

## Response to RoHS Exemption Application N<sup>o</sup> 2013-2

Nanoco is a well-established UK-based developer and manufacturer of CFQD™ cadmium-free quantum dots, free of cadmium and other toxic heavy metals, which can be used in many applications including display screens, lighting, solar cells and biological imaging. Dow Electronic Materials, a division of The Dow Chemical Company, is a well-known supplier of specialty chemical products and applications into the electrical and electronic manufacturing industry for over 50 years.

In January 2013, Dow Electronic Materials entered into a global licensing agreement with Nanoco to manufacture, market and sell CFQD™ cadmium-free quantum dots. Small-scale manufacture is currently undertaken in the UK and larger scale manufacture is scheduled to be online by mid-2014. A pilot launch of the first TVs using CFQD™ cadmium-free quantum dots is planned for the first half of 2014, with full commercial production expected within the following 12 months. We would like to jointly submit the following response to the public consultation on this exemption application. Prior to responding in detail to the issued list of questions, we include a summary of our understanding of the application's key issues. We also include an overview of the application of quantum dot technology into both displays and solid-state lighting devices.

### 1. Exemption Justification: Key Issues

- i. *There is no viable cadmium-free quantum dot alternative available or likely for at least 5 years*  
We shall show that Nanoco's CFQD™ cadmium-free quantum dots are both available and viable. Their optical emission performance currently meets the requirements for commercial LCD screens, in terms of enhanced screen colour range and lifetime (at least 30,000 hours). Whilst the applicant has compared their cadmium-based quantum dots to indium phosphide, Nanoco's CFQD™ cadmium-free quantum dots are not made from indium phosphide. Although containing indium, they are made from a unique, alloyed semiconductor matrix with quite different properties.
- ii. *OLEDs as an alternative consume too much energy*  
OLEDs are certainly another viable alternative and TVs expect to capture 17 % of the OLED market by 2014. Energy usage is currently higher than for LCD TVs but likely to reduce dramatically over coming years.
- iii. *Quantum dot technology offers approximately 20 % improved energy efficiency over conventional TVs*  
Any energy savings from use of quantum dots would apply to both cadmium-based and CFQD™ cadmium-free quantum dots. However, we understand that energy savings are associated with improved efficiency of the LED backlights and not the down-converting material; LEDs are more efficient than previously used backlight sources, e.g. fluorescent tubes.
- iv. *Indium is EU listed as a critical resource*  
We estimate that incorporation of CFQD™ cadmium-free quantum dots into LCDs will increase the total indium content of these devices by just 15 %. Substitution of indium tin oxide (the major use of indium in an LCD) with indium-free materials is being investigated. Recovery and

recycling of indium has already been developed and a leading indium supplier predicts supplies are sufficient to last another 50 to 100 years, as recycled indium already accounts for around 65 % of global supply.

v. *The wording of the exemption should be changed to extend the scope*

The applicant's use of quantum dots is quite different from the original Exemption 39 (2010) which is why they have suggested extending the scope. The proposed new wording is ambiguous (in relation to the "light-emitting area") and this could increase the allowed cadmium in a TV 10,000-fold over the original request. Indeed, the original applicant has chosen not to apply for an extension to Exemption 39, but has submitted a new application (request 2013-5), which is for the same use as this application (request 2013-2).

vi. *Environmental and safety impact is small*

Since cadmium in Electrical and Electronic Equipment is controlled 10-fold more than the other "RoHS" substances, its impact cannot be considered small. With a toxicity (LD<sub>50</sub>) of 100 – 300 mg/kg (rats and mice, oral)<sup>i</sup> cadmium's use and pathways into the environment will always be significant.

The applicant's own report suggests that cadmium can be released from cadmium-based quantum dot components certainly under acidic conditions making the risk not insignificant to both health and environment.

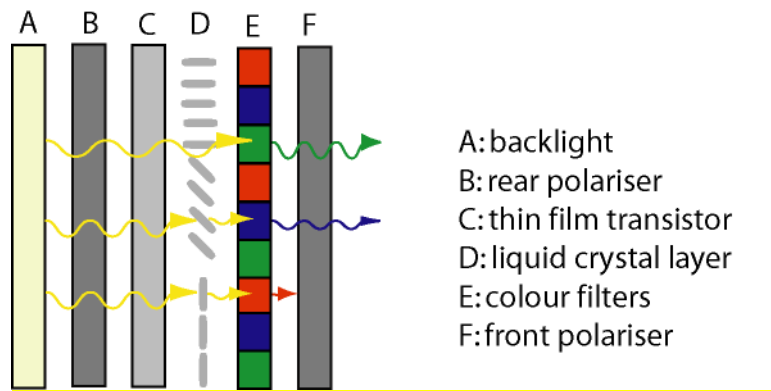
The link between the claimed energy saving and reduced emissions of cadmium from coal burning for power generation raises some questions. Firstly, the energy mix in Europe is different from the USA and the data presented may not be applicable. Secondly, emissions from power generation are already being reduced through various policies and regulations in Europe. Finally, the principle of justifying the use of cadmium in consumer products through off-setting against power generation emissions in this way may create a precedent for a greatly increased number of exemption requests in the future.

