

A direct arylation approach for the preparation of benzothiadiazole-based fluorophores for application in luminescent solar concentrators

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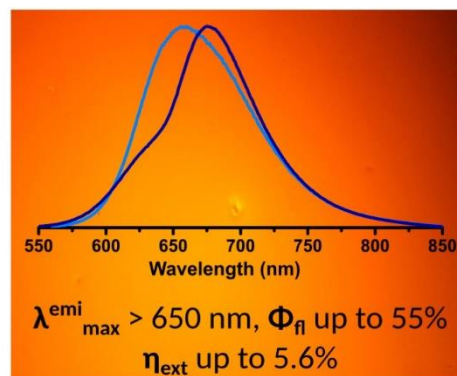
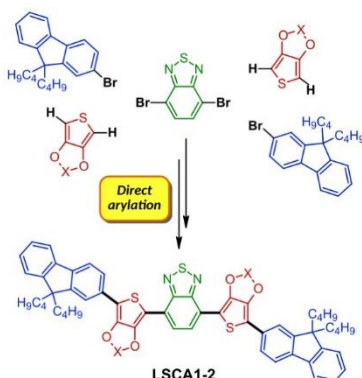
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Dedicated to Prof. Masahiro Murakami on the occasion of his retirement from Kyoto University



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Abstract A straightforward synthetic protocol featuring direct C-H arylations as key steps has been optimized to prepare two benzo-2,1,3-thiadiazole (BTD)-based organic fluorophores. Their light absorption and emission properties, as well as their affinity to PMMA as the chosen polymer matrix, were found suitable for application in luminescent solar concentrators (LSC). Solar concentration devices were fabricated with both emitters and their relevant optical and photovoltaic properties were presented.

Key words Direct arylation, Fluorophore, Heterocycles, Luminescent Solar Concentrator, Photovoltaics.

Organic luminescent materials have attracted increasing attention over the past few years, since they can find application in several different fields such as the fabrication of organic light-emitting diodes (OLEDs),¹ optical communication and interconnection technologies,² biomedicine³ and photovoltaics (PV).⁴

Concerning the latter, several studies have been focused on their application in luminescent solar concentrators (LSCs), a class of optical devices that can be used to generate electric power from sunlight. LSC technology has been studied since the 1970s^{5,6} and operates with common plastic (*e.g.*, poly(methyl methacrylate), PMMA) panels doped with a fluorescent dye. The fluorophore must be capable of absorbing sunlight and emitting it at longer wavelengths: thanks to the different refractive indexes between air and the plastic material, the emitted radiation is mainly concentrated, via total internal reflection, at the edges of the panel (where conventional silicon solar cells can be placed). The key advantages of such devices are that they are transparent and lighter than common silicon panels and can also absorb indirect light; as such, they can be easily incorporated into building components, furniture, roofs, and façades.⁷ To obtain efficient LSCs, it is mandatory to carefully optimize the

materials used for their fabrication, among which the fluorophore is key.⁸

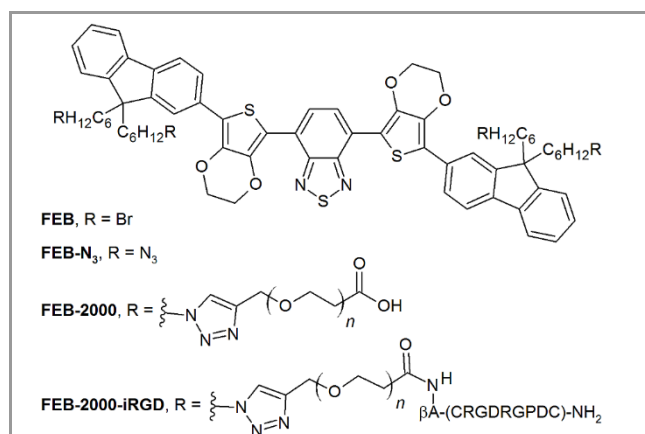


Figure 1 Structure of the FEB molecules based on the benzo-2,1,3-thiadiazole core (see ref. 18).

