



LIGHTINGEUROPE

THE VOICE OF THE LIGHTING INDUSTRY

**LightingEurope request for a
new exemption for the use of
cadmium in luminescent
material for on-chip application
on LED semiconductor chips
(lighting), Annex III of RoHS
Directive 2011/65/EU**

Date of submission: 29 September 2017

1. Name and contact details

1) Name and contact details of applicant:

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2. Reason for application:

Please indicate where relevant:

Request for new exemption in: ANNEX III

Request for amendment of existing exemption in

Request for extension of existing exemption in

Request for deletion of existing exemption in:

Provision of information referring to an existing specific exemption in:

Annex III

Annex IV

No. of exemption in Annex III or IV where applicable: _____

Proposed or existing wording: _____

Duration where applicable: _____

Other: _____

3. Summary of the exemption request / revocation request

Applicant requests a new exemption under the RoHS Directive (2011/65/EU) for the use of cadmium in luminescent material for on-chip application on LED semiconductor chips, to be added to Annex III of the aforementioned Directive. This specific use of cadmium will enable significant energy savings.

This request is submitted as per the recommendation of Oeko Institut to clarify the questions that could not be answered during the assessment of the request to extend RoHS exemption 39 in Annex III (Gensch, et al., 2016). It was recognized by Oeko Institut that the use of cadmium provides energy saving benefits in certain applications, but an exemption could not be phrased as insufficient information was available to accurately limit the scope (Gensch, et al., 2016). In the Commission Delegated Directive of August 7, 2017 it is indicated that “*it is always possible to submit a request for exemption in the future when information is available for applicants to demonstrate that cadmium-based specific illumination applications have benefits over other light source alternatives, so to meet one of the criteria for RoHS exemptions*”¹.

For this reason, we are in this new exemption request proposing an exemption (wording) that is more narrowly limited to the specific use of this new technology in LED semiconductor chips.

The wording for the new exemption is proposed as follows: “Cadmium (<1000 ppm) in luminescent material for *on-chip* application on LED semiconductor chips for use in lighting applications of at least CRI 80.”

Introduction to luminescent material

Conventional solid-state lighting technology is based on blue LEDs exciting a garnet and red phosphor (phosphorescent light downconverter) to generate green, yellow and some red light, which is mixed to form white light for illumination purposes. To bring LED illumination closer to the high color quality of incandescent light sources it is necessary to add a significantly higher amount of red phosphor of longer wavelengths to produce the warm tones missing from the garnet phosphor spectrum. The broad spectrum of conventional red phosphors causes a large drop in luminous efficacy as the emission further reaches deep red and infrared wavelengths where the eye sensitivity is low. Similar to incandescent bulbs, a significant part of the generated light is wasted as infrared radiation. One of the key R&D priorities of the LED industry is therefore to develop new high efficiency, narrow line-width downconverter materials, of which quantum dot luminescent material is the most promising technology currently available.

Quantum dots (QDs) are a relatively new material class that, like phosphors, downconvert light from higher energy wavelengths of typically blue light to lower energy wavelengths in the visible and near-IR. Key characteristics of quantum dots are their potentially very high efficiency, their narrow emission spectrum, and that their emission wavelength can be accurately tuned across the entire visible spectrum. The narrow emission spectrum prevents the needless generation of invisible infrared radiation (see Figure 1). No other downconverter exists which exhibits narrow emission (<40 nm full width at half maximum, or FWHM), is wavelength-tunable to within 1 nm, and has very high photoluminescence quantum efficiencies, both at room temperature and LED operating temperatures. These features make QDs ideal to be used in improving the performance and energy efficiency

¹ Commission Delegated Directive - C(2017)5446/941186

of today's white phosphor-converted LEDs by replacing one or more of the phosphors used as a light downconverting elements.

At the moment, the only type of quantum dot that can be used in an on-chip configuration and has the aforementioned advantageous properties is a cadmium (Cd) containing quantum dot. The quantum efficiency and reliability under on-chip operating conditions has not been resolved for alternative non-cadmium materials. Cadmium is a component in II-IV semiconductor quantum dots (typically based on CdSe or CdS) and is used in the quantum dot core or quantum dot shell.

The use of Cd-containing Quantum Dots in on-chip LED applications will enhance the luminous efficacy of LEDs by 10-20 % (based on CCT and CRI) above best-available conventional phosphors. This provides significant energy savings that clearly outweigh the potentially negative effects of a rather limited amount of cadmium entering the market in a safely encapsulated form.

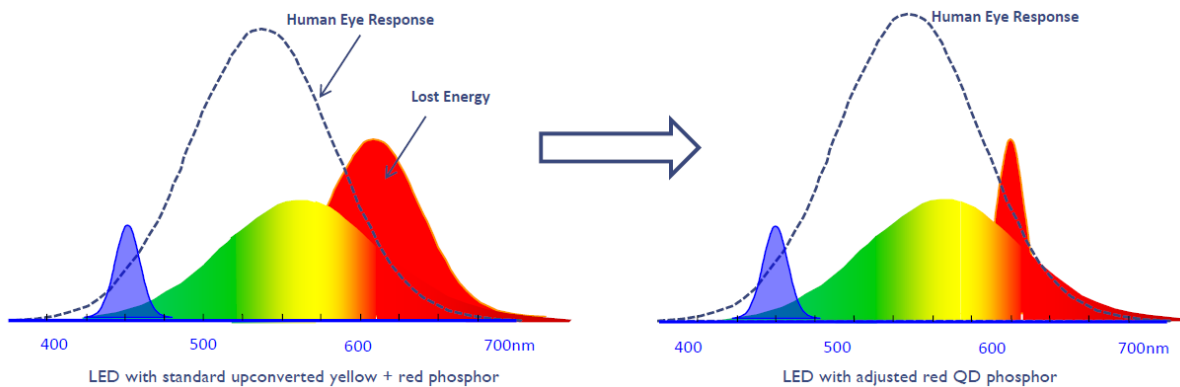


Figure 1: Comparison of QD and conventional phosphor spectrum (Source: Yole Développement, "Phosphors and Quantum Dots 2015: LED Downconverters for Lighting and Display Applications", 2015)