## **2. Overview of Quantum Dot Applications**

### **a) Liquid Crystal Display Backlight Unit (LCD BLU) Technology**

Quantum dots can be used in different ways in electronic displays. It is perhaps worthwhile giving a high level overview of how LCD BLU technology works, and how quantum dots may be integrated into the LCD BLU.

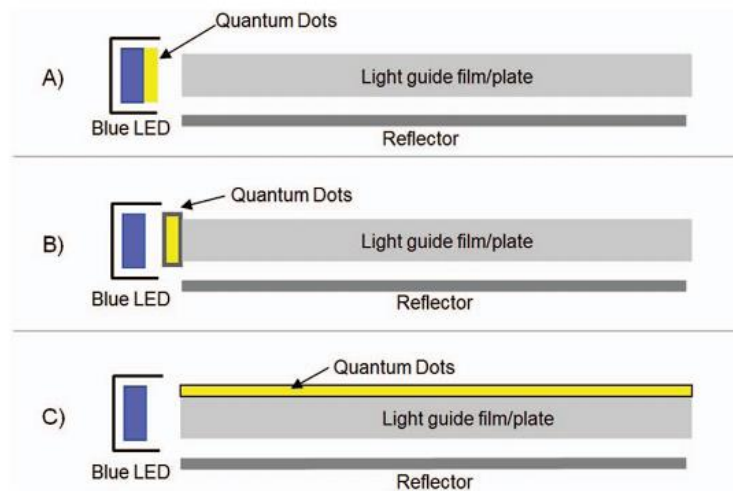
In an LCD BLU (**Figure 1**), the backlight comprises a white light source. Each pixel is controlled by an array of backlit thin film transistors (TFTs). The TFTs individually control each liquid crystal to determine whether light from the backlight is transmitted or blocked. The rear and front polarisers are aligned at 90° to one another. When a pixel transistor is turned off, the liquid crystal molecules rotate the polarised light through 90°, such that light passes through the colour filters and the front polariser to the screen. When a pixel transistor is turned on, the liquid crystal molecules align such that the light passes through the layer without being rotated, thus it is blocked by the front polariser.



**Figure 1:** Schematic diagram of an LCD BLU.

To produce white light, the backlight can comprise blue LEDs in combination with a down-converting material to absorb a proportion of the blue light, which is subsequently re-emitted at longer wavelengths. In conventional LCD BLUs, the down-converting material is a rare-earth phosphor such as cerium-doped yttrium aluminium garnet (Ce:YAG), which is integrated directly onto the LED chips. An alternative down-converting material comprises a combination of red and green quantum dots (QDs).

There are three potential strategies to integrate quantum dots into conventional LCD BLUs: “on-chip”, “on-edge” and “on-surface”, as defined by Coe-Sullivan *et al.* (Figure 2).<sup>ii</sup>



**Figure 2:** Integration strategies for QD-BLUs for LCD TV: A) on-chip, B) on-edge, and C) on-surface.

With on-chip geometry, the QDs are deposited directly onto the LED surface and are encapsulated within the LED package. The on-edge configuration has the QDs incorporated into a remote component, such as a capillary, that is situated in close proximity to the LED chips. Finally, on-surface configuration incorporates QDs into a remote film that covers the entire screen area. The on-chip design uses the least amount of QD material but is difficult to achieve in practice due to the thermal degradation of the quantum dots that are in direct contact with the LED source. In contrast, the on-surface design would have the highest quantum dot usage but would operate near to room temperature. The on-edge design is a compromise between temperature (on-chip) and quantity (on-surface) conformations.

The existing RoHS Exemption 39 is intended to cover the use of cadmium-based quantum dots in the on-chip design, whereas the requested extension and change of scope is to cover the on-edge and on-surface designs.

**b) Solid-State Lighting (SSL) Applications**

Quantum dots can also be used in down-conversion of light from solid-state LEDs, to provide “warm” white light with a high colour-rendering index (a measure of quality) and high luminous efficacy (a measure of efficiency). Typically, a blue LED is used with down-converting phosphors that re-emit longer wavelength light to create a white light appearance. One strategy uses two or more different colours (*e.g.* green and red) of quantum dots. Another strategy uses a green-yellow rare-earth phosphor and red quantum dots. Both technologies allow the appearance of LED lighting to be significantly improved for consumers compared to currently available low energy products. The quality of the light is “warmer” and colours appear more natural. As with LCD BLU display technology, quantum dots suffer from thermal degradation when in direct contact with the LED source, so SSL devices are likely to implement quantum dots in a remote component. Both cadmium-based and cadmium-free quantum dots can be used in this lighting technology.

## Questionnaire: Exemption Request N° 2013-2

### Exemption for “Cadmium in II-VI LED Downconversion”

1. The wording suggested by the applicant for an extension of the exemption is proposed to be “Cadmium II-VI color converting material ( $< 10 \mu\text{g Cd per mm}^2$  of light-emitting area) for LEDs for use in solid state illumination or display systems”.
  - a. Do you agree with the scope of the exemption as proposed by the applicant? Please suggest an alternative wording and explain your proposal, if you do not agree with the proposed exemption wording.

We consider the suggested wording of the proposed exemption extension vague and open to use throughout lighting and display applications with no effective limitation on the amount of cadmium that could be used in a device.

