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Synthesis of yellow fluorescent dyes derived from benzoxanthene that can be used in colour converters for remote phosphor LED systems

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A B S T R A C T

The current commercially available yellow organic dyes are not stable enough to be used for remote phosphor LED applications. Therefore new yellow benzoxanthene dicarboximide dyes to convert blue light from LED into light of longer wavelengths were synthesized. The spectral properties of the dyes and their stability in PET films were examined. The compounds showed high photoluminescence quantum yield and above all superior photostability under operation conditions (10% reduction in photoluminescence at 450 nm irradiance of 0.016 W/cm² at 60 °C). With extrapolated lifetimes up to 27000 h, a huge improvement in stability was established when compared to the commercially available yellow dyes exhibiting lifetimes lower than 1000 h.

1. Introduction

A possibility to generate white light with LED’s is the “multichip” approach in which LED’s of different colours like red, yellow, green and blue are combined [1]. A disadvantage when using different coloured LEDs, which overrules the benefit, is the assembly and the colour mixing which is rather complicated. Because of this, phosphor-converted LEDs (pc-LEDs) are currently the most common manner for white light generation.

Pc-LED’s are blue LEDs made from InGaN coated with an yttrium aluminium garnet phosphor doped with cerium (Y₃Al₅O₁₂:Ce³⁺; YAG:Ce) which emits additional yellow light (Fig. 1). When the colour characteristics should be improved, a red-emitting phosphor (for example a nitrido silicate) is added [1]. Partial conversion of the blue light in combination with the yellow and red emission results in a white light spectrum of the pc-LED. Colour tunability is possible by varying the thickness of the coating or by changing the concentration of phosphors in the coating. Typically, the inorganic phosphor layer is directly coated on top of the blue emitting LED. In this configuration, the phosphor conversion-related losses are high, the temperature of the phosphor can be above 160 °C, and the light intensities at the phosphor are ~ 100 W/cm². Pc-LEDs have significant light engine losses and heat management issues, which allows for gains in light engine efficiency. Optimal efficiency is limited for pc-LEDs because the phosphors emit light in all directions, including in the direction of the blue LED, leading to light losses. Moreover, some light is back reflected by the encapsulation to the blue LED. Besides lowering the optical output, also a rise in temperature in the LED junction is obtained lowering the total LED output.

A solution has been found for this problem and is called “the remote phosphor configuration”. In this case, the coating is assembled further away from the blue LED (Fig. 2). The inside of the capsule is coated with a highly reflective coating to ensure that the reflected waves are able to leave the device without optical losses and thermal quenching. In this way, the chance of reflected beams hitting the blue LED and being turned into heat is minimized; this results in a much more efficient electrical power to light conversion [2].

Lowering the price of the LED’s is an important drive in the lighting industry. In the case of the efficient remote phosphor configuration relatively more phosphor is needed as a result of the increased surface of the colour converting layer [3]. Inorganic phosphors as the colour converter materials in the remote phosphor configuration are not preferred due to their price. Organic phosphors can be a cheap solution for this problem if it wasn’t for their relative low stability in comparison to their inorganic counterparts. The lifetimes of commercially available dyes, that have high quantum efficiencies however, are very low (< 1000 h) [4], and certainly much too low for lighting applications. The challenge is to develop photostable luminescent dyes keeping good spectral properties (absorption/emission wavelengths) and a high photoluminescence quantum efficiency (PLQE).
In this paper, we wish to report the syntheses of new benzoxanthene derivatives with lifetimes above 10000 h. The lifetimes were measured in a poly(ethylene terephthalate) (PET) host matrix. The choice for this polymer host matrix was made after the finding that red dyes have a much longer lifetime in this polymer compared to poly(methylmethacrylate) and polycarbonate. The lifetime is defined as the time when 10% in absorption or emission spectrum is reduced, while operating at typical lighting conditions, i.e. 450 nm irradiance of 0.016 W/cm² at 60 °C in air [5]. Although the lifetime in real lighting applications depends on the spectral performance of the lamp, this 10% decrease is very useful to compare the various synthesised dyes with commercially available dyes.