On-chip application

Until now, it has not been possible to use QDs directly in LED packages because of thermal quenching, sensitivity to oxygen and water, and light density issues. Through 2016 they have been deployed only in a "remote" configuration where the QDs are separate from the blue LED and packaged as a separate optical element in the luminaire. Recently, technology has been developed which allows QDs to be deployed inside the LED package². This allows LED manufacturers to use the least amount of QD material per lumen of light, and is also the lowest cost and most flexible way to utilize quantum dots in either lighting or displays³. The added benefit of being able to use QDs directly in the LED package is utterly important for making this technology more economic and energy-efficient. However, solely cadmium-containing, high-performance QDs are applicable for on-chip LED application to-date. By design, QDs developed for use inside LED packages contain significantly less total cadmium than the remote QD implementations that are currently available and still preserve the performance benefits

² B. D. Mangum, T. S. Landes, B. R. Theobald, and J. N. Kurtin, "Exploring the bounds of narrow-band quantum dot downconverted LEDs," *Photonics Research*. 5, A13–A22 (2017).

³ K. T. Shimizu, M. Böhmer, D. Estrada, S. Gangwal, S. Grabowski, H. Bechtel, E. Kang, K. Vampola, D. Chamberlin, O. B. Shchekin, and J. Bhardwaj, "Towards commercial realization of quantum dot based white LEDs for general illumination," *Photon. Res.* 5, A1–A6 (2017).

of increasing energy efficiency, higher quality of light and better color gamut that have been documented in previous RoHS exemption applications for cadmium in lighting and display applications.

Rationale for the exemption

This request for a RoHS exemption is justified on the basis that the safe use of minimal amounts of cadmium leads to a significant increase in the luminous efficacy of LED lighting, especially for warm-white light sources of CRI of at least 80. The same energy savings cannot currently be reached with similar technologies while maintaining product reliability and lifetime. As a result, utilization of cadmium-containing quantum dots has an overall positive environmental impact due to their lower energy consumption compared with currently available technologies. With reference to Article 5(1)(a) third criterion, a specific exemption for the use of cadmium for lighting applications is therefore justified. In addition to the reduction in energy and CO₂ emissions, other emissions derived from power plants will be reduced, including cadmium emissions. In fact, the low amount of safely incorporated cadmium per QD LED is much smaller than the amount of cadmium emitted over the lifetime of the LED by the generation of the additional electricity required if less efficient LED packages or competitive technologies would be operated. Additionally, on-chip QD technology enables the use of significantly less cadmium than use in remote applications. This application for an exemption is dedicated to on-chip QD downconverters for energy efficient lighting applications. In this submission, we are describing the following:

- Why application at the chip level is necessary for integration into lighting.
- Products utilizing on-chip QDs for the lighting application and the benefits gained in both energy efficiency and color quality.
- The current status and timeline for use of Cd-free quantum dots at the chip level.
- Alternative technological approaches and the unique benefit that QDs provide.

There is no technical substitute developed yet for the cadmium-based on-chip quantum dot technology. This application is intended to demonstrate that potential Cd-free QD alternatives fall far behind the performance and stability requirements to reliably increase the efficiency of a white lighting LED by up to 20 % in combination with a precise control over the light output spectrum. Due to their wider emission peak width and poor performance at elevated temperatures, as well as poor reliability, Cd-free QD materials are inadequate for use in lighting applications. For the foreseeable future, there exists no other substitute that can match the benefits of the current technology based on Cd-containing QDs.

Total energy savings and total cadmium use by means of transition scenarios

As estimation of total energy savings, total QD cadmium use, and avoidable cadmium emissions related to energy savings is possible based on the total lighting capacity installed. In the EU, the lighting capacity is 10.77 Tlm (Tera lumen)⁴. The following table compares the scenarios of using LED packages based on conventional phosphors and LED packages based on cadmium containing quantum dots to provide the light output of 10.77 Tlm.

	Unit	Full transition (100%)		1% transition		2% transition		5% transition	
		QD LED	Conv	QD LED	Conv	QD LED	Conv	QD LED	Conv
Total light output in EU (2013)	Tlm	10.77	10.77	0.11	0.11	0.22	0.22	0.54	0.54
Light output per LED	lm	106.40	105,18	106.40	105.18	106.40	105.18	106.40	105.18
Number of LEDs required	bln #	101.22	102,39	1.01	1.02	2.02	2.05	5.06	5.12
Power consumption per LED	W	0.80	0.92	0.80	0.92	0.80	0.92	0.80	0.92
Power consumption of LEDs required	GW	80.56	94.70	0.81	0.95	1.61	1.89	4.03	4.73
Annual operating hours per LED ⁵	h	1,000.00	1,000.00	1,000.00	1,000.00	1,000.00	1,000.00	1,000.00	1,000.00
Total power consumption (per year)	GWh	80,564.71	94,698.84	805.65	946.99	1,611.29	1,893.98	4,028.24	4,734.94
Total amount of cd safely employed per LED (lifetime)	ug	1.61	-	1.61		1.61		1.61	
Total amount of cd safely employed in LEDs required	kg	162.97	-	1.63	-	3.26	-	8.15	-
Total power savings per year	GWh	14,134.13		141.34		282.68		706.71	
Total amount of cd emissions avoided per kwh	ug	3.80	-	3.80		3.80		3.80	
Total amount of cd emissions avoided per year	kg	53.71	-	0.54	-	1.07	-	2.69	-

If all light sources in the entire EU were converted to cadmium containing quantum dot LEDs overnight, an estimated 163 kg of cadmium would be required to subsequently save 14.134 GWh of energy and to reduce the emissions of cadmium by 54 kg per year. Noteworthy, this total transition is a fictional scenario generating grossly exaggerated values especially the amount of cadmium that would actually enter the EU market under this exemption. Therefore 3 transition scenarios more likely to reflect real margins are added (1%, 2% and 5% transition of total lighting capacity installed in the EU).

