cm²)</th>
<th>Hg (mass %)</th>
<th>Te (mass %)</th>
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<td>HgTe 3</td>
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<td>100</td>
<td>Not detected</td>
</tr>
<tr>
<td>HgTe 4</td>
<td>0.0022</td>
<td>100</td>
<td>Not detected</td>
</tr>
<tr>
<td>HgTe 6</td>
<td>0.0068</td>
<td>100</td>
<td>Not detected</td>
</tr>
</tbody>
</table>

The combination of XRF and NMR convincingly shows that we are displacing Z-type metal-dithiolates when exposing the QDs to methanol during the washing steps. The effect of this displacement on the optical properties is shown in Figure 4b of the main manuscript: a decrease in band gap emission quantum yield and a concomitant increase of the gain cross section per QD. The strong correlation between the stripping, the formation of mid-gap states and the increase in gain cross section, strengthen the proposed gain model of surface-mediated optical gain.

11 DFT Modeling

Pristine and Z-type displaced HgTe QDs of about 2.0 nm in diameter were cleaved from the bulk zinc-blende crystalline structure. For all cases, QDs exhibit a non-stoichiometric inorganic core with an excess of cation charge fully compensated by X-type thiolate ligands (see Supplementary Fig. 18). Their electronic structure was computed at the DFT level of theory using the PBE exchange-correlation functional and a double-zeta basis set as implemented in the CP2k quantum chemical package. Relativistic effects were incorporated using effective core-potentials. All geometries were fully relaxed in vacuum.
Supplementary Figure 18: Relaxed structures for Hg with increased Z-type ligand removal (left to right). See also Figure 4c, main text.

Oscillator strengths were computed from the matrix elements of the position operator using the QMWorks-NAMD interface to CP2k:

\[ f_{i\rightarrow j} = \frac{2}{3} E_{i\rightarrow j} \sum_{\mu=1}^{3} |\langle \phi_i | \mu | \phi_j \rangle|^2 \]

Here, \( E_{i\rightarrow j} \) is the one-electronic transition computed as an energy difference between Kohn-Sham states \( \phi_i \) and \( \phi_j \), and \( r_{\mu} \) is the position operator. The optical spectra are computed by convoluting the computed peaks with a 0.1 eV Gaussian to take into account line broadening due to thermal motion.

Supplementary Figure 19: Absorption Spectrum (on relaxed structure of each system) In the system with 1 and 4 Hg(SCH3)2 removed, the transition from the LUMO to the gap state has a non-negligible oscillator strength.

Supplementary Fig. 19 illustrates the optical spectrum of the pristine and Z-type displaced HgTe QDs. For all structures, the main peak is featured by two bands that can be ascribed to the X1 and X2 excitons, also seen in the tight-binding calculations. Upon removing 1 and 4 Z-type Hg(SCH3)2 ligands, the HgTe QDs experience substantial structural reorganization with the formation of stable 2-coordinated Te atoms at the surface. These atoms present non-bonding 5p orbitals that intrude the bandgap of the QDs. The oscillator strength from the CB edge to the surface traps are substantial as evinced in the computed spectra and in the Table below.
Supplementary Table 3: Characterization of the Z-type displaced QDs in terms of their surface states. Radiative lifetimes are calculated according to Eq. 14.

<table>
<thead>
<tr>
<th>Quantum Dot</th>
<th>Number of Traps</th>
<th>Oscillator Strength CB -&gt; Trap</th>
<th>Localization on Te-2c (%)</th>
<th>Calculated Radiative Lifetime (μs)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hg₆₇Te₅₅(SCH₃)₂₄</td>
<td>1</td>
<td>0.14312</td>
<td>58</td>
<td>7.1</td>
</tr>
<tr>
<td>Hg₆₄Te₅₅(SCH₃)₁₈</td>
<td>4</td>
<td>0.45921, 0.08899, 0.05664, 0.51411</td>
<td>47, 51, 52</td>
<td>2.2, 12.5, 17.8, 1.96</td>
</tr>
<tr>
<td>Cd₆₇Se₅₅(SCH₃)₂₄</td>
<td>1</td>
<td>0.00336</td>
<td>67</td>
<td>/</td>
</tr>
<tr>
<td>Cd₆₇Te₅₅(SCH₃)₂₄</td>
<td>1</td>
<td>0.00133</td>
<td>62</td>
<td>/</td>
</tr>
</tbody>
</table>

Table 3 illustrates also a comparison with similar II-VI QDs, with Cd instead of Hg and Se instead of Te. For the Cd based QDs the 2-coordinated surface trap is strongly localized, which renders it less optically active. For HgTe, the situation is reverse. The surface states are still localized, but much less and almost half of the mid gap orbital leaks on nearby atoms. This partial delocalization helps in increasing optical activity by increasing the overlap with the conduction band states. For the HgTe QD where one Z-type ligand has been displaced, the trap state appears at ~0.3 eV above the valence band maximum after structural relaxation. This is slightly higher than the experimental value of ~0.15 eV. We thus explored the effect of thermal motion on the position of the trap level by performing a molecular dynamic simulation of 5ps in a NVT canonical ensemble at 300 K. The simulation box was initially equilibrated for 2 ps using a velocity rescaling algorithm. A timestep of 1fs has been employed in all runs.

Supplementary Figure 20: Distribution of the energy difference between the trap and the valence band maximum on a 5ps NVT MD simulation at 300K.

In Supplementary Fig. 20 we plotted the distribution of the energy difference between the trap and the valence band maximum (VBM) throughout the dynamics. The trap level is fairly sensitive to the vibrational modes with a broad thermal distribution peaking at 0.1 eV, in much better agreement with the experiments. In some cases, for very short times, the trap level can be also found below the VBM, as evidenced by the negative distribution values.
Using the oscillator strength calculated above, we can make an estimation of the radiative lifetime of the gap state transition using: \(^{14}\)

\[
\tau^{-1} = \frac{e^2}{2\pi \varepsilon_0 c^3 m_e} \times n_s |f_{LF}|^2 \times \frac{\omega^2}{g} f
\]  

where reasonable estimates are: \(n_s = 1.45\) (solvent refractive index), \(f_{LF} = 0.3\) (local field factor), \(g = 4\) and \(f\) the oscillator strength, see table 3. We find lifetimes of \(ca. 20 \mu s\), fairly close to the observed microsecond lifetime of the gap state (see main text, Figure 1c). We note that the calculated lifetime is the radiative lifetime whereas the measured lifetimes are a combination of non-radiative and radiative contributions. As the QY for the gap state is far from unity, we should be cautious to make the direct comparison yet the calculated lifetimes give a good upper bound for the actual experimental lifetime(s).
12 References