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Subphthalocyanines as narrow band red-light emitting materials

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Abstract—A series of new light emitting subphthalocyanines, lower homologues of phthalocyanines, were synthesized having color points covering the red-orange region of the visible spectrum. Additionally, they were found to be of potential use as narrow band emitters for red-light emitting diodes.

The use of organic light emitting devices (OLEDs) for illumination systems, which promise to revolutionize the flat panel illumination market, has highlighted the need for efficient red luminescence molecules.[1,2] The main driver for this need is the desire to obtain warm white light sources. Such light sources inevitably contain a large component of a red emitter. Hence, the overall device efficiency will depend for a large part on the efficiency of the red OLED. To optimize the efficiency, it is desirable to use red emitters whose emission spectrum is narrow such that only a small fraction of the photons is emitted in the near infrared. Examples of emitters proposed are those making use of ruthenium,[3] iridium[4] or osmium complexes,[5] lanthanide complexes, such as europium[6] as well as platinum based porphyrins[7] and phthalocyanines (Pcs).[8] A less well-known type of red emitters are the subphthalocyanines (SubPcs), which are fluorescent emitters with high quantum yields that have narrow emission spectra in solution.[9] Recently, very efficient white light emitting diodes have been obtained using a fluorescent red light emitter, which was excited via exciton transfer from a green phosphorescent emitter, harvesting in this way both singlet and triplet excitons generated in the OLED.[10] This finding sheds new light on the desire and search for efficient fluorescent red light emitters.

SubPcs are macrocycles, known only as boron derivatives, formed by three N-coupled isoindole moieties having a delocalized 14 π-electron system. The preparation and properties of these subporphyrinoids have been recently reviewed and highlighted.[9a,b] Their aromatic characteristics along with their non-planar cone-shaped structure make them attractive compounds with singular chemical and physical properties.[11,12] Indeed, they are lowest homologues of Pcs, well-known two-dimensional 18 π-electron aromatic systems with unusual electrical and optical properties.[13] They are excellent antenna units that absorb in the 550–650 nm region with excitation energies above 2.0 V; they possess low reorganization energies, and their overall physical characteristics may be tuned by the introduction of different peripheral and axial substituents. Structural modifications of these compounds[14] and novel applications[15] have been also reported. Particularly, their high thermal and chemical stability, electron transfer abilities, and tunable solubility, make SubPcs suitable candidates for applications in OLEDs.

Herein, we report a series of SubPcs that exhibit narrow photoluminescence spectra with maxima ranging from 577 to 613 nm. Additionally, we prepared a solution processable OLED structure by dispersing two representative compounds in a suitable charge transporting matrix, which confirmed the narrow emission and serves as a proof of principle for the use of SubPcs in OLEDs.

Keywords: Subpthalocyanine; Fluorescence; Light emitting diodes.

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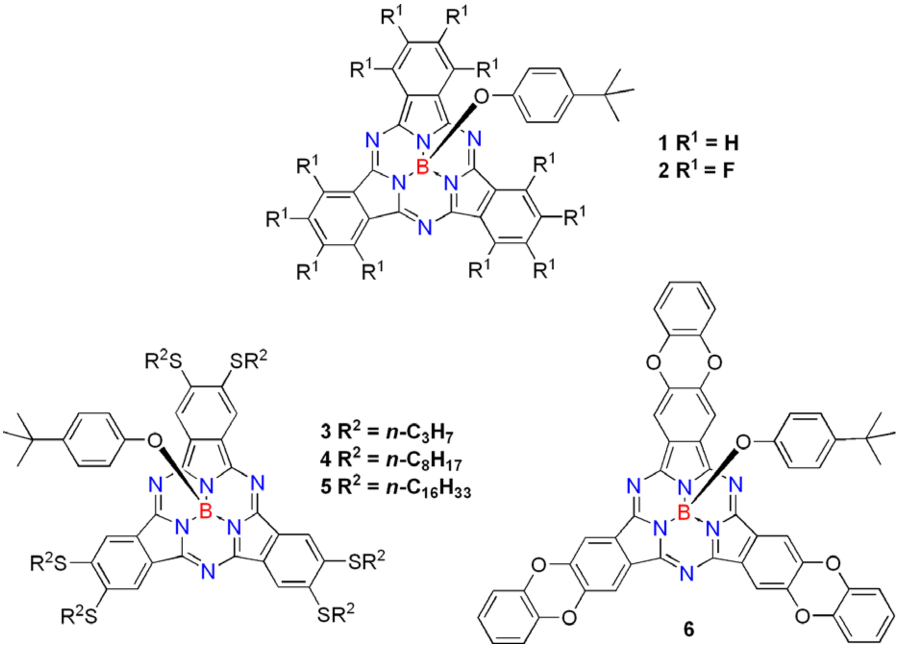


Figure 1. Subphthalocyanines **1**–**6** synthesized for this work.