⁴ VHK, "Model for European Light Source Analysis (MELISA) version 0", prepared for the European Commission, Brussels, 31 January 2015

⁵ VHK states annual operating hours for LED between 500-1500 hours, therefore in this table an average of 1000 hours is used. See VHK, "Model for European Light Source Analysis (MELISA) version 0", prepared for the European Commission, Brussels, 31 January 2015, p10

4. Technical description of the exemption request / revocation request

(A) Description of the concerned application:

1. To which EEE is the exemption request/information relevant?

Name of applications or products: 1

a. List of relevant categories: (mark more than one where applicable)

- | | |
|---------------------------------------|-----------------------------|
| <input type="checkbox"/> 1 | <input type="checkbox"/> 7 |
| <input type="checkbox"/> 2 | <input type="checkbox"/> 8 |
| <input type="checkbox"/> 3 | <input type="checkbox"/> 9 |
| <input type="checkbox"/> 4 | <input type="checkbox"/> 10 |
| <input checked="" type="checkbox"/> 5 | <input type="checkbox"/> 11 |
| <input type="checkbox"/> 6 | |

LightingEurope is of the opinion that LEDs in general are category 5, because the majority is used for general illumination. However, they have some of the characteristics of components (used in luminaires). Some manufacturers of electrical equipment in other RoHS categories may install LEDs into their equipment for general illumination purposes and so they will need to use LEDs that comply with the RoHS directive, however the products that they place on the market are not category 5 but may be household appliances, medical devices or potentially in any RoHS category 1 - 11.

LightingEurope is aware of the difficulty to classify certain LEDs unambiguously in the category set out by RoHS legislation. For LED lighting producers it is essential to have legal certainty regarding the possibility to put the products on the market irrespective of the planned application as we are not able to control the use of the LEDs in products falling in other categories or out of the RoHS scope.

b. Please specify if application is in use in other categories to which the exemption request does not refer: N/A

c. Please specify for equipment of category 8 and 9:

The requested exemption will be applied in

- monitoring and control instruments in industry
- in-vitro diagnostics
- other medical devices or other monitoring and control instruments than those in industry

2. Which of the six substances is in use in the application/product?

(Indicate more than one where applicable)

- Pb Cd Hg Cr-VI PBB PBDE

3. Function of the substance:

Cadmium (Cd) is used to meet (and increase) the quantum efficiency and reliability requirements for on-chip applications.

The only type of quantum dots featuring high optical performance over temperature, narrow FWHM, and good stability over time that can currently be used in LED packages are quantum dots which contain cadmium. Cd is a component in II-IV semiconductor quantum dots, either as the group II element in the semiconductor core (based on CdSe, CdS, Cd_{1-y}Zn_ySe or Cd_{1-y}Zn_yS) or as the group II element in the semiconductor shell (based on CdSe or CdS or Cd_{1-y}Zn_yS). The cadmium element is bound by covalent bonds within the semiconductor material, the semiconductor is protected by an additional inorganic coating, and the final particles themselves are safely embedded inside a silicone matrix cured on top of the LED chip.

Quantum dots serve as a replacement for conventional phosphors. They enable higher color quality and higher energy efficiency. At this time there are no alternatives to cadmium in quantum dots that can withstand the operation condition inside an LED package while providing the necessary performance and stability. The only quantum dot compositional system to date that has been proven to directly replace phosphors in LED packages is the Cd-based core/shell system.

Quantum dots perform the same function as the phosphor in an LED. As an example, Quantum dots as produced by one of the QD suppliers (Pacific Light Technologies) are provided in powdered form with a mean particle size of (5-7) μm embedded in a carrier matrix substance such as silicone. The QD material converts shorter-wavelength light to longer-wavelength light. Figure 2 shows the absorption and emission characteristics of on-chip QDs. Key characteristics of QDs are that the emitted light is narrow in spectral width, the emission wavelength can be very accurately engineered to within +/- 1 nm, and all visible colors can be produced. Self-absorption of light is effectively avoided via a separation of excitation (absorption) and emission wavelengths (see blue and red curves in figure below). A fundamental feature of QDs is that the light emission can be targeted much more efficiently than phosphors, resulting in a higher overall LED energy efficiency as measured in lumens per watt.

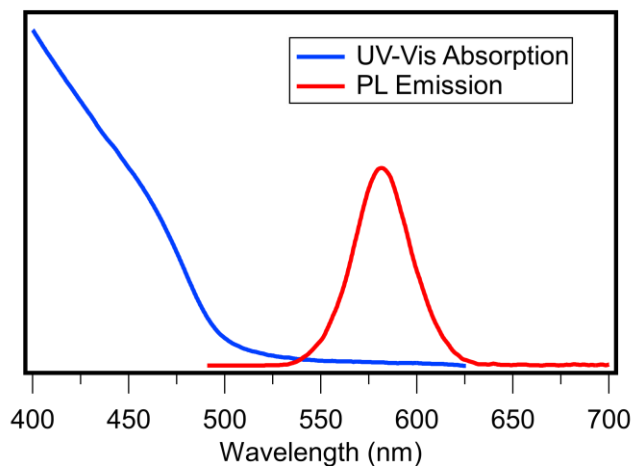


Figure 2: absorption and emission characteristics of on-chip QDs

4. Content of substance in homogeneous material (%weight):

The concentration (by weight) of cadmium in the luminescent material is $\leq 0.1\%$ (≤ 1000 ppm)⁶. The luminescent material is typically a mixture of silicone, phosphor and/or quantum dots forming a solid layer on top of the LED chip.

5. Amount of substance entering the EU market annually through application for which the exemption is requested:

Please supply information and calculations to support stated figure.

An estimation on the amount of cadmium entering the EU market annually through application for which the exemption is requested, is provided in the table on page 5.

A total amount of cadmium is expected to enter the market between 1.6 kg (1 % transition scenario) and 8.1 kg (5 % transition scenario).

6. Name of material/component:

- Cadmium selenide
- Cadmium zinc selenide
- Cadmium sulfide
- Cadmium zinc sulfide
- Cadmium selenide sulfide
- Cadmium zinc selenide sulfide

7. Environmental Assessment:

LCA: Yes
 No

(B) In which material and/or component is the RoHS-regulated substance used, for which you request the exemption or its revocation? What is the function of this material or component?

The substance is used in the form of cadmium selenide, cadmium sulfide, and alloys of cadmium, zinc, selenium, and sulfur in the luminescent material used as the downconverter in LED packages. The cadmium element is bound by covalent bonds within the semiconductor quantum dot material, the semiconductor is protected by an additional inorganic coating, and the final particles are themselves embedded inside a highly stable silicone encapsulant (lens) cured on top of the LED chip.