2. Experimental

2.1. Materials and instrumentation

4-Bromonaphthalic anhydride was purchased from TCI. All the other reagents and solvents were of reagent-grade quality and obtained from commercial suppliers. Column chromatography was performed using silica gel (Acros Organics, ultra pure, 40-60 μm, 60 Å). Dyes F083, solvent yellow 98, dispersive yellow and fluorescent yellow 43 were obtained from BASF, CIBA, Bayer and Nippon Kayaku, respectively. Their structures are presented in Fig. 3.

Amorphous PET films with dye concentration of 200 ppm (w/w) are made by extrusion.

Invista Polyclear T94N PET (bottle grade polymer) is dried in a dehumidifying dryer at 140 °C for > 6 h. An amount of dye, about 300 g, was added. After a few minutes the dye containing film comes out of the slot die of the extruder and is gathered. When there is no change in colour of the film anymore, observed by bare eye, the film is gathered on a winder.

Before making the films, the extruder is flushed with clear polymer until a clear film, with the right dimensions, is obtained. At that moment the blend of polymer and dye is added into the hopper of the extruder. After a few minutes the dye containing film comes out of the slot die of the extruder and is gathered. When there is no change in colour of the film anymore, observed by bare eye, the film is gathered on a winder.

Just before the hopper is empty, the gathering of the film stops and the hopper is filled with clear polymer to flush the dye out of the extruder, until it is clean again to produce the next film.

²H NMR spectra were recorded on either a VNMRS spectrometer with a 7.05 Tesla magnet from Oxford Instruments and an indirect detection probe at 300 MHz, or a MP300 spectrometer with a 7.05 Tesla magnet from Oxford Instruments containing a 4 nuclei autoswitchable probe. Chemical shifts are denoted in δ (ppm) referenced to the residual protic solvent peaks. The splitting patterns are designated as follows: s (singlet), d (doublet), dd (double doublet), t (triplet), q (quartet), sept (septuplet), m (multiplet), br (broad). ¹³C NMR spectra were recorded on the MP300 spectrometer (at 75 MHz). Mass spectra were recorded on Agilent 1200 series and Agilent 6130 mass detector.

Absorption spectra were measured on a Perkin Elmer Lambda 950 UV-vis spectrometer. The films were measured in transmission on a plate which allows light pass through a 4 mm × 3 mm area. The absorption data are given for 175 μm films with 200 ppm (W/W) of one of the dyes.

Photoluminescence spectra were taken on a Perkin Elmer LS55 fluorescence spectrometer. The films were fixed between a glass and metal plate. Both excitation and emission spectra were measured. QE was measured on the setup which had an integrating sphere, a blue laser emitting at 450 nm, and an Ocean Optics spectrometer. Films were stuck to the sample holder. A measurement of the light intensity at every wavelength was done with and without the sample. PLQE was obtained by calculating the ratio between the emitted photons and absorbed photons by the dye. The lifetime of the dyes was measured as decrease of the photoluminescence of the dyes (photo bleaching).

2.2. Synthesis

2.2.1. 4-Bromo-N-(2,6-diisopropylphenyl)-1,8-naphthalimide (2)

A mixture of 4-bromonaphthalic anhydride (10 g, 36.1 mmol) and 2,6-diisopropylaniline (16.2 mL, 86.0 mmol) in AcOH (300 mL) was refluxed overnight. A solution of NaHCO₃ was added. The mixture was cooled and poured into water. The precipitate was filtered and concentrated. Puriﬁcation by column chromatography (SiO₂, DCM/ heptane 2/1) gave pure compound 2 (12.6 g, 80% yield) as a white powder.

²H NMR (300 MHz, CDCl₃, ppm): δ = 8.75 (d, 1H, J = 7.7 Hz), 8.68 (d, 1H, J = 8.4 Hz), 8.51 (d, 1H, J = 7.7 Hz), 8.12 (d, 1H, J = 8.4 Hz), 7.92 (t, 1H, J = 7.7 Hz), 7.49 (t, 1H, J = 7.6 Hz), 7.35 (d, 2H, J = 7.6 Hz), 2.73 (sept, 2H, J = 6.9 Hz), 1.17 (d, 12H, J = 6.9 Hz).