As far as we were aware, no report on their potential use in OLEDs has ever been published, despite their intense fluorescence.

We prepared a number of SubPcs **1**–**6** (Fig. 1), with the aim of having high fluorescence quantum yields and a low tendency towards aggregation. SubPcs **2** and **4** are known[6] and were synthesized following the procedures previously described, giving physical characteristics identical to the reported ones. Compounds **1**, **3**, **5**, and **6** are new and were synthesized using our previous reported method,[16] albeit with slight modifications. Full characterization data for the new compounds are given in Supplementary data (S3–S5). Thus, BCl_3-templated cyclotrimerization of the appropriate substituted phthalonitrile and subsequent in situ nucleophilic substitution of the axial chloride atom of the Cl-substituted SubPc intermediate allowed the preparation of SubPcs **1**–**6** in good overall yields.

The absorption and photoluminescence spectra of the SubPcs are depicted in Figure 2. Regarding the absorption spectra, the fine tuning of the position of the Q-band in the SubPc derivatives has been addressed in the present case by introduction of appropriate peripheral substituents. The small shift in emission maximum versus the absorption maxima for each individual SubPc is a consequence of the 0–0 transition dominating the emission spectrum. The most interesting feature of the emission spectra is its small width at half of the maximum intensity (WHM), which is ranging from 60 to 90 nm for the different compounds investigated. Such a small WHM is rarely observed for organic fluorescent compounds. It originates from the fact that there are a limited number of configurations leading to a narrow density of states of the HOMO and LUMO energies. Such a feature has been observed as well in other rather rigid molecules, such as porphyrins and Pcs, with comparable values in some cases, but it is generally not associated with a high photoluminescence quantum yield.

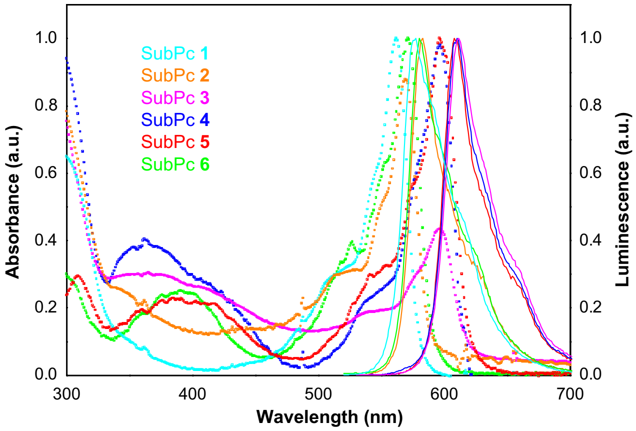


Figure 2. Absorption (dotted lines) and emission (solid lines) spectra in toluene solution of the SubPcs **1**–**6**.

The photoluminescence quantum yields of SubPcs **1**–**6** in deaerated toluene solution have been determined using $Ru(bpy)_3Cl_2$ as reference[17] and are shown in Table 1. Strikingly the values obtained range from a mere 2% to some 56%. Especially the values corresponding to SubPcs **1** and **6** are indicative of the high photoluminescence efficiencies the SubPcs can possess.

At this point, the question arises whether these complexes maintain their narrow emission width also in electroluminescence. This is an interesting question, as it is the first step in obtaining OLEDs using this attractive class of emitter molecules. Thus, SubPcs **5** and **6** were selected and tested in solution processable OLED

Table 1. Selected photophysical properties of SubPcs **1**–**6** in solution[a]

Compound	Abs[a] 298 K	Emission 298 K	
	λ (nm)	λ (nm)	φ_{em}[b]
1	562	577	0.56
2	570	579	0.02
3	596	613	0.16
4	596	611	0.17
5	596	612	0.10
6	570	584	0.34

[a] Absorbances were recorded from acetonitrile solutions.
[b] Luminescence emission quantum yields (±10%).

devices since they offered the best compromise between processability, photophysical, and solubility properties of the SubPcs series presented in this work. The SubPcs were dispersed in a standard blue emitting polymeric OLED using a polyspirofluorene–arylamine copolymer, Spiroblue,[18] as the emitting polymer. Homogenous transparent films were obtained as long as the concentration of the SubPcs remained below 20 wt % OLEDs were prepared by spincoating a toluene solution containing Spiroblue and compound **5** or **6** in a 4:1 ratio on extensively cleaned ITO covered glass plates. To enhance the hole injection and the device stability, prior to the light emitting layer a 100 nm PEDOT:PSS (HC-Starck) was deposited.[19] Finally, a barium cathode capped with silver was thermally evaporated under high vacuum. Device characterization was performed under inert atmosphere. For further details see Supplementary data. Using such a non-optimized and simple architecture we were able to obtain the electroluminescence spectra of these compounds (Fig. 3). From these data it is clearly observed that the emission spectra are virtually unchanged with respect to that of the solution based photoluminescence data, retaining their narrow width.

