



Colourless *p*-phenylene-spaced bis-azoles for luminescent concentrators



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ABSTRACT

We report on the synthesis of new push-pull imidazole-benzothiazole and thiazole-benzothiazole fluorophores obtained in good yields by using direct C–H arylation synthetic strategies. Spectroscopic investigations in CHCl₃ solution evidenced that the 1,4-phenylene-spaced imidazole-benzothiazole bearing an electron-donating dimethylamino group achieved a trade-off between fluorescence maximum (516 nm), Stokes shift (165 nm) and a quantum yield higher than 0.4. Dispersions of the selected fluorophore in poly (methyl methacrylate) (PMMA) thin films mostly maintained the optical features in solution with significant light transmittance in the visible region (90% at 440 nm), and a brilliant green emission at 500 nm. Photocurrent experiments performed on PMMA thin films coated over high purity transparent glasses promoted their use in the development of colourless luminescent solar concentrators with optical efficiencies close to 6%.

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1. Introduction

Sunlight concentration is a promising path to cost-effective photovoltaic (PV) technologies. Solar concentration is achieved by collecting the sun radiation incident on a large surface and redirecting it on a smaller area, thus allowing to reduce the amount of photoactive materials, which has the largest impact on the final costs [1–3]. There are mainly two kinds of solar concentrators, one type is based on geometrical optics [4] and another category resides on luminescent components [3,5]. Compared to standard concentrators based on geometrical optics, luminescent solar concentrators (LSCs) show several advantages: low weight, high theoretical concentration factors, ability to work well with diffuse light and no needs of sun tracking or cooling apparatuses. LSCs demonstrate an entirely new standard for very large area and highly adoptable solar windows that can translate into improved building efficiency,

enhanced UV-barrier layers, and lower cost solar harvesting systems. LSCs consist in a slab of transparent material doped with a fluorophore able to absorb the solar spectrum [6]. The higher refractive index of the host compared to the environment allows to trap a fraction of the emitted photons by means of total internal reflection. Photons are then collected at the edges of the device to produce electric power by means of PV cells. Moreover, the use of commodity plastics such as poly (methyl methacrylate) (PMMA) and polycarbonate (PC) and well consolidated and economic industrial processes for the preparation of LSCs offer encouraging means to include solar energy to the built environment.

However, conventional LSCs are often plagued by a multitude of unfavourable processes that hinder their ability to deliver light to PV cells, in particular fluorescence quenching due to aggregation phenomena between luminescent species [6,7]. These issues triggered a great flurry of research in the field, leading to a large number of solutions that took into account fluorophore features, polymer hosts and their effective combinations [6]. In the recent years, the research on PV devices based on LSC technology has been focusing on achieving high power conversion efficiencies [8–18]. A

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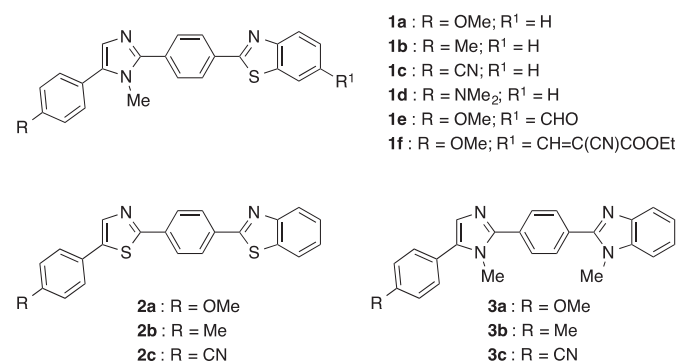
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simple approach for higher concentrations is to enhance the spectral window of absorption of the LSC, therefore increasing the number of available photons. To this end, multiple dye systems have long been proposed to cope for the narrow absorption characteristic of organic dyes as well as new design solutions [14,19,20]. Sloff et al. [18] described a stacked device with a power conversion efficiency of 7.1%, which is, at best of our knowledge, the highest efficiency ever reported for LSC-PV systems. Conversely, a dye mixture in a single slab offers the possibility of cascading of emission via non-radiative processes such as the fluorescence resonance energy transfer (FRET) [19,21]. Nevertheless, the maximum efficiencies for LSCs were recorded for PMMA device embedding perylene-based fluorophores [8,10,22]. Lumogen F Red 305 is a red-emitting perylene fluorophore, which is considered the state-of-the-art in dyes for LSC applications [6] since it shows a quantum yield (QY) of about 1 even at high concentration (>300 ppm) in polymers [23] and a good photostability [24].

However, the strong absorption in the visible spectrum of perylene-based fluorophores leads to a large degree of colored tinting. In order to overcome this issue, visible-transparent LSCs based on NIR-emissive cyanine salts have been recently proposed as innovative devices with transparency of near 90% in the visible spectrum [12]. This technology is considered very promising and it has received much attention in the scientific community due to LSCs potential application as architectural windows [12,25,26].

In connection with these findings, we exploited the potentiality offered by the new 1,4-phenylene-spaced azoles as near-UV absorbing fluorophores characterized by large Stokes shifts (SS) and green emission to be used in colorless LSC with optical efficiencies close to 6. Mixed imidazole-benzimidazole analogues were already proposed by us as fluorophores with SS near 100 nm, very high Φ , and with a bright blue-green emission well retained in the solid state. Notwithstanding their excellent emission features, their fluorescence peaked at $\lambda < 430$ nm did not match the working window of a Si-based PV cell ($\lambda \geq 500$ nm) [27], thus impeding their application in LSCs technology [28]. Therefore, new push-pull imidazole-benzothiazole and thiazole-benzothiazole fluorophores, **1a–f** and **2a–c** (Scheme 1), were efficiently synthesized aimed at retaining the features of imidazole-benzimidazole analogues (**3a–c**), while shifting their emission to longer wavelengths. Notably, high Φ is still required to maximize the LSC efficiency. Indeed, increasing SS of the fluorophore reduces reabsorption but radiationless internal conversion processes become more probable when the electronic excitation energy decreases, relative to the energy of molecular vibrations [29]. Therefore, an effective trade-off between SS and Φ should be achieved [30,31].

Thin-film LSC devices were then prepared by dispersing fluorophores in poly(methyl methacrylate) (PMMA) films coated over high optical quality glass slab. **1d** and **1f** 1,4-phenylene-spaced



Scheme 1. Chemical structure of compounds **1a–f**, **2a–c**, and **3a–c**.

azoles were selected being their emission higher than 500 nm. The LSCs optical efficiencies were discussed and compared to that measured for LSCs with the same geometry and containing Lumogen F Red 305.

2. Experimental part

2.1. Materials

Unless otherwise stated, all reactions were performed under argon by standard syringe, cannula and septa techniques. 2-(4-(5-(4-Methoxyphenyl)-1-methyl-1H-imidazol-2-yl)phenyl)-1-methyl-1H-benzo [d]imidazole (**3a**), 1-methyl-2-(4-(1-methyl-5-(*p*-tolyl)-1H-imidazol-2-yl)phenyl)-1H-benzo [d]imidazole (**3b**), 4-(1-methyl-2-(4-(1-methyl-1H-benzo [d]imidazol-2-yl)phenyl)-1H-imidazol-5-yl)benzotrile (**3c**), and 2-(4-bromophenyl)-1-methyl-1H-benzo [d]imidazole (**6**) were prepared as previously described by us [28]. All the other commercially available reagents and solvents were used as received. Poly(methyl methacrylate) (PMMA, Aldrich, Mw = 350,000 g/mol, acid number <1 mg KOH/g).

2.2. General procedures for the Palladium-catalysed direct 5-arylation of 1-methyl-1H-imidazole (**8**) and thiazole (**9**) with aryl bromides **10a–c** [28,32].

Pd(OAc)₂ (11.2 mg, 0.05 mmol), Bu₄NOAc (0.60 g, 2.0 mmol), and aryl bromide **10** (1.5 mmol), if a solid, were placed in a flame-dried reaction vessel. The reaction vessel was fitted with a silicon septum, evacuated, and back-filled with argon. This sequence was repeated twice more. DMA (5 mL), aryl bromide **10** (1.5 mmol), if a liquid, and the appropriate azole **8** or **9** (1.0 mmol) were then added successively under a stream of argon by syringe at room temperature. The resulting mixture was stirred under argon for 24 h at 70 °C when thiazole (**9**) was employed, or at 110 °C when 1-methyl-1H-imidazole (**8**) was the coupling partner. After cooling to room temperature, the reaction mixture was diluted with AcOEt, filtered through a plug of Celite and eluted with additional AcOEt and CH₂Cl₂. The filtrate was concentrated under reduced pressure and the residue purified by flash chromatography on silica gel. This procedure was used to prepare compounds **4a–c** and **5a–c**.

2.2.1. 5-(4-Methoxyphenyl)-1-methyl-1H-imidazole (**4a**)

The crude reaction product, which was obtained by Pd-catalysed reaction of 1-methyl-1H-imidazole (**8**) with 4-bromoanisole (**10a**), was purified by flash chromatography on silica gel with a mixture of CH₂Cl₂ and MeOH (96:4) as eluent to give **4a** (0.15 g, 82%) as a light-yellow solid, m.p. 106–108 °C. ¹H NMR (200 MHz, CDCl₃): δ 7.48 (s, 1H), 7.30 (m, 2H), 7.02 (s, 1H), 6.96 (m, 2H), 3.83 (s, 3H), 3.61 (s, 3H) ppm. ¹³C NMR (50.3 MHz, CDCl₃): δ 159.1, 138.3, 132.3, 129.6 (2C), 127.1, 121.8, 113.9 (2C), 55.1, 32.1 ppm. MS (EI): m/z (%) = 189 (12), 188 (100), 174 (10), 173 (82), 145 (17). The spectral properties of this compound are in agreement with those previously reported [33].

2.2.2. 1-Methyl-5-(*p*-tolyl)-1H-imidazole (**4b**)

The crude reaction product, which was obtained by Pd-catalysed reaction of 1-methyl-1H-imidazole (**8**) with 4-bromotoluene (**10b**), was purified by flash chromatography on silica gel with a mixture of CH₂Cl₂ and MeOH (96:4) as eluent to give **4b** (0.14 g, 81%) as a yellow oil. ¹H NMR (200 MHz, CDCl₃): δ 7.49 (s, 1H), 7.26 (m, 2H), 7.25 (m, 2H), 7.07 (s, 1H), 3.63 (s, 3H), 2.39 (s, 3H) ppm. ¹³C NMR (50.3 MHz, CDCl₃): δ 138.7, 137.6, 133.3, 129.3 (2C), 128.3 (2C), 127.6, 126.7, 32.4, 21.2 ppm. MS (EI): m/z (%) = 173 (13), 172 (100), 171 (17), 144 (14), 130 (16). The spectral properties of this compound are in agreement with those previously reported [34].

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