2.2.2. 2-(2,6-Diisopropylphenyl)-6-(2-methoxyphenyl)-1H-benzo[de]isoquinoline-1,3(2H)-dione (3)

Compound 2 (3.2 g, 7.33 mmol), 2-methoxyphenylboronic acid (3.0 g, 20.0 mmol), Pd(PPh₃)₄ (300 mg, 0.3 mmol) and Na₂CO₃ (2.1 g, 19.8 mmol) were added to a degassed mixture of EtOH (2 mL), toluene (70 mL), 1,4-dioxane (6 mL) and water (6 mL) under nitrogen. The mixture was reacted at 100 °C for 1 day. The reaction was quenched by addition of water and extracted with DCM (3 x). The combined organic layers were washed with water, brine, dried (Na₂SO₄), filtered and concentrated under reduced pressure. The crude solid was purified by column chromatography (SiO₂, DCM/heptane 2/1) to give 3 (2.9 g, 87% yield) as a white powder.

²H NMR (300 MHz, CDCl₃, ppm): δ = 8.71 (d, 1H), 8.66 (dd, 1H), 8.05 (dd, 1H), 7.74 (d, 1H), 7.69 (t, 1H, J = 7.6 Hz), 7.40 (t, 1H, J = 7.7 Hz), 7.34 (d, 1H, J = 7.6 Hz), 2.73 (sept, 2H, J = 6.9 Hz), 1.17 (d, 12H, J = 6.9 Hz).

2.2.3. 2-(2,6-Diisopropylphenyl)-6-(2-hydroxyphenyl)-1H-benzo[de]isoquinoline-1,3(2H)-dione (4)

BBr₃ (1.8 mL, 19.1 mmol) was added to a solution of 3 (2.9 g, 6.4 mmol) in DCM (200 mL) at 0 °C under nitrogen. The mixture was stirred at 40 °C overnight, cooled to 0 °C and a solution of NaHCO₃ was added. The mixture was extracted with DCM (2x) and then with EtOAc (2x) and the combined organic layers were washed with water and brine, dried (Na₂SO₄), filtered and concentrated. Purification by column chromatography (SiO₂ eluent: DCM/TBME 60/1) gave pure compound 4 (2.8 g, 97% yield) as a white solid.

²H NMR (300 MHz, CDCl₃, ppm): δ = 8.77 (d, 1H), 8.72 (dd, 1H), 8.15 (dd, 1H), 7.83 (d,
1H). 7.78 (t, 1H), 7.50 (t, 1H), 7.46 (td, 1H), 7.36 (d, 2H), 7.32 (dd, 1H), 7.16 (t, 1H), 7.08 (d, 1H), 4.87 (s, 1H), 2.78 (sept, 2H), 1.18 (d, 1H), 1.11 (d, 6H), 1.10 (d, 6H), 1.07 (d, 6H), 1.06 (d, 6H). 13C NMR (75 MHz, CDCl3, ppm): δ = 29.28, 24.24. M + H = 540.2.

2,6-Dibromo-2(2,6-diisopropylphenyl)-1H-xantheno[2,1,9-def]isoquinoline-1,3(2H)-dione (6)

A solution of bromine (20.7 mL, 402.4 mmol) in CHCl3 (60 mL) was added dropwise over 6h to a solution of compound 5 (15 g, 33.5 mmol) in CHCl3 (1.5 L) at 60 °C under nitrogen. The mixture was stirred at 60 °C for a further 28h. TLC (SiO2, DCM/heptane 2/1) indicated complete conversion to product 6. The mixture was cooled to room temperature and concentrated under reduced pressure. The mixture was triturated with hot heptane, filtered and evaporated again under reduced pressure to give compound 6 (19.5 g, 96% yield) as a yellow solid. 1H NMR (300 MHz, CDCl3, ppm): δ = 9.54 (dd, 1H), 8.88 (s, 1H), 8.85 (s, 1H), 7.65 (td, 1H), 7.56 (dd, 1H), 7.49 (t, 1H), 7.44 (t, 1H), 7.35 (d, 2H), 2.72 (sept, 2H), 1.18 (d, 12H).

