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Luminescent QR codes for smart labelling and sensing

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ABSTRACT

QR (Quick Response) codes are two-dimensional barcodes composed of special geometric patterns of black modules in a white square background that can encode different types of information with high density and robustness, correct errors and physical damages, thus keeping the stored information protected. Recently, these codes have gained increased attention as they offer a simple physical tool for quick access to Web sites for advertising and social interaction. Challenges encompass the increase of the storage capacity limit, even though they can store approximately 350 times more information than common barcodes, and encode different types of characters (e.g., numeric, alphanumeric, kanji and kana). In this work, we fabricate luminescent QR codes based on a poly(methyl methacrylate) substrate coated with organic-inorganic hybrid materials doped with trivalent terbium (Tb^{3+}) and europium (Eu^{3+}) ions, demonstrating the increase of storage capacity per unit area by a factor of two by using the colour multiplexing, when compared to conventional QR codes. A novel methodology to decode the multiplexed QR codes is developed based on a colour separation threshold where a decision level is calculated through a maximum-likelihood criteria to minimize the error probability of the demultiplexed modules, maximizing the foreseen total storage capacity. Moreover, the thermal dependence of the emission colour coordinates of the Eu^{3+}/Tb^{3+}-based hybrids enables the simultaneously QR code colour-multiplexing and may be used to sense temperature (reproducibility higher than 93%), opening new fields of applications for QR codes as smart labels for sensing.

1. Introduction

QR (Quick Response) codes, introduced by Denso Wave Incorporated in 1994, are bi-dimensional barcodes composed of black and white modules. Since then, QR codes were certified by international standard norms becoming a world known codification scheme with numerous applications in distinct areas, e.g., food (to track and certify the products quality and also to avoid counterfeiting [1,2]), security (combined with encryption techniques to improve identification documents security [3]), medicine (to easily manage the patients-related information [4]), among other, like pharmaceutics [5], marketing [6], and tourism [7]. The unequivocal implantation of QR codes is well demonstrated by its popularity increase in the last years, in particular, in daily routines as they offer a simple physical tool for quick access to web sites, advertising, and social interaction [8].

The popularity of QR codes lies on their unique characteristics, such as fast and easy readability independently from the orientation, ability to correct errors and physical damages, which make them a very robust code in what concerns information protection. Despite the fact that they can store approximately 350 times more information than common barcodes and encode different types of characters (numeric, alphanumeric, kanji and kana) [9], their storage capacity is still reduced, limiting a wider use.

The information capacity limit has been addressed in the literature involving the use of colour schemes and/or multiplexing methods. In particular, information multiplexing can be achieved by replacing the modules with special characters (*e.g.* \, /, <, >, ^) associating them to a unique array of *n* bits, creating a unique QR code, increasing the storage limit up to *n* times; so far a 3 times

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increase was already demonstrated [10]. Another approach proposes a multi-view scheme in which three QR codes are translated into a planar projection of a three-dimensional shape with a cubic form, where the QR codes are placed on the sides of the cube, allowing a 1.5 increase of information storage [11]. Other possibility to deal with QR code storage limitation is the use of colour schemes that consist in the use of multiple colours, defining each module with more than one bit of information, which is the same principle as the one behind the use of special characters. One example is based on predefining a standard colour pallet for each set of bits combination permitting to double the QR code storage capacity using four colours [12] and quadruple using 16 colours [13]. However, practical disadvantages are envisaged due to the sensitivity to reading conditions, as the colour scheme decoding process must be able to match the colour detected with the colour pallet pre-established to process the decoding. Another possibility, reported by some of us, to codify each QR code consists in the use of the primary colours (red, R, green, G, or blue, B) with an addictive colour method, resulting in an eight-colour pallet [14]. In this case, since the primary colours are orthogonal among them, the final images can be decoded by separating colours in the RGB components, obtaining the original three monochromatic QR codes. An increase of storage capacity per unit area by a factor of six, when compared to the normal QR code, may be foreseen using multilevel encoding in each primary colour [14].

The methodology we present here is based on the former principle of colour adding using the RGB components. As a proof of concept, we work only with one RGB component, but the materials and processing techniques here reported allow the incorporation of more than one colour. To experimentally implement this strategy, visible light-emitting organic-inorganic hybrids were used to design RGB luminescent multiplexed QR codes. The advantage of organic-inorganic hybrids lies on the fact that they are easily processed at room temperature with the desired shape and thickness, combining the flexibility of the organic counterpart with the mechanical stability of the inorganic one [15–17]. Moreover, the possibility of incorporating optically active centres with light emission properties tuned along the visible spectral range is of great advantage, as distinct multiplexing colours may be selected. Therefore, beta-diketonate complexes of trivalent lanthanide ions (Ln^{3+}, Ln = Eu, Tb) were selected as they are red and green emitters, respectively, under UV excitation [18], permitting the hybrids to keep their transparency under day light illumination, keeping codified and enabling the multiplexing of information. This later aspect arises from the fact that UV illumination is required to activate the emission and, therefore, to enable the information reading, ensuring security features. We propose to multiplex luminescent QR codes based on transparent Ln^{3+}-doped organic-inorganic hybrid materials with a standard black-white QR code. In this case, instead of having three black-white QR codes and add them, we propose the use of one printed black and white QR code (base code) combined with a QR code made of Ln^{3+}-doped organic-inorganic luminescent hybrids deposited over a transparent poly(methyl methacrylate) (PMMA) substrate. We demonstrate the applicability of the methodology to decode the multiplexed based QR codes on the RGB addictive colour method [14] using a green-emitting luminescent QR code. The methodology to decode the multiplexed is developed based on colour separation threshold, where a decision level is calculated trough probability density functions. Furthermore, taking advantage of the emission thermal dependence of the luminescent QR code layer, we demonstrate the ability of these codes to potentially realise the simultaneously sensing of the temperature (5–50 °C), prospecting luminescent QR codes for higher storage capacity smart labelling.