Semiconductor quantum dots (QDs) are materials whose physical dimensions, without further processing, are on a nanometer scale, typically between 2 and 10 nm. Minor

⁶ In current QD based LEDs, the Cd concentration ranges between ~ 100 and ~ 1000 ppm based on CCT; this equates to a range between ~ 0.3 and ~ 3 μg of Cd per LED. See K. T. Shimizu, M. Böhmer, D. Estrada, S. Gangwal, S. Grabowski, H. Bechtel, E. Kang, K. Vampola, D. Chamberlin, O. B. Shchekin, and J. Bhardwaj, "Towards commercial realization of quantum dot based white LEDs for general illumination," Photon. Res. 5, A1–A6 (2017).

alterations in size or shape ultimately result in a measurable shift in their optical, electronic, and mechanical properties⁷. Essentially, QDs are semiconductor materials which are quantum confined in all three dimensions, distinguishing them from quantum wells or nanowires. Colloidal QDs are synthesized and processed in solution, giving them a unique combination of size-dependent solid-state properties with the handling methodologies of synthetic chemistry⁸. There is a sufficient amount of atoms present that the lattice parameters of the crystallites are similar to those of the bulk material, and the electronic properties are variations of those of the bulk semiconductor. Because of quantum confinement, the absorption and photoluminescence (PL) spectra of quantum dots shift to the blue in a very predictable manner upon reduction of QD size. Sharp absorption features and narrow PL line-widths indicate a narrow particle size distribution. By exerting synthetic control over the particles, emission wavelengths between the UV- and Near Infrared (NIR) range can be generated. The emission spectra of semiconductor quantum dots are typically very narrow (<35 nm) and the emission wavelength can be placed within a 1 nm accuracy. Other useful optical properties of semiconductor quantum dots include: fast (nanosecond) radiative lifetimes, very high (>90 %) quantum efficiency, and high absorption cross section (“potency”), which results in a high number of downconverted photons per unit mass.

Semiconductor quantum dots based on Cd (cadmium selenide CdSe, cadmium sulfide CdS and alloys of cadmium, zinc, selenium, and sulfur) are the most well-studied of the different classes of semiconductor nanomaterials.

The product containing the Cd-based downconverting quantum dot is the light emitting diode package. A slurry is formed by mixing quantum dot materials (which have been processed further to form a dry powder of micron-sized particles), one or more phosphors, and any other additives such as scatterers, into an LED-grade optical silicone encapsulant. A layer of the slurry is applied on the top of a blue LED chip, and serves to downconvert part of the blue light to light of a longer wavelength, forming a white LED package. The white LED package is then used as a component in solid-state luminaires.

(C) What are the particular characteristics and functions of the RoHS-regulated substance that require its use in this material or component?

Other than quantum dots, no other downconverter exists which has a narrow emission band (<35 nm FWHM at room temperature), is emission tunable to within 1 nm⁹, and has very high luminescence quantum efficiencies, both at room temperature and LED-operating temperatures. These attributes allow QDs to increase the efficiency of a white

⁷ Brus, L. E. “A simple model for the ionization potential, electron affinity, and aqueous redox potentials of small semiconductor crystallites” J. Chem. Phys. 1983, 79, 5566 71

⁸ Peng, X. G.; Wickham, J.; Alivisatos, A. P. Kinetics of II VI and III V colloidal semiconductor nanocrystal growth: “Focusing” of size distributions. J. Am. Chem. Soc. 1998, 120, 5343 5344. Steigerwald, M. L., Brus, L. E. Semiconductor crystallites: A class of large molecules. Acc. Chem. Res. 1990, 23, 183 188. Murray, C. B.; Norris, D. J.; Bawendi, M. G. Synthesis and characterization of nearly monodisperse CdE (E = sulfur, selenium, tellurium) semiconductor nanocrystallites. J. Am. Chem. Soc. 1993, 115, 8706 15 Peng, Z. A.; Peng, X. Nearly monodisperse and shape controlled CdSe nanocrystals via alternative routes: Nucleation and growth. J. Am. Chem. Soc. 2002, 124, 3343 3353

⁹ The efficiency penalty in the case of a warm white 90 CRI LED example is approximately 1 % per nm of QD peak wavelength. For example, if the peak wavelength of the intended target is off by 5 nm then an efficiency penalty of 5 % would occur. This is also confounded by the CRI /R9 requirement where the CRI and R9 would also change dramatically. Similar to the efficiency, the CRI can change by ~1 pt per nm and R9 by ~10 pts per nm.

lighting LED by up to 20% while giving the LED manufacturer precise control over the light output spectrum (and therefore color quality). The efficiency benefit will significantly reduce the cost per lumen for the consumer and drive the adoption of solid-state lighting, thus having a very meaningful net benefit to the environment due to lower energy consumption.

The key advantage of Cd-based QD materials designed for lighting products is the ability to operate reliably directly on the LED chip, qualifying as a direct replacement for current phosphor materials. Furthermore, the utilization of such quantum dots results in the application of the minimal required cadmium for this purpose and necessitates little to no re-design of either the lamp or luminaire.

Key on-chip performance factors for QDs are resistance to thermal and intensity quenching¹⁰. Thermal quenching is either the loss of quantum efficiency and/or phosphor photoluminescence output as the temperature is increased. The intensity quenching is the loss of quantum efficiency or phosphor photoluminescence output as the incident blue light intensity is increased. Most phosphor materials show some characteristic of thermal and intensity quenching at different temperatures and different flux intensities. In the case of QDs, the quenching occurs in the form of quantum efficiency loss which negatively affects both color stability and overall LED efficiency. Temperatures at the downconverter level are typically (100-125) °C, and can reach as high as 150 °C in very high-power LED chips. The flux intensity felt by the downconverter is usually in the range of (50-100) W/cm². Cd-based QD materials have been engineered to be reliable under conditions of high temperature and high flux. The result is that Cd-based QDs approach similar thermal and intensity quenching to red phosphor whereas Cd-free QDs suffer significantly higher quenching

In summary, Cd-based quantum dot materials have overcome all the technical challenges related to operating on chip, and therefore are able to deliver the full benefit of the QD materials to lighting products with the lowest quantity of cadmium possible.