Fundamentally, however, we do not see an on-going need for this exemption, either as originally intended (the original applicant’s “on-chip” configuration, see **Overview of Quantum Dot Applications, Figure 2**) or as in the applicant’s proposed rewording, since a cadmium-free alternative (Nanoco’s CFQD™ cadmium-free quantum dots) is available.

The proposed change is intended to allow cadmium-based quantum dots to be used in any part of the lighting/display system, rather than directly on the LED chips (“on-chip”) that provide the primary light source. To the best of our knowledge, no commercial lighting or display systems using this architecture have been produced under the current exemption. The only marketed systems are those where the cadmium QDs have been positioned remotely from the LEDs. This is highly significant since the amount of cadmium QDs required is much greater the further away from the LED chips. The proposed wording “light-emitting area” is ambiguous. The original RoHS Exemption 39 request related to the use of cadmium as a colour-converting material in an on-chip configuration. In this context, the “light-emitting area” was in relation to the surface area of each LED chip (the light emitter), not to the total backlight area or the surface area of the filters or the area of the display screen, each of which might be interpreted as a light-emitting area. The proposed wording of the exemption could, therefore, be used to define the whole screen surface area to allow much higher quantities of cadmium per unit than the original Exemption 39 area of each LED chip in the backlight. This is illustrated in **Table 1**, which compares the light-emitting area for three different QD BLU designs with a 40” screen and a 16:9 aspect ratio. All calculations are based on a specific commercially available cadmium quantum dot LED TV, which utilises cadmium-based QD down-converting technology and has been available on the EU market since June 2013. The TV screen is double-edge-lit, comprising two full-length QD-containing capillaries, each illuminated by a row of blue twin-chip solid-state LEDs. Calculations of the sum of the LED areas within each chip, the approximate surface area of each glass capillary (which acts as the colour-converting component), and the screen area have been used. The corresponding maximum “allowed” cadmium content per device, according to the  $10 \mu\text{g per mm}^2$  light-emitting area limit proposed in the exemption request, is tabulated.

**Table 1:** Estimated light-emitting area and the corresponding maximum “allowed” cadmium concentration (according to the proposed exemption request) for on-chip, on-edge and on-surface QD BLU designs, for a 40” screen.

BLU DESIGN	ESTIMATED LIGHT-EMITTING AREA, mm <sup>2</sup>	MAXIMUM Cd CONTENT “ALLOWED” (EX. 39)
On-chip	48 (light-emitting area, based on LED area within each chip <sup>1</sup> of the two LED light bars)	480 µg
On-edge	$1 \times 10^4$ (surface area <sup>2</sup> of two glass capillaries)	100 mg
On-surface	$4 \times 10^5$ (display area <sup>3</sup> of a 16:9, 40” screen)	4 g

For this specific cadmium quantum dot LED TV, the volume of resin within each capillary was estimated to be approximately 1 cm<sup>3</sup>. Independent analysis of the resin by inductively coupled plasma mass spectrometry (ICP-MS) measured the cadmium concentration to be 1,060 ppm (see **Table 2**). Thus, assuming the density of the cured resin to be in the region of 1.2 g cm<sup>-3</sup>, at a concentration of 1,060 ppm the amount of cadmium would fall in the region of 2.5 mg per TV (two capillaries), *i.e.* around five times the maximum cadmium concentration that would be permitted under the proposed wording of the exemption request if the light-emitting area is properly interpreted to be that of the LED chips. If the light-emitting area is taken to refer to the area of a colour-converting film, then up to 4 g of very toxic cadmium<sup>iii</sup> would be permitted per TV, almost a 10,000-fold increase compared to the area of the LED chips. This clearly illustrates that the proposed wording could lead to no effective control of the amount of cadmium that could be used in each TV or similar device.

**Table 2:** Independent ICP-MS analysis on the resin from a commercially available cadmium quantum dot LED TV.

ANALYSIS	RESULTS	UNITS
Concentration of Cadmium	1060	mg/kg
Concentration of Chromium	<0.3	mg/kg
Concentration of Lead	<0.2	mg/kg
Concentration of Mercury	<0.02	mg/kg

It would seem more logical and in keeping with the original intention of Exemption 39 that the total amount of cadmium allowed per TV should be linked and limited to the LED chip area.

However, we would like to repeat our comment that whilst CFQD™ cadmium-free quantum dots are available, this exemption is no longer justified.

<sup>1</sup> Based on the LED chip size, the light-emitting area of each LED light bar, comprising 48 twin-chip LED chip packages, each consisting of two 0.5 mm x 0.5 mm LED chips, is 48 x 2 x 0.5 mm x 0.5 mm = 24 mm<sup>2</sup>.

<sup>2</sup> The surface area of each oval shaped capillary with dimensions of 2 mm x 4 mm x 510 mm was estimated to be [(2 mm x π) + 4 mm] x 510 mm = 5244 mm<sup>2</sup>.

<sup>3</sup> The screen dimensions for a 40”, 16:9 display are 34.86” x 19.61”;  $34.86'' \times 19.61'' \times (25.4 \text{ mm}/'')^2 = 4.4 \times 10^5 \text{ mm}^2$ .