In particular, the exploitation of small organic molecules as emitters appears very interesting, offering many advantages such as ease of preparation, tunability of the photophysical properties, and low costs. In this context, we have approached the study of molecules with donor-acceptor-donor (D-A-D) architectures, having one (or more) strong electron-donating moiety (D) connected to a highly electron-poor motif, the acceptor (A).⁹⁻¹² This kind of structures might favor strong intermolecular charge transfer (ICT) processes upon photoexcitation, leading to red-shifted emissions and large Stokes shift (SS) values, which are possibly beneficial to limit re-absorption phenomena in the devices.¹³ Such molecular design allowed us to obtain LSCs characterized by excellent optical properties, in some cases even superior to those provided by state-of-art commercial fluorophores (such as BASF LR305).^{14,15} The emission maxima of those compounds

were usually limited to the 460-550 nm range; nevertheless, a further red-shift of the emission could be useful not only to improve the match with the absorption of Si solar cells and, consequently, to enhance the PV efficiency of the resulting LSCs, but also to extend the palette of available colors of the devices. Furthermore, emitters with photophysical properties compatible with chlorophylls (*i. e.* absorption in the green region of the spectrum and emission in the red region) could be useful to fabricate LSCs applicable in the growing fields of greenhouse- and photobioreactor-integrated PV.^{16,17} For these reasons, we decided to investigate the effect of adding to the molecular scaffold further aromatic moieties to obtain a π -D-A-D- π sequence. We were inspired by the fluorescent probe, **FEB-2000** (Fig. 1), reported by Yang and co-workers in 2017 for tumor imaging applications.¹⁸ Such compound includes a benzo-2,1,3-thiadiazole (BTD), 3,4-ethylene-dioxythiophene (EDOT) and fluorene moieties in a typical π -D-A-D- π structure, resulting in an emission centered at 675 nm, coupled with a high fluorescence quantum yield (85% in toluene solution). Given such promising properties, we devised to prepare and apply in LSC two new compounds based on the **FEB-2000** structure, that is **LSCA1**, having simple butyl chains on the fluorene moieties, and **LSCA2** having a bis-*n*-pentylpropylenedioxy-thiophene (ProDOT) unit replacing EDOT (Fig. 2).

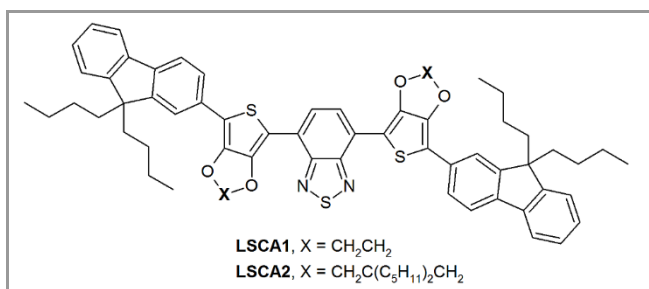
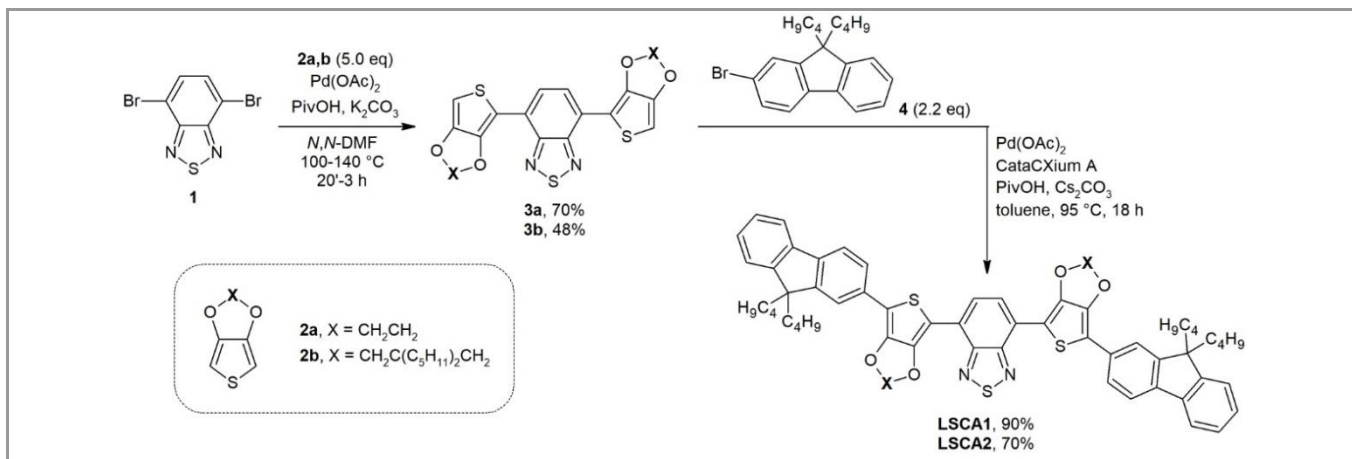


Figure 2 Structures of the two emitters **LSCA1** and **LSCA2**.