QD Applications

Lighting around the world consumes 20 % of generated electricity and there are numerous efforts to make lighting more energy efficient to ultimately minimize greenhouse gases and pollutants generated by fossil fuel burning power plants. Solid state lighting based on semiconductor LEDs is penetrating the lighting market and taking a major share from incandescent bulbs as they are much more energy efficient and longer lasting (25,000-50,000 h vs 2,000 h). LEDs are also suitable for dimming or turning off to save energy and, unlike fluorescent lamps, LEDs do not lose lifetime when switched on and off frequently.

Solid state lighting technology is based on phosphor conversion of blue LEDs. The use of a single broad green/yellow phosphor such as Ce:YAG creates LEDs that are inexpensive, efficient and create reasonably good light (>80 CRI). To produce very good quality of light as defined by CRI $R_a > 90$ & $R_9 > 50$, it is necessary to add an additional red phosphor to produce the warm tones missing from the YAG phosphor spectrum. This is particularly true at lower color temperature (CCT), which relates to how “cold” or “warm” a white light source appears. Figure 3 exemplifies spectra for different CCT values.

¹⁰ Quenching is a process in the quantum dot whereby the excited state produced, by the blue light, relaxes to the ground state without producing visible radiation. The lost energy is dissipated as heat

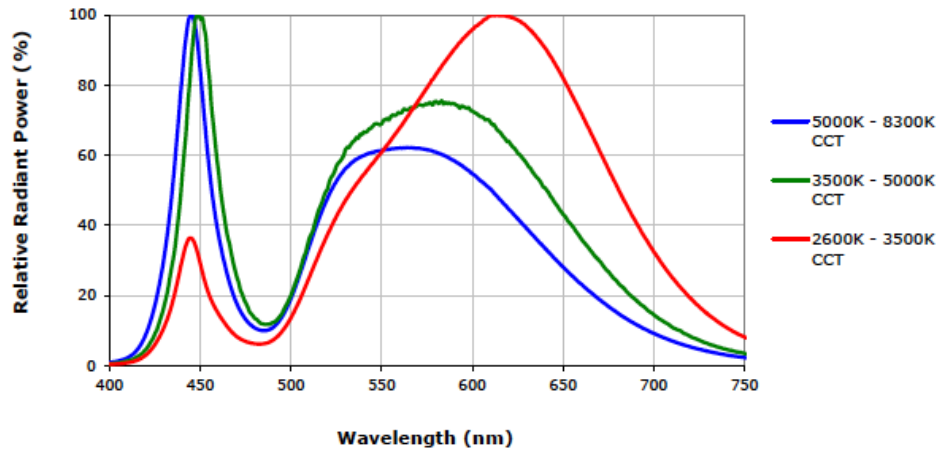


Figure 3. Spectra of conventional phosphor LEDs at various CCT values.

The drawback of red phosphors is the existence of a broad wavelength spectrum and low spectral efficiency relative to green phosphors. LEDs with CRI >90 are always less energy efficient than LEDs that have CRI <80 because of the red phosphor spectral inefficiency. The broad wavelength spectrum of red phosphors reaches deep red and IR wavelengths where the eye sensitivity is low to none. In fact, a significant proportion of the efficiently produced LED light is wasted by emission in the near-infrared range where the human eye is not sensitive at all as shown in Figure 4.

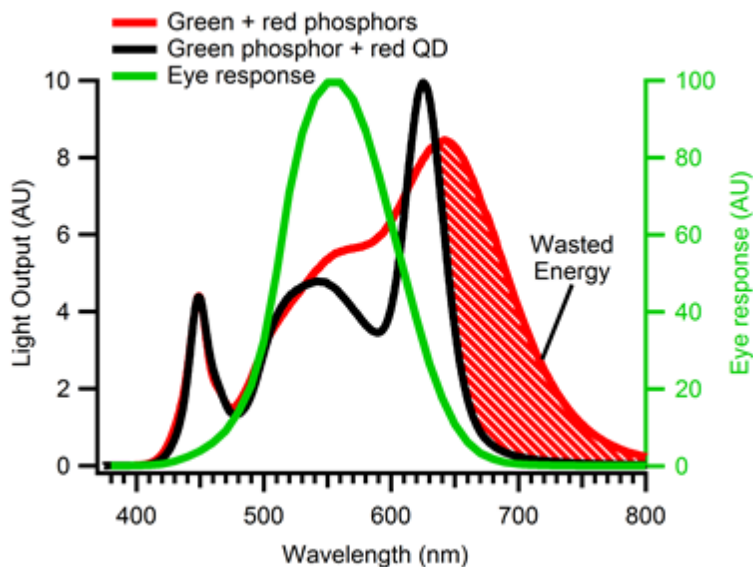


Figure 4. LED light output from downconverting phosphor systems. The red curve is a two phosphor system, the black curve consists of the same LED chip, the same green phosphor, but replaces the red phosphor with a red QD. The green line indicates the human photopic (eye sensitivity) response (right axis).

The benefits that quantum dots bring to lighting are their high light conversion efficiencies, narrow linewidths, and precise emission peak placement. QDs can improve the efficiency of warm-white LEDs by up to 25%, depending on the color rendering index and color temperature. The higher the CRI and/or the lower the CCT, the greater the red content and therefore the greater the visual impact and benefit of the quantum dots.

Downconverters in solid state lighting must maintain their optical properties over very long time (>25,000 h), under high temperature and extremely high blue light intensity. They must pass a variety of humidity tests with no special packaging to prevent degradation due to moisture-driven reactions. Without stability under these conditions, quantum dots can only be used in very specialized “remote” designs outside of the LED package. In order to make a real impact on both the market and on energy efficiency, QDs must be made to perform as well as their conventional phosphor counterparts under the same conditions – inside the LED package – on chip.

To summarize, replacing the red phosphor in today’s high-CRI LED packages with quantum dots results in cost-effective solutions for the illumination/lighting market that provides high quality of light with up to 20% increase in energy efficiency.

5. Information on Possible preparation for reuse or recycling of waste from EEE and on provisions for appropriate treatment of waste

1) Please indicate if a closed loop system exist for EEE waste of application exists and provide information of its characteristics (method of collection to ensure closed loop, method of treatment, etc.)