- b. Please state whether you either support the applicant's request or whether you would like to provide argumentation against the applicant's request. In both cases provide detailed technical argumentation/evidence in line with the criteria in Art. 5 (1) (a) to support your statement.

Nanoco Technologies Limited (Nanoco) is a UK-based company that has developed and manufactures CFQD™ cadmium-free quantum dots. In January 2013, Nanoco and Dow Electronic Materials entered into a global licensing agreement for the manufacture, marketing and sale of Nanoco's CFQD™ cadmium-free quantum dots in electronic displays. Large-scale manufacture is planned for mid-2014.

Noting Article 5(1)(a) of the 2011 RoHS Directive, granting this exemption to use cadmium would weaken the environmental and health protection in the community when CFQD™ cadmium-free quantum dots are an available, better alternative to the environment and health. Nanoco's CFQD™ cadmium-free quantum dots are nanocrystals with an alloyed matrix composed of a complex semiconductor material, free of any RoHS regulated heavy metal. As with cadmium-based QDs, Nanoco's CFQD™ cadmium-free quantum dots can down-convert blue LED light (re-emitting across the visible spectrum); fine tuning of the particle size determines the quantum dot emission wavelength. CFQD™ quantum dots are synthesised by Nanoco's unique, patented "molecular seeding" method, enabling the production of particles with a narrow size distribution.<sup>iv</sup>

Extending the duration of Exemption 39 is not appropriate since other technologies have now been developed that are able to effectively substitute for the use of cadmium quantum dots in illumination and display systems. These include CFQD™ cadmium-free quantum dot material developed by Nanoco, as well as non-quantum dot alternatives such as OLED. Nanoco's CFQD™ cadmium-free quantum dots are an effective, efficient and reliable down-converting material. Herein, we will provide supporting data for both solid-state illumination and display applications (see Questions 2 and 3). We envisage that televisions containing CFQD™ material will be commercially available within the next 12 months. We envisage that CFQD™ quantum dot-containing colour-converted LED lighting (SSL) will be available by the end of 2015. Therefore, we expect technology incorporating CFQD™ quantum dots to be commercially available well within the five year extension to Exemption 39 requested by the applicant and as such believe that the request is unjustified.

2. The application mentions that possible substitutes are OLEDs, RGB LEDs, CFQDs.
  - a. Please provide information concerning these possible substitutes or developments that may enable substitution or elimination at present or in the future. If possible please provide data to establish reliability of possible substitutes.

An organic light-emitting diode (OLED) is an electroluminescent organic film. In contrast to quantum dot down-conversion, OLEDs do not require a backlight. In display applications, OLEDs offer an advantage over LCD displays in that they can produce a wider viewing angle due to their direct light emission.

RGB LEDs comprise red, green and blue solid-state LEDs to produce white light. They are able to provide high luminous efficacies (the ratio of produced visual sensation to the electrical power required to produce the light), and light down-conversion is not required.

Quantum dot technology, described by the applicant, is a backlight down-conversion technology. This applies whether the quantum dots are cadmium-containing or cadmium-free, like Nanoco's CFQD™ quantum dots. Nanoco manufactures cadmium-free quantum dots, so our response will focus on the reliability of CFQD™ material as an effective alternative to cadmium-based quantum dots.

Nanoco devotes its entire research, development and manufacturing capacities to the production of cadmium-free, RoHS compliant quantum dot materials and their associated technological applications. As such, Nanoco is best placed to comment on the performance of cadmium-free quantum dots. Nanoco's CFQD™ quantum dot performance far exceeds that suggested in the exemption request; the applicant's own research into indium phosphide quantum dots is somewhat behind the advancements made by Nanoco. Other cadmium-free quantum dot materials with superior performance to indium phosphide are available, one example being Nanoco's CFQD™ cadmium-free quantum dots, nanocrystals with a unique, alloyed semiconductor matrix.

The exemption request suggests that indium phosphide quantum dot material (which is by nature cadmium-free) is not yet a candidate for LED down-conversion applications since it gives a relatively broader emission full-width at half-maximum (FWHM) compared to cadmium-based II-VI materials, presenting a significant barrier to achieving commercial performance. FWHM represents the distribution of emission wavelengths within the ensemble of quantum dots. Scientific literature well-documented that indium phosphide quantum dots display broader FWHM values than II-VI quantum dots (such as CdSe). In part this is due to stronger quantum confinement effects of visible-emitting indium phosphide nanoparticles which results in a large emission wavelength change from a small change in particle size.<sup>v</sup> However, Nanoco's CFQD™ cadmium-free quantum dot material is not indium phosphide and has superior properties. The alloyed matrix of elements in CFQD™ quantum dots ensures that both the semiconductor band gap and the strength of the bonding interactions within the nanoparticles can be manipulated, reducing the strength of the quantum confinement effects and thus the range of wavelengths (*i.e.* the FWHM) emitted by a given size distribution of quantum dots. As a result, a given size distribution of CFQD™ quantum dots exhibits a significantly narrower wavelength distribution than that exhibited by the same size distribution of indium phosphide quantum dots. As shown in the device data that follow, Nanoco's patented molecular seeding technology can be used to synthesise CFQD™ quantum dots with FWHM and photoluminescence quantum yield (the ratio of light absorbed to light emitted) values with comparable performance for display and lighting applications.