The previously reported synthesis of **FEB** (precursor of **FEB-2000**, Fig. 1) consisted of four synthetic steps and involved the preparation of two tin-containing intermediates, required to assemble the final molecule through the Stille-Migita cross-coupling reaction (Scheme S1, Supporting Information).¹⁸

Despite the overall yield of the final compounds being quite satisfactory, we decided to design a different and more sustainable synthetic approach to **LSCA1-2**, based on the direct C-H arylation process.¹⁹ Such a procedure enables facile coupling of aryl halides with non-substituted heteroaryls and has been recognized as a very efficient synthetic tool for producing well-defined and high-performance π -conjugated materials,²⁰ also as a part of sequential domino protocols.²¹ Our approach to prepare the two fluorophores is reported in Scheme 1. Commercially available 4,7-dibromo-2,1,3-benzothiadiazole (**1**) and EDOT (**2a**), or the previously reported ProDOT (**2b**),²⁰ were reacted under optimized direct arylation conditions, employing Pd(OAc)₂ as palladium source, K₂CO₃ as base, pivalic acid (PivOH) as additive, and DMF as solvent. Upon heating, the desired intermediates **3a** (140 °C, 3h)²² and **3b** (100 °C, 20 min) were recovered, after workup and purification, in 70% and 48% yield, respectively. In the subsequent step, **3a** and **3b** were reacted with 2-bromo-9-dibutyl-fluorene (**4**) using Pd(OAc)₂, *bis*(adamantyl)-*n*-butylphosphane (CataCXium® A) as ligand, Cs₂CO₃ as base, PivOH as additive, and toluene as solvent. The choice of ligand was based on previous results obtained by our research group, showing an efficient functionalization of ProDOT-containing compounds under direct arylation conditions.²⁰ After heating at 95°C for 18 h, the final fluorophores **LSCA 1-2** were obtained in very good yields after purification (90% and 70% respectively). Thus, the two syntheses proceeded with yields comparable to that of the original preparation of FEB compounds, although they were conducted under more sustainable conditions, without the use of pre-formed or toxic organometallics.

The two emitters have been fully characterized and their optical properties were analyzed *via* UV-Vis and fluorescence emission spectroscopy in solution. Toluene was selected as a solvent since it has a similar refractive index (1.496) to that of PMMA (1.491), the most common polymer used in LSC, thus providing a relevant reference for the foreseen application. The spectra were also recorded in a more polar solvent such as dichloromethane to check the occurrence of positive emission solvatochromism, usually observed for conjugated donor-acceptor fluorophores because of excited state stabilization.



Scheme 1 Synthetic route leading to compounds **LSCA 1-2**.

Table 1 Spectroscopic properties of **LSCA1** and **LSCA2** in dichloromethane (DCM) and toluene solution.

Compound	Solvent	λ_{abs} (nm)	ϵ ($\times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$)	λ_{em} (nm)	SS (eV)	$\Phi_{\text{F}}(\%)$
LSCA1	DCM	550 [385] ^a	4.97 [7.18] ^a	670	0.40 [1.37] ^a	-
	Toluene	550 [387] ^a	4.81 [6.49] ^a	650	0.35 [1.30] ^a	66
LSCA2	DCM	528 [371] ^a	3.11 [5.07] ^a	662	0.47 [1.47] ^a	-
	Toluene	531 [374] ^a	3.17 [4.68] ^a	638	0.39 [1.37] ^a	68

^a In parentheses, values of λ_{abs} , ϵ , SS relative to a second absorption peak at a shorter wavelength are reported.

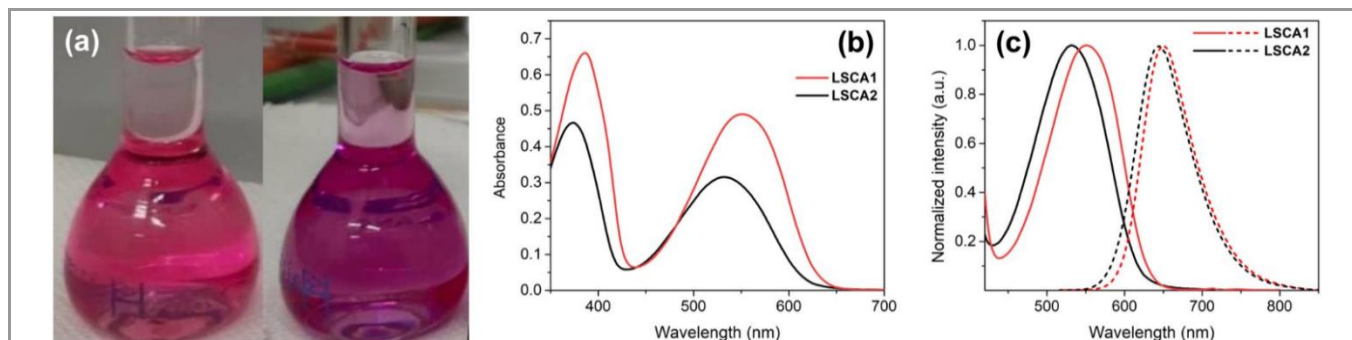


Figure 3 (a) Pictures of 0.01 mM toluene solution of **LSCA1** (left) and **LSCA2** (right); (b) Absorption spectra of **LSCA1** (red line) and **LSCA2** (black line) in toluene solution, 0.01 mM; (c) normalized absorption (solid lines) and emission (dot lines) spectra of **LSCA1** (red) and **LSCA2** (black) in toluene solution, 0.01 mM, with λ_{exc} at 550 and 531 nm, respectively.

Spectroscopic data are reported in Table 1. Both dyes exhibited similar shapes of the visible spectra in the two solvents, characterized by two broad absorption ranges, an absorption peak at a shorter wavelength (370–390 nm), corresponding to a localized $\pi \rightarrow \pi^*$ transition, and another one between 500 and 600 nm, corresponding to the ICT photoexcitation process.²³ The absorption intensity increased with concentration, with a comparable trend in both solvents (Fig. S10). For both absorption maxima, **LSCA1** exhibited a higher ϵ than **LSCA2** (Fig. 3b), corresponding to a better light-harvesting ability. The emission spectra of the two dyes were also registered in both solvents, after excitation at the maximum absorption wavelength. They showed only one peak, centered at 650–670 nm for **LSCA1** and at 638–662 nm for **LSCA2**, respectively, depending on the solvent (Fig. S11). In general, large Stokes shifts, around 100–130 nm, and limited overlap between absorption and emission spectra were observed in agreement with a strong ICT effect in both solvents (Fig. 3c). Moreover, the regular shapes of the emission spectra proved the absence of emissive aggregates. Remarkably, due to the presence of alkyl chains, both fluorophores showed good solubility in a nonpolar solvent such as toluene. Such behavior might entail an easy

dispersion into the polymer matrix used for LSC, facilitating device fabrication, and offering an important advantage on large-scale applications.

The two compounds were then characterized in a polymer matrix. Films with a $25 \pm 5 \mu\text{m}$ thickness were prepared by dispersion into transparent and totally amorphous PMMA, at different concentrations (range: 0.4–2.0 wt.%). Both compounds gave homogenous films with negligible macroscopic phase separation at the surface, even at the highest fluorophore content, as confirmed by epifluorescence microscopy images (Fig. S13). UV-Vis spectra of **LSCA1-2** in PMMA at different concentrations (Fig. S14) also showed a regular increase of absorbance with fluorophore concentration. The emission spectra of the two fluorophores were also recorded at different concentrations showing a red-shift of the maximum wavelength, accompanied by a moderate decrease of fluorescence quantum yield (Fig. 4a,b). This is a typical trend, the red-shift being due to the increase of self-absorption, usually worsening with the concentration of the fluorophore, as well as fluorescence quenching phenomena potentially arising from dipole-dipole or surface-dipole interactions, occurring more frequently in more concentrated matrices.²⁴

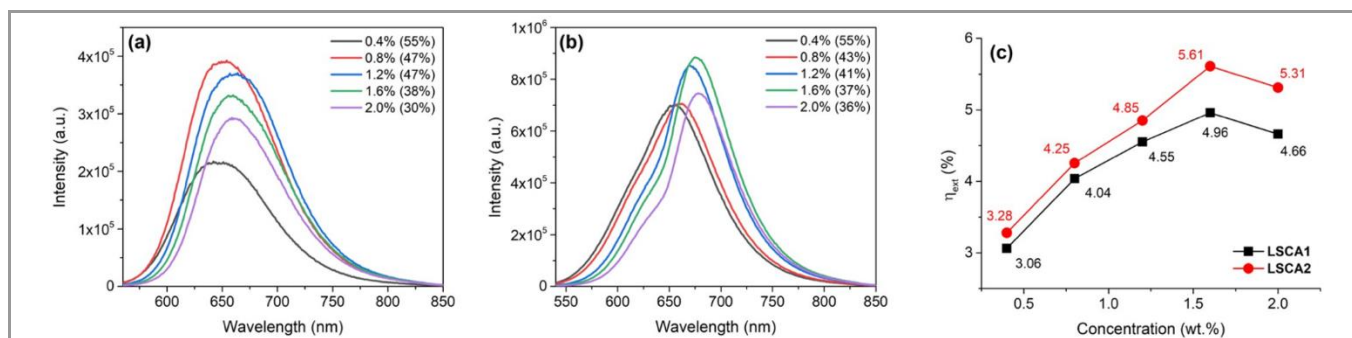


Figure 4 Emission spectra of **LSCA1** (a) and **LSCA2** (b) in PMMA at different concentrations (wt. %). Fluorescence quantum yields are reported in brackets; (c) External photonic efficiencies (η_{ext}) of LSCs built with **LSCA1-2** emitters vs. their wt.% concentration in PMMA films.

Finally, the efficiency of the corresponding LSC devices was evaluated.²⁵ The external (η_{ext}) and internal (η_{int}) photonic efficiencies were recorded for all different concentrations (see SI for definitions and experimental details). The two emitters showed a comparable behavior, with maximum η_{ext} values of 4.96% and 5.61% for **LSCA1** and **LSCA2**, respectively, obtained in both cases at 1.6 wt. % fluorophore concentration (Fig. 4c). On the contrary, the highest η_{int} values were found at the lowest concentration, in agreement with the above-mentioned trend of the fluorescence quantum yield of the two fluorophores in PMMA (Fig. S12). This is not surprising since, the η_{int} parameter is calculated based on the number of photons actually absorbed by the LSC, and thus depends only on the light emission and re-absorption phenomena occurring within the polymeric film. Then, to assess the LSC performances in the direct light-to-electricity conversion, the photovoltaic efficiency (η_{dev}) parameter was measured, connecting two Si-PV cells in series to an edge of the thin-film LSCs and measuring the electric power generated by the devices under simulated solar irradiation (see SI for details). In agreement with η_{ext} measurements, the best η_{dev} values were also recorded at 1.6 wt.% (0.70 and 0.72 % for **LSCA1** and **LSCA2**, respectively), indicating that at such concentration the devices had the highest capability of converting light into electricity. The fact that both the best η_{ext} and η_{dev} values were obtained at relatively high concentrations in the matrix highlights the efficacy of the chosen π -D-A-D- π design in reducing self-absorption phenomena thanks to the resulting large Stokes shifts, suggesting the possibility to employ this kind of emitters in large scale concentration devices.²⁶

In conclusion, we have prepared two π -D-A-D- π luminescent compounds using an efficient and high-yielding two-steps direct arylation protocol that avoids the use of highly flammable reagents, such as *n*-butyllithium, or highly toxic agents, such as organotin compounds. Both emitters showed physical and optical properties suitable for application in LSC devices. In particular, the chosen molecular design was confirmed to yield compounds with a strong absorption in the middle of the visible region and fluorescence emission centered above 600 nm, resulting in large Stokes shifts and a good match with Si solar cells absorption. Preliminary results showed that both compounds had excellent dispersibility in PMMA matrix, and their LSC devices reached external photonic efficiencies close to or above 5.0% (at 1.6 wt.%), which were comparable or superior to those recently obtained with other donor-acceptor type organic fluorophores measured under similar conditions.²⁷⁻³⁰ Therefore, their favorable spectral features, excellent physico-chemical properties and simple synthetic procedures make **LSCA1-2** derivatives very promising candidates for scaled-up LSC applications.

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Supporting Information

YES (this text will be updated with links prior to publication)

Primary Data

NO.

Conflict of Interest

The authors declare no conflict of interest.

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