Final applications (luminaires and lamps) are in the scope of EU Directive 2012/19/EU–WEEE (Recast). Take back systems are installed in all EU Member States: end users and most commercial customers have to bring back the application free of charge.

European legislation on Waste Electrical and Electronic Equipment (WEEE) makes producers responsible for end of life products. Target setting as consequence of the present legislation is 45 % of Electrical and Electronic Equipment placed in the market by 2016, rising to 65 % in 2020 per year for all categories.

In general, the following channels have been established in the respective member-states providing countrywide coverage:

- Direct collection from large end users:
 - Containers have been made available, ad hoc or permanently, and will be collected upon notification by the end user that the container is full.
- Collection through distribution:
 - Wholesalers and Retailers place collection means at their premises respectively in their shops. Collection is done upon notification.
- Collection through municipalities:
 - Where infrastructure allows collection means are placed at municipality depots.

2) Please indicate where relevant:

- Article is collected and sent without dismantling for recycling
- Article is collected and completely refurbished for reuse

- Article is collected and dismantled:
 - The following parts are refurbished for use as spare parts: _____
 - The following parts are subsequently recycled: _____
- Article cannot be recycled and is therefore:
 - Sent for energy return
 - Landfilled

3) Please provide information concerning the amount (weight) of RoHS substance present in EEE waste accumulates per annum:

- In articles which are refurbished _____
- In articles which are recycled 100%
- In articles which are sent for energy return _____
- In articles which are landfilled _____

6. Analysis of possible alternative substances

(A) Please provide information if possible alternative applications or alternatives for use of RoHS substances in application exist. Please elaborate analysis on a life-cycle basis, including where available information about independent research, peer-review studies development activities undertaken

There is a significant research effort on Cd-free quantum dot luminescent materials such as indium phosphide (InP) and copper indium selenide sulfide (CuInSe_xS_{2-x}). These and similar compositions are generally considered to be 3 to 5 years behind Cd-based QDs in term of stability, quantum efficiency, and spectral efficiency (peak width).¹¹ The most advanced cadmium-free quantum dot compositions are based on InP cores. However, their spectral width, quantum efficiency and stability remain inferior to CdSe compositions.¹² Their use in commercial products is limited to displays with costly remote downconverter elements such as sheets, which avoid the on-chip implementation.

In displays, where Cd-free QDs are employed in a remote configuration, the broad FWHM and low converter efficiency of InP-based QDs results in lower system efficacy. [Oeko 2016] Similar trade-offs between FWHM and system efficacy have been described for lighting applications. [<https://doi.org/10.1364/PRJ.5.000A13>] Even if InP QDs could be used on-chip, their performance would be fall behind phosphor-converted LEDs due to their broad FWHM and low conversion efficiency. For red InP QDs, the FWHM is currently 46nm while Cd-based QDs are typically less than 35 nm, as shown in Figure 8 for commercially available displays, and summarized in Table 1.

¹¹ Yole 2015, p. 267

¹² Yole 2015, p. 180

Table 1. Summary red FWHM for displays and material employed.

Display	Material	Red FWHM (nm)
Philips 276E	Cd Qds	32
Samsung Q series	InP QDs	46

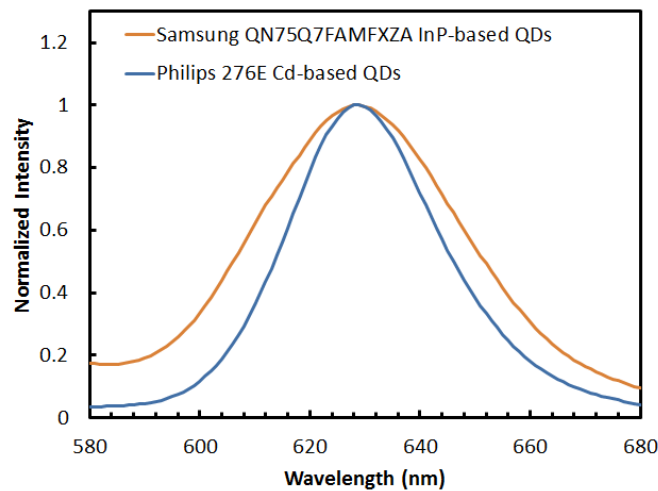


Figure 8. Red portion of spectra of displays employing Cd and Cd-free QDs.

(B) Please provide information and data to establish reliability of possible substitutes of application and of RoHS materials in application

Given the immaturity of Cd-free QDs and their rate of development, it is estimated that Cd-free QDs will be precluded from practical use in on-chip LED configurations for the next >5 years.¹³ There are no commercially available Cd-free QDs available for on-chip comparison to Cd-containing QDs. Measurements of LEDs incorporating Cd-free materials in development have been hindered by rapid degradation of optical characteristics once exposed to representative temperature and blue light flux conditions in the package.¹⁴ The applicants have evaluated Cd-free QDs which completely degrade in on-chip conditions with days or even hours.

¹³ Oeko 2016, p.74

¹⁴ CREE Inc., Santa Barbara Technology Center, Consultation Questionnaire Regarding Cd Exemptions, submitted 11.1.2016, p. 5, available under: http://rohs.exemptions.oeko.info/fileadmin/user_upload/RoHS_Pack_10/Cd_Quantum_Dot_Evaluation/CREE_RoHS_Cd_exemption_consultation.pdf

Advantages of Cd-containing QD over InP-alternatives:

It is widely accepted and numerous described in literature that InP-based QDs possess significantly lower photoluminescence quantum yields compared to the current gold-standard CdSe/CdS-QD.¹⁵ Despite tremendous efforts to increase quantum yields of InP-derived QD, Cd-based QDs still remain superior. It is noteworthy that photoluminescence quantum yield is a key property directly related to lower energy consumption. Interestingly, the group of Brandi Cossairt from Yale University demonstrated that the addition of cadmium (in chemical form of cadmium salts) dramatically improved photoluminescence quantum yield of InP-QD.¹⁶ This finding underlines the necessity of cadmium for current state-of-the-art QD design to ensure that QDs with the highest efficacy are applied to realize minimization of energy consumption. Most importantly, the technical incompatibility of incorporating InP-QDs onto chip arrays still remains challenging without solutions to overcome this application-limiting pitfall in the near future.