Nanoco's molecular seeding method of synthesis has been demonstrated to be scalable. Plans to scale up production are already underway and are expected to be achieved by mid-2014. CFQD™ LCD displays are expected to be launched within the next 12 months, and CFQD™ lighting applications by the end of 2015.

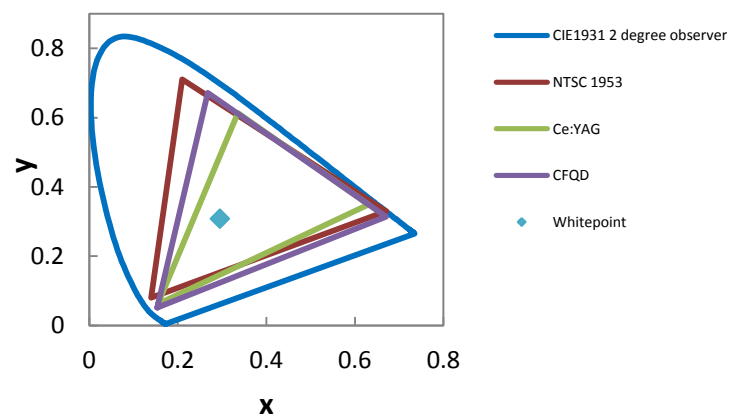


## CFQD™ BLU Performance

The applicant describes three different configurations for quantum dot colour-converted LCDs: “on-chip”, “on-edge” and “on-surface”, (**Figure 2**). CFQD™ backlight units (BLUs) have been compared using the on-chip and on-surface geometries.

### On-Chip

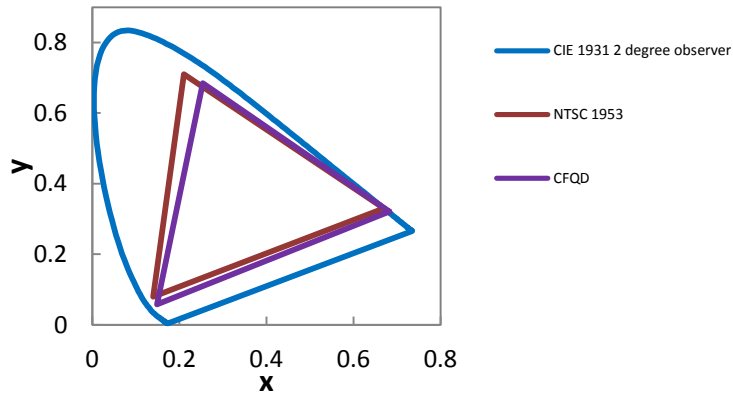
In the on-chip geometry, CFQD™ material has been incorporated into a 22” LCD display. The light bar from a commercially available LCD TV, comprising LEDs with a conventional rare-earth (Ce:YAG) phosphor, was replaced with a light bar consisting of 60 colour-converted CFQD™-LEDs. In doing so, the colour gamut was increased from 67 % to 92 % of the area of the United States National Television Systems Committee (NTSC) 1953 colour triangle, an internationally recognised standard, as shown in **Figure 3**. As discussed by the applicant in response to the clarification questions from Öko and Fraunhofer, quantum dots (both cadmium-containing and cadmium-free) cannot currently withstand the harsh conditions of the on-chip environment to provide the necessary performance lifetimes for display applications. However, the results show that CFQD™ quantum dots can be used instead of cadmium QDs to significantly improve the colour gamut with respect to that of a rare-earth phosphor colour-converted TV.



**Figure 3:** Colour triangle of an on-chip CFQD™ BLU (*purple*) compared to that of a conventional Ce:YAG BLU (*green*) and the NTSC 1953 standard (*red*).

### On-Surface

In the on-surface geometry, CFQD™ quantum dots have been incorporated into a film displaying 97 % NTSC 1953 area (89 % NTSC 1953 overlap), as shown in **Figure 4**. The colour gamut is comparable to that displayed by the commercially available cadmium quantum dot LED TV. Although the colour gamut of this TV is reported as 100 % of the NTSC 1953 standard, our internal measurements found that the maximum overlap with the NTSC 1953 colour triangle was just 91 %, as shown in **Table 3**.



**Figure 4:** Colour triangle of an on-surface CFQD™ BLU (*purple*) compared to that of the NTSC 1953 standard (*red*).

**Table 3:** Summary of the display settings of a commercially available cadmium quantum dot LED TV and the corresponding optical performance compared to the NTSC 1953 standard.

Condition	Picture Setting	Colour Setting	Colour Space	Format	Area NTSC, %	Overlap NTSC, %
A	photo-vivid	default	sRGB	ITU601	61	60
B	photo-vivid	max	sRGB	ITU601	46	46
C	photo-vivid	max	Adobe RGB	ITU601	91	89
D	photo-vivid	max (red also set to max)	Adobe RGB	ITU601	100	91
E	photo-vivid	max	Adobe RGB	ITU601	66	58
F	photo-vivid	max	Adobe RGB	ITU709	85	84
G	photo-original	max	Adobe RGB	ITU709	80	78

The conditions to which quantum dots are exposed in the on-surface geometry are much milder than those of the on-chip geometry. To assess the performance lifetime, a CFQD™ film was prepared and irradiated at 2.5 mW cm<sup>-2</sup> to simulate the conditions of an on-surface environment. The photoluminescence intensity remained stable during 3,000 hours of testing. Extrapolating the data using a logarithmic curve suggests a lifetime of at least 30,000 hours.<sup>4</sup>

Overall, CFQD™ cadmium-free quantum dots can be used to achieve similarly performing display devices to cadmium quantum dot-containing TVs already available on the EU market, in terms of both optical performance and lifetime.