2,6-Diisopropylphenyl)-5-bromo-11-phenoxy-1H-xantheno[2,1,9-def]isoquinoline-1,3(2H)-dione (7)

A mixture of 6 (1.4 g, 2.31 mmol), phenol (1.2 g, 12.75 mmol) and K2CO3 (2.2 g, 15.92 mmol) in NMP (60 mL) was stirred at 90 °C under nitrogen overnight. Then, the content of the flask was poured into a cold 20% acetic acid solution in water. After 5 min, 2 N aqueous HCl was added and the mixture stirred for 10 min and the precipitated solid was filtered, washed neutral with warm water and vacuum dried at 60 °C. The residue was coated on silica gel and purified by column chromatography (SiO2, eluent: dichloromethane/heptane 1/1 to 2/1). 1H NMR (300 MHz, CDCl3, ppm): δ = 8.85 (dd, 1H), 8.76 (s, 1H), 8.29 (s, 1H), 7.46 (m, 5H), 7.30 (d, 2H), 7.25 (m, 1H), 7.19 (t, 1H), 7.11 (d, 2H), 2.65 (sept, 2H), 1.15 (d, 6H), 1.10 (d, 6H).

2,6-Diisopropylphenyl)-5,11-diphenyl-1H-xantheno[2,1,9-def]isoquinoline-1,3(2H)-dione (8)

To a clear solution of compound 7 (600 mg, 0.97 mmol) in THF (80 mL) and MeOH (10 mL) under nitrogen was added 10% Pd/C (100 mg) and the reaction was placed under hydrogen atmosphere using a balloon. The mixture was stirred at 30 °C overnight and then filtered over Celite. The crude solid was purified by column chromatography (SiO2, eluent: toluene/chloromethane 3/2). Compound 8 (540 mg, 98%) was obtained as a yellow solid. 1H NMR (300 MHz, CDCl3, ppm): δ = 8.85 (dd, 1H), 8.61 (d, 1H), 8.33 (s, 1H), 7.44 (m, 6H), 7.32 (d, 2H), 7.22 (m, 2H), 7.12 (d, 2H), 2.72 (sept, 2H), 1.15 (d, 6H), 1.11 (d, 6H). 13C NMR (75 MHz, CDCl3, ppm): δ = 163.81, 163.35, 156.47, 155.91, 152.27, 148.81, 145.83, 133.45, 132.12, 131.22, 130.55, 129.62, 129.12, 128.19, 127.93, 125.28, 124.32, 124.21, 123.98, 121.82, 121.15, 118.50, 117.71, 115.35, 110.63, 29.28, 24.24. M + H = 540.2. λmax (ethyl acetate) = 428 nm, ε = 479 nm and 506 nm.

2,6-Diisopropylphenyl)-5,11-diphenyl-1H-xantheno[2,1,9-def]isoquinoline-1,3(2H)-dione (10)

Compound 6 (18 g, 29.7 mmol), phenylboronic acid (29.0 g, 237.8 mmol), Pd(PPh3)4 (1.3 g, 1.1 mmol) and Na2CO3 (9.4 g, 89.2 mmol) were added to a degassed mixture of EtOH (32 mL), benzene (600 mL) and water (60 mL) under nitrogen. The mixture was reacted at 80 °C overnight. The reaction was quenched by addition of water and extracted with DCM (3 x). The combined organic layers were
washed with water, brine, dried (Na₂SO₄), filtered and concentrated under reduced pressure. The crude solid was purified by column chromatography (SiO₂, eluent: DCM/heptane 2/1). Compound 10 (16 g, 90% yield) was obtained as a yellow solid. ¹H NMR (300 MHz, CDCl₃, ppm): δ = 8.77 (s, 1H), 8.57 (s, 1H), 7.81 (d, 2H, J = 8.36 Hz), 7.56 (m, 7H), 7.49 (t, 2H, J = 7.4 Hz), 7.35 (dd, 1H, J = 8.4, 7.0, 1.5 Hz), 7.35 (d, 2H, J = 7.5 Hz), 7.23 (dd, 2H, J = 12.3, 1.3 Hz), 6.87 (dd, 1H, J = 8.3, 7.0, 1.5 Hz), 2.79 (sept, 2H, J = 6.9 Hz), 1.20 (d, 6H, J = 7.1 Hz). ¹³C NMR (75 MHz, CDCl₃, ppm): δ = 164.15, 164.05, 152.81, 152.61, 145.87, 141.87, 137.48, 136.21, 135.61, 134.23, 131.59, 131.38, 131.25, 129.79, 129.72, 129.66, 129.33, 129.26, 128.79, 128.55, 128.27, 124.27, 124.16, 121.30, 119.77, 118.22, 115.13, 29.36, 24.25. M + H = 460.3. λₘₐₓ (ethyl acetate) = 436 nm, ε = 17700 and 455 nm, ε = 15600. λ(εm) (ethyl acetate) = 489 nm and 516 nm.