7. Proposed actions to develop possible substitutes

(A) Please provide information if actions have been taken to develop further possible alternatives for the application or alternatives for RoHS substances in the application.

The technical breakthrough of cadmium quantum dot material in on-chip configurations paves the way for alternative quantum dot materials. It is possible that some of the techniques developed to stabilize Cd-based QDs for on-chip use can also be applied to InP and other Cd-free quantum dot materials. The development of efficient downconverter materials is a high R&D priority in LED technology and cadmium quantum dot technology may serve as a stepping-stone to eventual cadmium-free quantum dots. As described above, in order to be considered viable for commercial use, these Cd-free

¹⁵ J. P. Park, J.-J. Lee, and S.-W. Kim, "Highly luminescent InP/GaP/ZnS QDs emitting in the entire color range via a heating up process," *Sci. Rep.* 6, 30094 (2016).; A. Narayanaswamy, L. F. Feiner, and P. J. van der Zaag, "Temperature dependence of the photoluminescence of InP/ZnS quantum dots," *J. Phys. Chem. C* 112, 6775–6780 (2008); M. J. Anc, N. L. Pickett, N. C. Gresty, J. A. Harris, and K. C. Mishra, "Progress in non-Cd quantum dot development for lighting applications," *ECS J. Solid State Sci. Technol.* 2, R3071–R3082 (2013); S. J. Yang, J. H. Oh, S. Kim, H. Yang, and Y. R. Do, "Realization of InP/ZnS quantum dots for green, amber and red down-converted LEDs and their color-tunable, four-package white LEDs," *J. Mater. Chem. C* 3, 3582–3591 (2015)., and are notoriously air-sensitive (S. Tamang, C. Lincheneau, Y. Hermans, S. Jeong, and P. Reiss, "Chemistry of InP nanocrystal syntheses," *Chem. Mater.* 28, 2491–2506 (2016).

¹⁶ J. L. Stein, E. A. Mader, B. M. Cossairt: Luminescent InP Quantum Dots with Tunable Emission by Post-Synthetic Modification with Lewis Acids. *J. Phys. Chem. Lett.* **2016**, 7, 1315-1320.

alternatives must meet or exceed the efficiency and stability performance already proven for Cd-based QDs in on-chip configurations.

(B) Please elaborate what stages are necessary for establishment of possible substitute and respective timeframe needed for completion of such stages.

In order to be considered viable for commercial use, Cd-free alternatives must meet or exceed the spectral efficiency, downconversion efficiency, and stability characteristics already demonstrated for Cd-based QDs in on-chip configurations. This is a daunting task for immature Cd-free compositional systems such as InP, and in fact some characteristics such as emission peak width (now >45nm for InP QDs) may be fundamentally (and not technically) limited by the material itself. All Cd-free QD alternatives will require a coating which limits oxidative and hydrolytic degradation reactions, but such coatings would not prevent intrinsic defects (such as vacancies) from forming. In short, based on reported progress to date, we anticipate that obtaining Cd-free QDs with parity performance to Cd-based QDs will take at least five years.

8. Justification according to Article 5(1)(a):

(A) Links to REACH: (substance + substitute)

1) Do any of the following provisions apply to the application described under (A) and (C)?

- Authorisation
 - SVHC
 - Candidate list
 - Proposal inclusion Annex XIV
 - Annex XIV
- Restriction
 - Annex XVII
 - Registry of intentions
- Registration

2) Provide REACH-relevant information received through the supply chain.

Name of document: N.A. Material will be below 1 metric tonne.

(B) Elimination/substitution:

1. Can the substance named under 4.(A)1 be eliminated?

Yes. Consequences? _____

No. Justification:

At the moment, the only type of quantum dot that can be used in an on-chip configuration meeting the efficiency and reliability requirements is a cadmium containing quantum dot.

2. Can the substance named under 4.(A)1 be substituted?

Yes.

Design changes:

Other materials:

Other substance:

No.

Justification:

Given the current state of Cd-free QDs and their rate of development, it is estimated that they will be precluded from practical use in on-chip configurations for the next >5 years.”¹⁷ Measurements of LEDs made with these materials have been hindered by rapid degradation of the QD quantum yield and lifetime once blended into LED encapsulant silicones.”¹⁸

3. Give details on the reliability of substitutes (technical data + information):

See paragraph 6.

4. Describe environmental assessment of substance from 4.(A)1 and possible substitutes with regard to

1) Environmental impacts: See LCA_____

2) Health impacts: _____

3) Consumer safety impacts: _____

Ad 2 and 3)

Without exposure to the quantum dot, there is no health risk¹⁹. Similar to display products, quantum dot solid-state lighting products are not likely to be handled, mechanically treated, or otherwise modified by a consumer in such a way that cadmium could be released. The cadmium element is bound by covalent bonds within the semiconductor material, the semiconductor quantum dots themselves are in turn bound inside the carrier silicone matrix cured on top of the LED chip, thus forming an LED package, which is in turn integrated into the lamp or luminaire, so the risk of consumer exposure to cadmium during the use phase is extremely low. Similarly, exposure of consumers to cadmium released to the environment from these products as a consequence of end-of-life or recycling operations is very unlikely. We have performed leaching tests on LED packages that contain cadmium quantum dots. Cadmium could not be detected in the leachate, showing that the cadmium is securely bound inside the LED package.

In production, cadmium can be handled safely so as to pose no risk to workers. Cadmium is used in various production processes, e.g. for nickel-cadmium (NiCd) batteries, electrical contacts, and filter glass. Adequate measures are in place to safeguard workers

¹⁷ Oeko 2016, p.74

¹⁸ CREE Inc., Santa Barbara Technology Center, Consultation Questionnaire Regarding Cd Exemptions, submitted 11.1.2016, p. 5, available under: http://rohs.exemptions.oeko.info/fileadmin/user_upload/RoHS_Pack_10/Cd_Quantum_Dot_Evaluation/CREE_RoHS_Cd_exemption_consultation.pdf

¹⁹ [3M Display Materials & Systems Division, "Re: 1st Questionnaire Regarding CdQD Exemptions", 2015](#)

in factories. The industry has extensive experience with handling dangerous substances and can do so safely.