### CFQD™ Solid-State Lighting (SSL) Performance

The performance of SSL is typically assessed in terms of luminous efficacy, colour-rendering index (CRI) and correlated colour temperature (CCT).

<sup>4</sup> Note, when quoting extrapolated lifetimes, current protocols state that LEDs must be tested for at least 10 % of the time quoted.

- Luminous efficacy is a measure of the ability of a light source to produce a visual sensation on the human eye, and is quantified in terms of the ratio of the produced visual sensation to the electrical power required to produce the light.
- CRI is a marker of the ability of a light source to reproduce the colours of an object as viewed under an ideal light source, such as the Sun (which has a CRI of 100).
- CCT quantifies the shade of white light emitted with respect to that emitted by a black-body radiation source; warm white light (CCT ~ 3,500 K or less) appears reddish, while cool white light (CCT ~ 4,000 K or more) appears bluish.

Further discussion on metrics for white SSL can be found in an article by Pimputkar *et al.*<sup>vi</sup>

The applicant suggests that cadmium-free quantum dots do not display sufficiently narrowband emission for SSL applications. This comment is misleading since for high CRI, high luminous efficacy lighting the FWHM requirements depend on a number of factors. These include the emission wavelength, the CCT, CRI and efficacy target performance values, and the implementation strategy.

1. One strategy uses only quantum dot down-converting materials with a blue LED backlight. In this case, a number of emission wavelengths of quantum dots (“colours”) would need to be combined to make the desired broad emission needed for white light. Combining many colours of quantum dots with narrow FWHM or fewer colours with broader FWHM can achieve the same goal.
2. A second strategy is to use red quantum dots in combination with a broadband green-yellow phosphor.

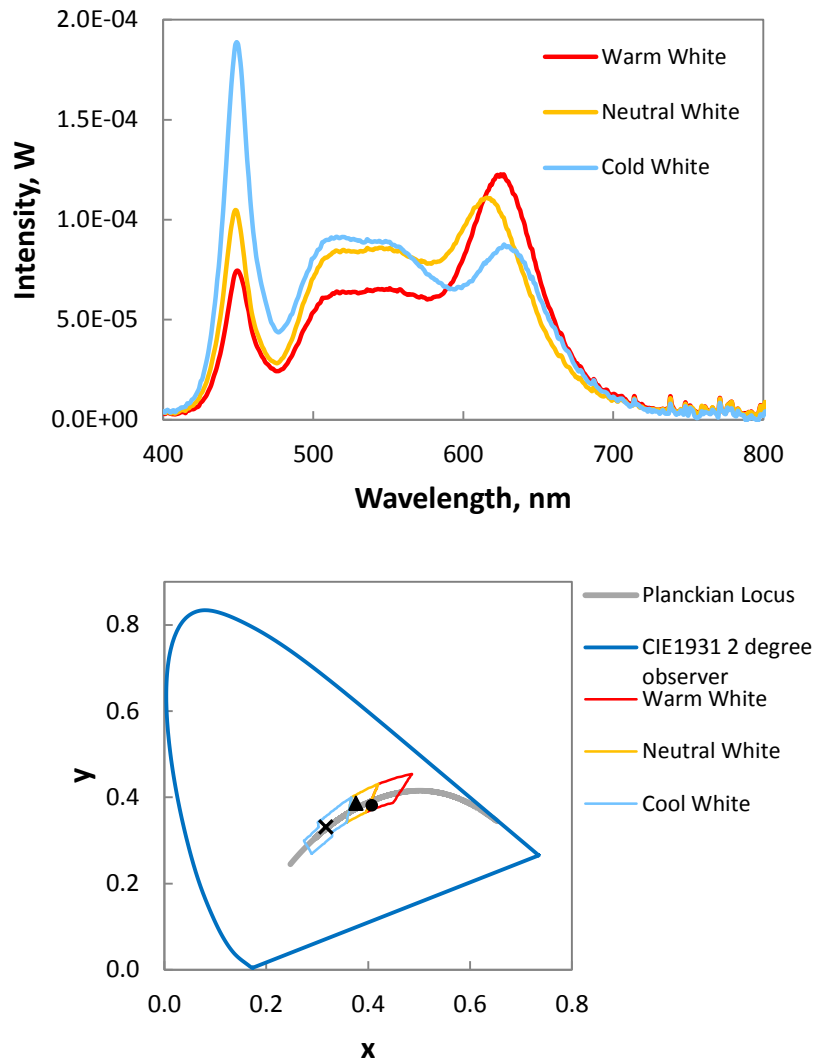
In this case, a quantum dot FWHM of 60 – 70 nm is ideal to maximise both efficacy and CRI at a target CCT. However, the choice of rare-earth phosphor determines the ideal quantum dot emission wavelength and FWHM, so it may be that the applicant has not had experience with a wide range of rare-earth phosphors, and that this has led them to make this claim.