2.2.9. 2-(2,6-Diisopropylphenyl)-11-phenoxy-5-phenyl-1H-xantheno[2,1,9-def]isoquinolino-1,3(2H)-dione (9)

Compound 7 (400 mg, 0.66 mmol), phenylboronic acid (396 mg, 3.25 mmol), Pd(PPh₃)₄ (40 mg, 0.03 mmol) and Na₂CO₃ (130 mg, 3.25 mmol), in degassed 1,4-dioxane (15 mL) was added to a degassed mixture of EtOH (1 mL), benzene (15 mL) and water (2 mL) under nitrogen. The mixture was reacted at 90 °C under nitrogen overnight. The mixture was cooled to room temperature and the solvent removed under reduced pressure. The residue was dissolved in dichloromethane and SiO₂ (3 g) was added. The dichloromethane was removed under reduced pressure and the product coated on silica was poured on top of a column containing silica gel. The column was eluted with a 1:1 mixture of dichloromethane/heptane. After isolation, the compound was washed with hot heptane on a glass filter and dried under vacuum. Compound 11 (1.0 g, 48%) was obtained as a yellow solid. ¹H NMR (300 MHz, CDCl₃, ppm): δ = 8.84 (dd, 1H, J = 8.2, 1.5 Hz), 8.40 (s, 1H), 8.28 (s, 1H), 7.33–7.48 (m, 6H), 7.31 (d, 2H, J = 7.5 Hz), 7.20 (m, 3H), 7.14 (d, 4H, J = 8.3 Hz), 2.70 (sept, 2H, J = 7.0 Hz), 1.16 (d, 6H, J = 6.8 Hz), 1.15 (d, 6H, J = 6.8 Hz). ¹³C NMR (75 MHz, CDCl₃, ppm): δ = 163.05, 162.94, 152.81, 152.61, 145.87, 141.87, 137.48, 136.21, 135.61, 134.23, 131.59, 131.38, 131.25, 129.79, 129.72, 129.66, 129.33, 129.26, 128.79, 128.55, 128.27, 124.27, 124.16, 121.30, 119.77, 118.22, 115.13, 29.36, 24.25. M + H = 603.3. λₘₐₓ (ethyl acetate) = 436 nm, ε = 17700 and 455 nm, ε = 15600. λ(εm) (ethyl acetate) = 489 nm and 516 nm.

3. Results and discussion

3.1. Design concept of the dyes

Preliminary studies with commercially available yellow emitting fluorescent dyes were performed in PET (polyethylene terephthalate) films. This polymer showed to be a matrix with the highest lifetime of the dyes [5]. The lifetime was defined as the duration before the dye had bleached 10% and consequently emitted only 90% of the initial yellow intensity. Assuming a much longer lifetime for the initial blue emitting diode, the colour point of the device would show an unacceptable shift. The lifetime also depends on the initial blue intensity. The measurements were performed at relative high intensities (> 0.5 W/cm² and 60 °C). However, the results are presented after recalculation to 0.016 W/cm² using the fact that accelerated degradation measurements showed a linear dependence of the photostability and the light intensity at 450 nm [5]. Although various applications in the lighting industry perform with different intensities, the mentioned intensity is used throughout this publication in order to be able to compare the various dyes.

Thus the lifetimes of commercially available yellow emitting dyes F083, solvent yellow 98, disperse yellow and fluorescent yellow 43 (see Fig. 3) were measured and found to be very low (< 1000 h) [4]. Despite the high PLQ (in all cases higher than 0.95 measured in PET) the low lifetime makes them not suitable for remote phosphor applications.

Among those available dyes, Solvent yellow 98 showed an increased lifetime, but still lower than 1000 h. In several measurements it was shown that oxygen plays an important role in bleaching (photo oxidation) of fluorescent molecules. Solvent yellow 98 contains a sulphur atom susceptible for photo-oxidation. Its oxidation to the benzo [k,l] thioxanthone-3,4-dicarboxylic acid imide-7,7-dioxide would give a compound with an absorption maximum around 380-400 nm [6] too far from the 450 nm emitted by the blue LED. It was then decided to investigate the oxygen analogues of Solvent yellow 98 as potential yellow converting fluorescent dyes.

Compound yellow X is such an analogue but unfortunately emits at too short wavelength (around 470 nm) and is therefore not useful for the application [7]. Furthermore such materials can potentially form aggregates that induce other optical effects and lowering of the quantum yield. To avoid this aggregation, steric hindrance has to be built into the molecule. Therefore, 2,6-diisopropylphenyl group was linked to the nitrogen atom of the imide moiety. This group turned out to be very successful in avoiding aggregation in several perylene derived fluorescent dyes [8]. In order to shift the emission spectrum to higher wavelengths, substitutions at position 5 and 11 (in Scheme 2) were performed. These positions seem to be the most accessible positions for reactions.

3.2. Synthesis

Benzoxanthene-3,4-dicarboximides have been prepared by substitution of 4-chloro-1,8-naphthalic anhydride with 2-nitrophenol, reduction, Pscherr cyclization and condensation with aniline [9–11]. Unfortunately, in our hands the Pscherr cyclization to benzoxanthene-3,4-dicarboxylic anhydride or imide was not reproducible often giving unsatisfactory yield due to reduction of the intermediate diazonium salt.

Prickett et al. reported the synthesis of benzoxanthene-3,4-dicarboxylic anhydride via a Suzuki coupling reaction of 4-bromo-1,8-naphthalic anhydride with 2-methoxymethylocarboxylic acid, removal of the methoxy protecting group and intramolecular oxidative cyclization [12]. Unfortunately the use of 3 equivalents of palladium acetate for the Suzuki coupling to proceed at least in 50% yield was necessary. On the other hand 4-bromo-1,8-naphthalenedicarboximide 2 was used successfully in a Suzuki reaction using a standard catalytic amount of
Therefore, 4-bromo-1,8-naphthalic anhydride was converted into 2 and subsequent Suzuki reaction gave the expected derivative 3 in 87% yield (see Scheme 1). After removal of the methoxy group with boron tribromide, phenol 4 was tested in a cyclization reaction to attempt to afford 5. Good results were obtained when 4 was heated in nitrobenzene at 200 °C with an excess of potassium carbonate. Compound 5 could be isolated in 85% yield after column chromatography. Once compound 5 was obtained, substituents had to be introduced to shift the emission spectrum to higher wavelengths (see Scheme 2). We envisaged to do so by means of 5,11-dibromo derivative 6.

Bromination of compound 5 proceeded readily using chloroform as solvent. Even with a large excess of bromine almost no byproducts were formed after several days of reaction. Dibromo compound 6 could then be isolated in 90% yield.

Reaction of compound 6 with phenol to afford dye 11 was...
Suzuki coupling with phenylboronic acid gave compound groups on position 5 and 11. Therefore, reduction of a hydrogen atmosphere a giving 7 only one phenoxy group was isolated instead of target compound 11. The use of a catalyst was then envisaged to introduce a second phenoxy group. Therefore an Ullmann coupling reaction was tested with copper (I) iodide and Cu(I)/N,N′-dimethylethylenediamine but almost no substitution of the second bromide was observed. Finally, reaction with copper (I) iodide and N,N-dimethyl glycine as ligand was successful and yielded target dye 11 [15].

The regio selectivity of the substitution of the bromide on position 11 giving 7 could be used to form products substituted by different groups on position 5 and 11. Therefore, reduction of 7 with Pd/C under a hydrogen atmosphere afforded mono phenoxy derivative 8 and Suzuki coupling with phenylboronic acid gave compound 9 both reactions in almost quantitative yields.

Suzuki coupling of dibromide 6 with phenyl boronic acid was also performed. The reaction gave dye 10 in very good yield. 1H NMR and mass spectra confirmed that both positions 5 and 11 were arylated.

3.3. Spectral properties and stability measurement

The emission spectra of 5 and of the four new dyes 8, 9, 10 and 11, recorded in ethyl acetate solution are presented in Fig. 4. Those measurements showed that the four new dyes have similar spectral properties; the emission spectra are red shifted compared to that of original structure 5. While compound 5 is less applicable in phosphor converters due to its short emission wavelength, the other compounds are applicable and especially the double substituted compounds 9, 10 and 11. Removal of one side group of 11 forming 8 resulted in a blue shift. Replacement of the phenoxy groups in 11 into phenyl groups 10 resulted in a small blue shift.

PET films containing the dyes were prepared and PLQE and lifetime measurements were performed. The results are presented in Table 1. All new dyes showed very high PLQE between 0.92 and 0.96. The excitation and emission spectra of commercial dye F083, and dyes 5 and 10 in PET are presented in Fig. 5. The emission spectra are redshifted compared to the spectra measured in ethyl acetate. Moreover, the emission differences between 5 and 10 are less pronounced than in ethyl acetate. This is probably due to the fact that unsubstituted 5 is more sensitive to the solvatochromic effect when changing from ethyl acetate to PET. The excitation spectra show that dyes 5 and 10 are eligible for using 450 nm blue light as excitation source.

Compound 5 showed a lifetime of about 2800 h in PET. Yellow dyes 8, 9 and 11 have an improved lifetime of more than a factor of 4 compared to 5. For compound 10 the lifetime is even increased to a factor of about 9 (27000 h) measured under the same conditions. Thus, yellow dye 10 showed to be the best performing organic dye with the highest lifetime under the applied conditions. Next to it’s superior lifetime the small red shift of 10 (in PET) as compared to F083 and 5 is also favorable for the optical properties and lamp efficiencies.

The fact that bromination of 5 results in substitution at carbon position 5 and 11 (see Scheme 2) and that the substituted compound 10 has a higher lifetime than unsubstituted 5 as well as mono substituted 8 may indicate that these positions play an important role in the degradation of these dyes. In compound 10 these reactive sites are blocked by phenyl groups and therefore preventing photo oxidation. This may explain the relatively high lifetime of 10.

4. Conclusions

Four new substituted benzoxanthene dicarboximide yellow dyes were synthesized. All four dyes have an absorption near 450 nm to convert part of the blue light emission of InGaN LED to light of a longer wavelength. PET films of the dyes showed high photoluminescence quantum efficiencies and more notably lifetimes above 10000 h. In the case of 5,11-diphenyl benzoxanthene dicarboximide derivative (10) the lifetime even increased to 27000 h therefore making this dye one of the most photostable fluorescent organic yellow dyes. Its properties makes it suitable to be used in colour converters for remote phosphor LED systems.

Conflicts of interest

J. Lub is an employee of Philips Electronics Nederland B.V.
P.A. van Hal J.M. Jansen and R.A.M. Hikmet are employees of Philips Lighting B.V.
S.L.J. Hamon and T.J. Visser are employees of Syncom B.V.

![Fig. 4. Emission spectra of (from left to right) dyes 5 (blue line), 8 (red line), 10 (purple line), 9 (green line), and 11 (brown line) in ethyl acetate. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)](image-url)
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Fig. 5. Excitation (dotted lines) and emission spectra (straight lines) of F083 (grey lines), S (blue lines) and 10 (red lines) in PET. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)