- ⇒ Do impacts of substitution outweigh benefits thereof?
Please provide third-party verified assessment on this: [See SEA](#)

(C) Availability of substitutes:

- a) Describe supply sources for substitutes: please see paragraph 6. _____
- b) Have you encountered problems with the availability? Describe: see paragraph 6. _____
- c) Do you consider the price of the substitute to be a problem for the availability?
 Yes No
- d) What conditions need to be fulfilled to ensure the availability? See paragraph 6. _____

(D) Socio-economic impact of substitution: SEA

- ⇒ What kind of economic effects do you consider related to substitution?
- Increase in direct production costs
 - Increase in fixed costs
 - Increase in overhead
 - Possible social impacts within the EU
 - Possible social impacts external to the EU
 - Other: _____
- ⇒ Provide sufficient evidence (third-party verified) to support your statement:

9. Other relevant information

Please provide additional relevant information to further establish the necessity of your request:

Quantum dots (QD) toxicity studies:

The assessment of QD toxicity for living organisms still remains somewhat difficult and confusing. A review article published by R. Hardman from Duke University in North Carolina, USA clearly highlights that QD toxicity is strongly influenced by a wide variety of physicochemical properties as well as environmental factors. Combined with the lack of standardized testing procedures, there are discrepancies in scientific literature with

respect to health risks derived from QD²⁰. Referring to toxicity studies of cadmium-containing QD on cells conducted by Hanaki *et al.*²¹, Voura *et al.*²², Jaiswal *et al.*²³, Chen *et al.*²⁴ as well as toxicity studies on rodents conducted by Larson *et al.*²⁵, Voura *et al.*²², Balou *et al.*²⁶, and Derfus *et al.*²⁷, no toxic effects were determined.

Furthermore, numerous scientific publications are available putting QD in the spotlight for consideration as potential platform for various biological and human medical applications (therapeutics/diagnostics).

Human Centric Lighting

Human Centric Lighting supports health, well-being and performance of humans by combining visual, biological and emotional benefits of light. Light has been known for a long time to enable sight, safety and orientation. However, light is not limited to facilitate vision, it has the potential to achieve far more than this. Science has shown that light facilitates powerful non-visual effects on humans. Light has the ability to improve cognitive performance, it can energize, increase alertness or ease relaxation. It can improve mood, as well as stabilize the sleep-wake cycle of people. Therefore, it can be understood that light impacts people's wellbeing and performance. In fact, the true value of light lies in the combination of excellent visual, biological and emotional effects of light.²⁸ The narrow bandwidth of quantum dots increases the design freedom and efficiency of human centric lighting (HCL) spectra²⁹

Other relevant information on QD lighting applications submitted during the consultation on Exemption 39.

Lumileds Germany GmbH, Input for stakeholder consultation for RoHS exemption requests, submitted 08.01.2016, available at

http://rohs.exemptions.oeko.info/fileadmin/user_upload/RoHS_Pack_10/Cd_Quantum_Dot_Evaluation/Lumileds_20160108_LCA_Results_final.pdf

²⁰ R. Hardman: A Toxicologic Review of Quantum Dots: Toxicity Depends on Physicochemical and Environmental Factors. *Environmental Health Perspectives* **2006**, *114*, 165-172.

²¹ K.-I. Hanaki, A. Momo, T. Oku, A. Komoto, S. Maenosono, Y. Yamaguchi: Semiconductor quantum dot/albumin complex is a long-life and highly photostable endosome marker. *Biochem. Biophys. Res. Commun.* **2003**, *302*, 496-501.

²² E. B. Voura, J. K. Jaiswal, H. Mattoussi, M. S. Simon: Tracking metastatic tumor cell extravasation with quantum dot nano-crystals and fluorescence emission-scanning microscopy. *Nat. Med.* **2004**, *10*, 993-998.

²³ J. K. Jaiswal, H. Mattoussi, J. M. Mauro, S. M. Simon: Long-term multiple color imaging of live cells using quantum dot bioconjugates. *Nat. Biotechnol.* **2003**, *21*, 47-51.

²⁴ F. Q. Chen, D. Gerion: Fluorescent CdSe/ZnS nanocrystalpeptide conjugates for long-term, nontoxic imaging and nuclear targeting in living cells. *Nano. Lett.* **2004**, *4*, 1827-1832.

²⁵ D. R. Larson, W. R. Zipfel, R. M. Williams, S. W. Clark, M. P. Bruchez, F. W. Wise: Water-soluble quantum dots for multiphoton fluorescence imaging in vivo. *Science* **2003**, *300*, 1434-1436.

²⁶ B. Ballou, B. C. Lagerholm, L. A. Ernst, M. P. Bruchez, A. S. Waggoner: Noninvasive imaging of quantum dots in mice. *Bioconjugate Chem.* **2004**, *15*, 79-86.

²⁷ A. Derfus: Probing the cytotoxicity of semiconductor quantum dots. *Nano. Lett.* **2004**, *4*, 11-18.

²⁸ http://lightingeurope.org/images/publications/position-papers/LightingEurope_and_IALD_Position_Paper_on_Human_Centric_Lighting_-_February_2017.pdf

²⁹ H.C. Yoon, J.H. Oh, S. Lee, J.B. Park, Y.R. Do: Circadian-tunable Perovskite Quantum Dot-based Down-Converted Multi-Package White LED with a Color Fidelity Index over 90, <http://www.nature.com/articles/s41598-017-03063-7> **2017**

Lumileds Germany GmbH, Input for stakeholder consultation for RoHS exemption requests, submitted 14.12.2015, available at http://rohs.exemptions.oeko.info/fileadmin/user_upload/RoHS_Pack_10/Cd_Quantum_Dot_Evaluation/20151214_Oeko_Institut_consultation.pdf

CREE Inc., Santa Barbara Technology Center, Consultation Questionnaire Regarding Cd Exemptions, submitted 11.1.2016, p. 5, available under: http://rohs.exemptions.oeko.info/fileadmin/user_upload/RoHS_Pack_10/Cd_Quantum_Dot_Evaluation/CREE_RoHS_Cd_exemption_consultation.pdf

10. Information that should be regarded as proprietary

Please state clearly whether any of the above information should be regarded to as proprietary information. If so, please provide verifiable justification:
