Lifetime prediction of encapsulated CdSe$_x$S$_{1-x}$ quantum platelets for color conversion in high luminance LED microdisplays: supplement

E. QUESNEL,[1,*] **S. PONCET,**[1] **S. ALTAZIN,**[1] **Y. P. LIN,**[2] **AND M. D'AMICO**[2]

[1]*Université Grenoble-Alpes, CEA, LETI, MINATEC Campus, 17 rue des Martyrs, F-38054 Grenoble cedex, France*
[2]*NEXDOT, 102 avenue Gaston Roussel Biotech-bâtiment Pasteur, 93230, Romainville, France*
[*]*etienne.quesnel@cea.fr*

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Note S1: Effect of QP concentration on aging curve

We observe some blue absorption (A_b) variation among the different samples tested (Table 1 of paper). It is thus necessary to check the influence of A_b on aging kinetic. Figure S1 compares samples with different QP concentrations aged at same blue irradiation power density P_b=6 W/cm^2. Between 60 and 90% of blue absorption, the aging kinetics are similar, within our margin of measurement accuracy. When A_b becomes low, the aging kinetic slightly accelerates. This result was expected since the blue light irradiation power emitted by the LED decreases in the thickness of conversion layer. It is maximal (6 W/cm^2) for the QPs located at the conversion coating-LED interface and decreases when approaching the conversion coating-air interface. This decrease is less when the QP concentration is lower; so the aging conditions are more severe for low QP concentration, than for high QP concentration.
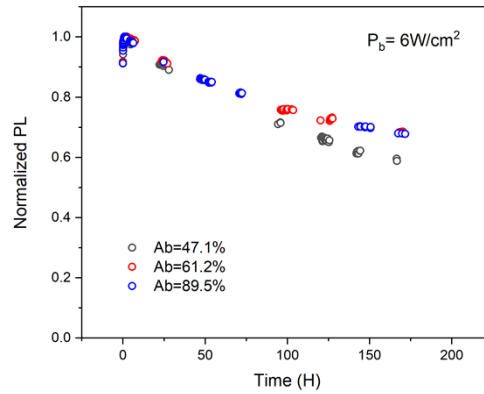

Fig. S1. Comparison of PL decays measured under same blue power irradiation density P_b (6 W/cm^2) on samples exhibiting different blue absorptions A_b (different QP concentrations).

Note S2: Stability of neat blue LED and of conversion layer absorption during aging test.

Fig S2 shows the emission variation over time of a neat blue LED, without any QP coating, and, as an example, the evolution with aging time of the blue absorption of QPs-based coating submitted to a very high blue LED fluence of 7.5 W/cm^2. We observe for the neat LED a PLED variation of $\pm0.15\%$ and a variation of $\pm0.7\%$ for the QPs based coating absorption. Actually, in most cases and test conditions it was limited to $\pm0.5\%$. This result shows that the PL decay (several 10%) observed in all our aging tests is neither due to the variation of LED blue emission nor to those of blue absorption by the QPs coating. In other words, the red PL decay can be clearly attributed to the creation of photo-induced defects that impact the radiative recombination, hence the resulting PL quantum yield.
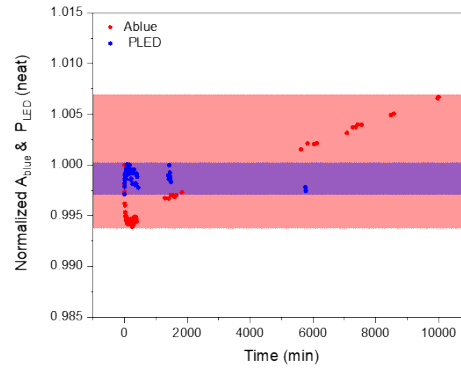

Fig. S2. In blue, variation over time of the relative radiant power PLED emitted by a neat blue LED (without coating) operated at 6W/cm^2 and room temperature. In red, relative variation of the blue absorption of a conversion layer deposited on a blue LED operated at room temperature and 7.5 W/cm^2.

Note S3: Determination of actual QP temperature during aging test.

Our aging tests are performed in ambient air (~25 °C) with the sample temperature monitored by a control module (heating resistance associated with a Peltier cooling system) inserted in the sample holder. The LED is mechanically fixed to the metallic holder and is in contact with it through its star-shape PCB. The QP layer is separated from the LED by the sapphire substrate on which the LED was grown. The thermal contact between the conversion layer and the Peltier module is thus not optimal (see Fig. S3b). As a result, when the setup temperature significantly deviates from ambient temperature, the temperature of conversion layer when operated at high P_b, can stabilize at higher temperature, which could induce a shift of QP emission peak. The shift of red PL peak can be used to determine the actual aging temperature of QPs, provided the coefficient temperature TC governing this shift is known. For that purpose, the red PL emission spectra of QPs has been measured at different temperatures in the 15-45 °C range with the LED operated for a short time at low power (1.3 W/cm^2) to avoid any extra heating of the QPs brought by the blue radiant power. The deduced TC of QPs is found to be equal to 0.13 nm/K (Fig S3).
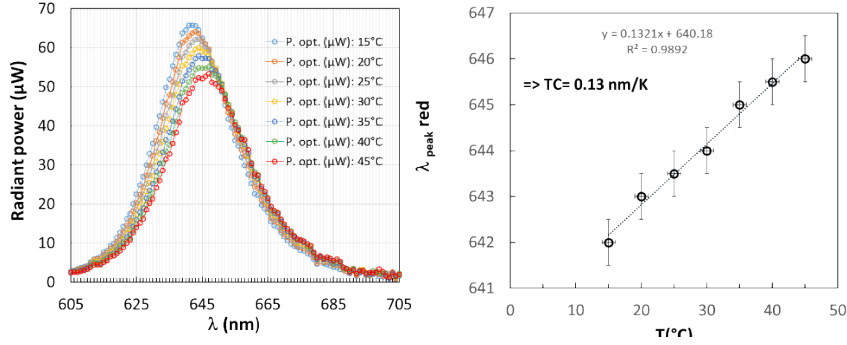

Fig. S3a. Shift of red PL peak versus temperature. The LED is operated at 1.3 W/cm^2. The temperature coefficient TC is the slope of linear fitting curve obtained with a rather good fitting accuracy (R^2~0.99).

On this basis, we have analyzed the PL shift of samples operated at different temperatures. Reference temperature is 25 °C. As an example, Fig. S4 shows how the red emission peak evolves during an aging test performed at 45 °C (setup T°) with a high blue radiant power of 6 W/cm^2. We observe that, when heating the substrate holder from 25 to 45 °C, the red PL peak red-shifts in the first minutes of aging by + 4 nm, which gives for the conversion layer +31 °C with respect to initial 25 °C. That is why in our graph of figure 3, we take an actual aging temperature of 329 K. The temperature of the other aging experiments has been determined using the same procedure.

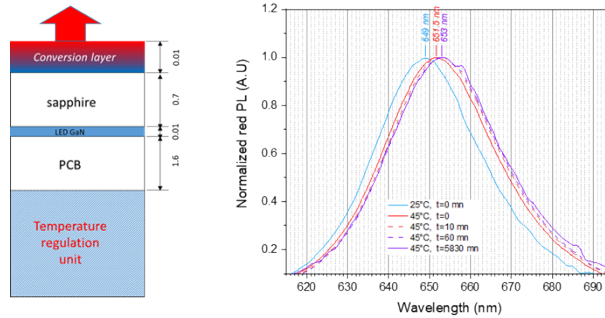Fig. S3b. Architecture of LED test sample and shift of red PL peak measured between 25 and 45 °C (setup T°) and 6 W/cm^2 permanent blue irradiation condition.

Note S4: Possible scenario for the photo-degradation mechanism.

A process has been proposed by V. A. Krivenkov et al [18] with a schematic representation of the ligand photo-oxidation process which occurs upon laser irradiation of QDs. If we adapt this process to our case, it could give the following sketch:
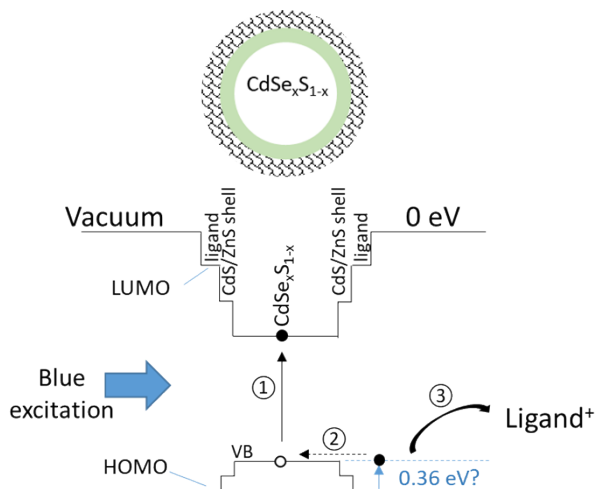

Fig. S4. Schematic representation of the ligand photo-oxidation process.

The photo-oxidation mechanism could be schematically seen as resulting from the following successive steps:

1 - Electron from valence band of $CdSe_xS_{1-x}$ moves to the first excited state upon blue excitation;

2 - Electron from highest occupied molecular orbital of ligand (HOMO) migrates to the vacant position in the VB of $CdSe_xS_{1-x}$ core via rapid tunneling through CdS/ZnS shell;

3 – Ligand$^+$ desorbs from the surface of QPs.

If this scenario is confirmed, the thermal activation energy governing the annihilation of emission centers deduced from our experiments (0.36eV) could correspond to the gap of energy between the VB of $CdSe_xS_{1-x}$ core and the HOMO level of ligand. The hole of VB by recombining with the "ligand electron" would prevent the radiative recombination.