Colour-converted LEDs were prepared with CCTs in the region of 4,000 K and 5,000 K, using Nanoco’s CFQD™ cadmium-free quantum dot material. **Table 4** compares the performance metrics with those of conventional  $AE_2Si_5N_8:RE$  (AE = alkaline-earth; RE = rare-earth) LEDs. Though the luminous efficacy was slightly lower than that for traditional LEDs with a similar CCT, the CRI for the CFQD™ quantum dot LEDs was comparable or higher.

**Table 4:** Comparison of luminous efficacy, colour-rendering index (CRI) and correlated colour temperature (CCT) for CFQD™ quantum dot colour-converted LEDs and conventional  $AE_2Si_5N_8:RE$  LEDs emitting with a CCT around 4,000 K and 5,000 K.

	4,000 K CCT		5,000 K CCT	
	CFQD™-LED	2-5-8 NITRIDE	CFQD™-LED	2-5-8 NITRIDE
<b>EFFICACY, lm/W<sub>opt</sub></b>	150.4	195.0	191.5	227.6
<b>CRI</b>	93	76	84	87
<b>CCT, K</b>	4,326	4,353	5,437	4,909

**Figure 5** shows the spectral intensity and coordinates in the Commission Internationale de l’Eclairage (CIE) 1931 colour space for warm, neutral and cool white LEDs produced by combining a blue solid-state LED with a commercially available green-yellow rare-earth phosphor and Nanoco’s red CFQD™ quantum dots. The LEDs displayed high luminous efficacies: 100 lm/W for cool and 84 lm/W for warm white light. The CCT was tuneable from 6,300 K to 3,300 K, with high CRIs (> 90).



**Figure 5:** Spectral intensity (*top*) and coordinates in the CIE 1931 colour space (*bottom*) for warm, neutral and cool white LEDs produced by combining a blue solid-state LED with a green-yellow rare-earth phosphor and red CFQD™ material.

As with the on-chip LCD display configuration, in order to commercialise QD SSL, issues relating to the lifetime of the nanoparticles in the LED environment need to be resolved. To the best of our knowledge, no commercial lighting devices using quantum dots (cadmium-based or cadmium-free) directly on LED chips are available. The applicant’s “Quantum Light Optic” product used cadmium QDs incorporated into a “lens” mounted away from the LEDs to reduce exposure to high temperatures. Even so, we understand that this still suffered from lifetime issues and was withdrawn from the US market in 2011.

- b. According to the applicant OLED are the only possible substitute relevant for the near future which could be used in applications similar to those relevant for QD-based LCDs. Please explain in detail, the current status of using OLED in comparison to applications using II-VI semiconductor down-conversion materials.

OLEDs emit, rather than down-convert, light and as such cannot directly substitute II-VI semiconductor down-conversion materials. OLEDs operate without a backlight or colour filters. Currently, OLEDs are commonly found in small- to medium-sized displays, such as smartphones and tablets. An online source<sup>vii</sup> summarises the status of OLED technology for larger display applications; 55" OLED TVs are currently on sale in the Korea, the UK and the US, while prototypes of a 56" OLED display have been unveiled at the Consumer Electronics Show. A leading OLED manufacturer plans to commercialise a 60" flexible, ultrahigh definition TV by 2017.

Current power consumption for OLED TVs is higher than for LCD TVs because it is not yet fully optimised. As the technology stabilises for mass production, power consumption is expected to improve dramatically, towards that of an LCD.

For in-depth analysis of the status of OLED technology, Öko-Institut and Fraunhofer IZM may wish to consult the market researcher Displaybank, which has published a number of reports on the subject.<sup>viii</sup>

- c. Furthermore please explain what display sizes cannot yet be manufactured with OLED? Is it possible to use OLED in the same applications using II-VI semiconductor down-conversion materials (can they replace one another), for instance in the small size displays?

Currently, OLED displays up to 55" are available on the Korean, UK and US markets. According to DisplaySearch,<sup>ix</sup> TVs are expected to account for 17 % of the OLED display market by 2014, with rapid OLED display area growth predicted during 2017.

For smaller displays, OLED technology is already commercially available in products including mobile phones, digital cameras, and monitors,<sup>vii</sup> for which equivalent II-VI semiconductor down-converted displays are not yet marketed. OLEDs and QD down-conversion materials will both be suitable for applications requiring smaller displays.

3. The applicant states that today there are no alternative semiconductor materials that can replace cadmium in II-VI down-conversion materials and retain sufficient performance to be useful.
  - a. Do you agree with the statement of non-existing alternatives made by the applicant?

Nanoco's CFQD™ cadmium-free quantum dots are clearly an available, viable alternative to cadmium in II-VI down-conversion materials, with demonstrated performance and efficiency.

- b. If not, please provide information about alternative semiconducting materials that can replace cadmium-containing semiconducting materials in the II-VI in LEDs for use in solid state illumination or display systems.

Nanoco's CFQD™ cadmium-free materials are an available, viable alternative to cadmium-containing semiconductor materials for LED down-conversion, with comparable performance and efficiency for both illumination and display applications (see detailed response to Question 2a).

4. Please indicate if the negative environmental, health and/or consumer safety impacts caused by substitution are likely to outweigh the environmental, health and/or consumer safety benefits. If existing, please refer to relevant studies on negative impacts caused by substitution.

Since its original drafting, the RoHS Directive has always recognised the human toxicity and environmental impact of cadmium in the community and sought to restrict its release through environmental pathways. Indeed, it is controlled to a level much higher than the other "RoHS" substances with a 10 times lower threshold permitted in Electrical and Electronic Equipment.

The only direct substitute to provide a positive health and environmental impact benefit over the use of cadmium-containing quantum dots is a quantum dot not containing a toxic material. Nanoco's CFQD™ cadmium-free quantum dots are free from heavy metals, RoHS compliant and do not present the toxicity risks associated with cadmium-containing II-VI QDs. Although the applicant states that the cadmium QD shell is cadmium-free and, as such, exposure to the resin of the colour-converting component presents no risk of cadmium exposure, a peer-reviewed article on the cytotoxicity of cadmium QDs presents evidence to the contrary. Brunetti *et al.* reported toxicity studies that show leaching of Cd<sup>2+</sup> from CdSe/ZnS QDs into human tissue *in vitro*, despite a two-monolayer ZnS shell.<sup>x</sup>

With regards to the disposal of cadmium-based QD-containing colour-converting components and devices, an investigation into the degradation of one of the applicant's lighting products (the "Quantum Light Optic") showed small releases of cadmium ions (< 0.10 mg/g polymer) in a range of stimulants, but significantly higher release of cadmium ions (1.10 – 1.20 mg/g polymer) in low pH fluids (1 M nitric and gastric acid).<sup>xi</sup> The study results suggest a risk of cadmium leaching from cadmium-based QD-containing colour-converting components and devices when exposed to low pH conditions that may be encountered in a landfill environment.

The applicant suggests cadmium-based quantum dots reduce energy consumption of up to 20 % compared to rare-earth LED down-converters (conventional LCD TVs). Any such energy saving would be likely to apply to CFQD™ quantum dot down-converted LEDs. However, our understanding of the energy savings associated with LED down-conversion technology is that it originates from the LED backlight rather than the QD colour converters; LEDs are more efficient than previously used backlight sources such as fluorescent tubes. As such, there should be little difference in energy consumption between QD-LED-LCD displays and standard LED-LCD displays.

Nanoco's CFQD™ quantum dots contain indium which, as highlighted in the exemption request, is an EC recognised critical material. Information received from a leading indium supplier projects that current indium supplies should last another 50 – 100 years, allowing sufficient time to develop alternative technologies to those that are heavily reliant on indium supplies (predominantly flat panel display and photovoltaic applications).<sup>xii</sup> Indium is three times more abundant than silver and is extracted as a by-product of mining and refining zinc, tin, copper, lead and iron. Extraction of the indium requires investment and this is currently increasing for new and existing refineries. Potential supplies are well-distributed globally, but China is currently the largest single producer. At present, indium supply and demand are well-matched. Indium production is forecast to meet rising demand, with much of the new capacity coming from outside China, reducing the influence of China on global supply balance and pricing. The small consumption of indium that will ensue from the introduction of CFQD™ lighting and display products onto the market is likely to have a relatively insignificant impact on global indium consumption. We estimate that for a CFQD™ quantum dot LCD with an on-surface configuration, the total indium content will only increase by approximately 15 % compared to that of a standard LCD. In the future, this small increase in indium consumption from the CFQD™ quantum dots could be offset by strategies to replace indium tin oxide in flat panel displays with indium-free transparent conducting oxides such as antimony tin oxide. Further, schemes to recycle indium are already in place,<sup>xiii</sup> with around 65 % of annual indium supply being generated by recycling,<sup>xii</sup> and include provisions to recycle indium from LCDs.<sup>xiv</sup> Thus it is reasonable to assume that strategies to recover indium from CFQD™ quantum dot LCDs could be developed.

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<sup>i</sup> Health Protection Agency, Cadmium Toxicological Overview, 2010:

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<sup>ii</sup> S. Coe-Sullivan, W. Liu, P. Allen and J.S. Steckel, *ECS J. Solid State Sci. Technol.*, 2013, **2**, R3026

<sup>iii</sup> <http://esis.jrc.ec.europa.eu/>

<sup>iv</sup> I. Mushtaq, S. Daniels and N. Pickett, Preparation of Nanoparticle Material. US Patent 7,588,828, 15<sup>th</sup> September, 2009.

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<sup>vi</sup> S. Pimputkar, J.S. Speck, S.P. DenBaars and S. Nakamura, *Nat. Photonics*, 2009, **3**, 180

<sup>vii</sup> <http://www.oled-info.com/oled-tv>

<sup>viii</sup> <http://www.displaybank.com/eng/research/report.html?cate=2>

<sup>ix</sup> <http://www.prweb.com/releases/2013/8/prweb11038981.htm>

<sup>x</sup> V. Brunetti, H. Chibli, R. Fiammengo, A. Galeone, M.A. Malvindi, G. Vecchio, R. Cingolani, J.L. Nadeau and P.P. Pompa, *Nanoscale*, 2013, **5**, 307

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