The preliminary results of these solution processable OLED confirm that SubPcs function as emitters in the Spiroblue host, as no residual blue emission is observed. The excited states can be created via energy transfer from excitons generated in the host to the SubPcs or by sequential trapping of holes and electrons. The latter seems the more dominant mechanism as the electroluminescence is more intense than the photoluminescence in the same films. This sequential trapping could also explain the relatively high turn-on voltage and rather low efficacies, 10 V (to reach 1 cd/m^2) and 0.1 cd/A (at 100 cd/m^2), respectively, for the first time OLEDs made of SubPcs.

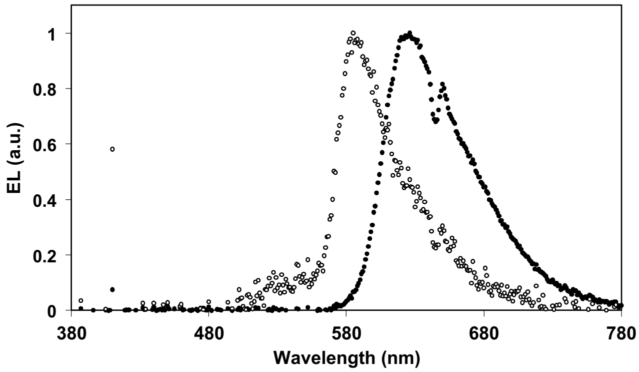
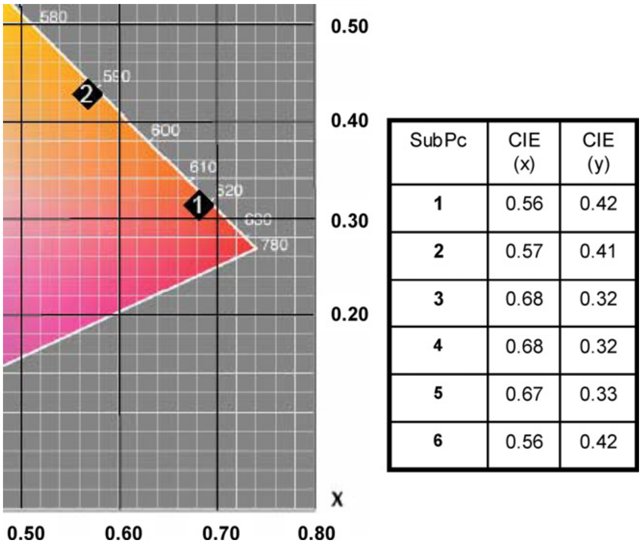


Figure 3. Electroluminescence spectra of OLEDs containing SubPcs **5** (full circles) and **6** (empty circles).



SubPc	CIE (x)	CIE (y)
1	0.56	0.42
2	0.57	0.41
3	0.68	0.32
4	0.68	0.32
5	0.67	0.33
6	0.56	0.42

Figure 4. Left: Amplified CIE 1933 color coordinate plot depicting the color points of SubPcs **3**, **4**, and **5** (black diamond nr 1) and SubPcs **1**, **2**, and **6** (black diamond nr 2). Right: Table with the color points of each SubPcs.

These emission maxima combined with the narrow width of the spectra showed above result in a range of orange to red color points, coming from orange to deep red in the amplified CIE coordinates plot (Fig. 4). Thus, using these compounds it is possible to obtain emitters that cover the red part of the visible spectrum by slightly modifying their chemical structures. The CIE coordinates of the light emitted from these electroluminescent devices containing SubPcs **5** and **6** are: $x = 0.67$, $y = 0.33$; and $x = 0.56$, $y = 0.42$, respectively. This demonstrates that SubPcs can indeed be used in solution processable OLEDs to generate an interesting narrow band red emission. Lastly, it is worth mentioning that current efforts are being made in fine tuning the position of the Q-band in subporphyrinoid systems,[14] though for other technological purposes (data storage, PDT, sensors, solar cells).[9b,13a,15]

In conclusion, we have described the photophysical properties of a new series of luminescent compounds that exhibit very narrow emission spectra resulting in color coordinates within the red and orange region useful for displaying and lighting applications. In spite of the narrow emission, the photostability of these SubPcs does not meet the requirements of OLEDs operating duration, but we believe that the modular synthesis of these compounds and different approaches to the device construction will allow much higher efficiencies in the future. In this sense, optimization of the device performance is currently underway by covalently linking the SubPcs to the charge transporting polymer chains and will be reported in due course.

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Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.tetlet.2007.05.036.

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