2. Experimental section

2.1. Materials synthesis and processing

2.1.1. Synthesis of $Tb(3Cl\text{-}acac)_3(H_2O)_2$

The $Tb(3Cl\text{-}acac)_3(H_2O)_2$ (3Cl-acac = 3-chloro-2,4-pentanedione) was prepared as detailed elsewhere [19]. A mixture of 1 mmol of $TbCl_3{\cdot}6H_2O$ (Sigma-Aldrich) and 3 mmol of 3-chloro-2,4-pentanedione was dissolved in 5 mL of H_2O and the pH of this solution was adjusted to 7 by adding an appropriate amount of an aqueous NaOH solution (10% w/v). The resulting mixtures were stirred at room temperature for 3 h to yield the $Tb(3Cl\text{-}acac)_3(H_2O)_2$ complex. The white solid products were filtered, washed with water, and dried in desiccators at room temperature. The molecular structure is depicted in Fig. 1.

2.1.2. Synthesis of $Eu_{0.25}Tb_{0.75}(tfac)_3(H_2O)$

The complex was synthesized according to the literature [20,21]. It started by adding 0.37 mL (3.0 mmol) of tfac (1,1,1-trifluoro-2,4-pentanedione, Sigma-Aldrich) to 10 mL of water. A certain amount of diluted ammonium solution (1.0 mol/L) was added and a two-phase solution was formed. The mixture was stirred at room temperature until a homogeneous solution was obtained, and pH value was kept around 8. Then 91.6 mg of $EuCl_3{\cdot}6H_2O$ (Sigma-Aldrich) and 280.1 mg of $TbCl_3{\cdot}6H_2O$ in 15 mL of water was added and the precipitate appeared. The mixture was further stirred at 50 °C and then placed at ambient condition overnight. The precipitate was filtered off, washed with water, and dried at 60 °C. The molecular structure is depicted in Fig. 1.

2.1.3. Synthesis of the doped di-ureasil, d-U(600), and tripodal tri-ureasil, t-U(5000), organic–inorganic hybrids

The d-U(600) di-ureasil is formed by polyether chains (with average molecular weight of 600 g mol^{-1}) covalently linked to a siliceous inorganic skeleton by urea bridges and the t-U(5000) host is a urea cross-linked tripodal siloxane-based hybrid, Fig. 1. The synthesis of d-U(600) and t-U(5000) involves two steps. For d-U(600), in the first step, 1.0 g (1.67 mmol) of Jeffamine® ED-600 (Sigma-Aldrich, 97%) was mixed with 1.0 mL of dried THF (tetrahydrofuran, Sigma-Aldrich, 99.9%). The mixture was stirred for 10 min at room temperature. Then 0.866 mL (3.34 mmol) of ICPTES (3-(triethoxysilyl)propyl isocyanate, 95%, Sigma–Aldrich) was added dropwise under stirring. The molar ratio Jeffamine® ED-600 to ICPTES is 1:2. The resulting transparent sol was stirred for 24 h at room temperature. The THF was evaporated and thus the precursor d-UPTES(600) was obtained (Fig. 1). The molar ratio of d-UPTES(600):H_2O is 1:6. The t-UPTES(5000) precursor (Fig. 1) was synthesized in an identical way, except for the Jeffamine® T-5000 used, which presents a branched chain structure with the amino groups located at the end of each branch, with a molecular mass of 5000 (Huntsman). The molar ratio of Jeffamine® T-5000: ICPTES is 1:3. The resulting solution was refluxed at 80 °C for 24 h. The solvent THF was evaporated using rotary evaporator under reduced pressure. The molar ratio of t-UPTES(5000):H_2O is 1:9.

In a second step, a solution of $Tb(3Cl\text{-}acac)_3(H_2O)_2$ (5.8 mg, 0.01 mmol) and 1 mL of ethanol (Fisher Scientific, 99.9%) was kept under magnetic stirring for 20 min and 2 g of t-UPTES(5000) were added, with 25 μL of water and stirred for 15 min. Then, 50 μL of 0.5 M HCl (Sigma Aldrich, 37%) were added to reduce pH from 9 to 2, to decrease the time necessary for the sol-gel transition. In these conditions the resulting material (tU5Tb), presents a sol-gel transition in ~3 h at 40 °C. For the synthesis of d-U(600) ureasil doped with the $Eu_{0.25}Tb_{0.75}(tfac)_3(H_2O)$ complex, 0.75 mL of EtOH was added to 1.0 g (0.914 mmol) of d-UPTES(600) and the mixture