A series of \(N1,N4\)-didodecyl-\(N1,N4\)-diphenylbenzene-1,4-diamine-based polysquaraines have been synthesized under microwave irradiation in the absence of any catalyst. The effect of the solvent of polymerization, on the squaric acid catenation (1,2 and 1,3 linkages), has been studied and polysquaraines integrating linear chains in their backbone have been advantageously obtained by using di-functional alcohol during the polymerization. Such obtained polymers exhibit a broad emission with a quantum yield up to 18%. The latter were then tested in OLED devices exhibiting a promising white emission.

Organic dyes have been widely studied for their strong absorption and integrated as semi-conducting materials in light emitting and absorbing devices. Squaric acid, first synthesized in 1959 by S. Cohen, J. R. Lacher and J. C. Park, and subsequently squaraine dyes are broadly studied dyes for their low band-gap and near infra-red absorption and emission. Organic dyes have then been integrated into various devices to study their optoelectronic properties. π-Conjugated polysquaraines could also be obtained via the condensation of a conjugated monomer with squaric acid. This approach remarkably works without the use of any transition metal catalyst and is only driven by the removal of water during the polymerization. Our group recently described that such obtained polysquaraines exhibited higher molar masses than the same polysquaraines synthesized using Suzuki and Stille cross-coupling reactions.

In the present work, the polymerization of the squaric acid monomer with an alkylated \(N,N\)-diphenyl-p-phenylenediamine in the absence of any catalyst and the impact of the alcohol used during the polymerization were studied. Various π-conjugated polymers containing squaraine units were then synthesized using conventional transition-metal catalyzed cross-coupling reactions and allowed to achieve materials with small band-gaps. They have then been integrated into various devices to study their optoelectronic properties. π-Conjugated polysquaraines incorporating di-functional alcohols as comonomers presented a broad emission and were integrated into OLED, exhibiting a white emission. The polycodensation was performed between squaric acid and \(N1,N4\)-dialkyl-\(N1,N4\)-diphenyl benzene or triphenyl diamine (TPDA). This monomer was chosen because of easy alkylation, high commercial availability and the presence of two conjugated nitrogens. Indeed, a conjugated nitrogen must be present in the monomer, as shown in the mechanisms proposed by Ronchi et al. in 2011. It was alkylation with a dodecane chain to ensure its solubility as well as the solubility of the final polymer.

All the polymers were synthesized following the same method (Scheme 1). Stoichiometric amounts of TPDA and squaric acid or 1,2-dichlorocyclobutene-3,4-dione (SqCl) were thus decreasing the cost of their optoelectronic devices. By enhancing the planarity and electron-donating character of difunctional monomers, Havinga et al. synthesized a polysquaraine alternating strong donor and acceptor subunits. In this report, squaric or croconic acid (considered as a stronger acceptor moiety) and benzobisthiazole or benzobisazole were respectively used as withdrawing (acceptor) and donating (donor) moieties. Various π-conjugated polymers containing squaraine units were then synthesized using conventional transition-metal catalyzed cross-coupling reactions and allowed to achieve materials with small band-gaps. They have then been integrated into various devices to study their optoelectronic properties. π-Conjugated polysquaraines could also be obtained via the condensation of a conjugated monomer with squaric acid. This approach remarkably works without the use of any transition metal catalyst and is only driven by the removal of water during the polymerization. Our group recently described that such obtained polysquaraines exhibited higher molar masses than the same polysquaraines synthesized using Suzuki and Stille cross-coupling reactions. In the present work, the polymerization of the squaric acid monomer with an alkylated \(N,N\)-diphenyl-p-phenylenediamine in the absence of any catalyst and the impact of the alcohol used during the polymerization were studied. Various π-conjugated polymers containing squaraine units were then synthesized using conventional transition-metal catalyzed cross-coupling reactions and allowed to achieve materials with small band-gaps. They have then been integrated into various devices to study their optoelectronic properties. π-Conjugated polysquaraines could also be obtained via the condensation of a conjugated monomer with squaric acid. This approach remarkably works without the use of any transition metal catalyst and is only driven by the removal of water during the polymerization. Our group recently described that such obtained polysquaraines exhibited higher molar masses than the same polysquaraines synthesized using Suzuki and Stille cross-coupling reactions.
allowed to react in a mixture of toluene plus an alcohol as a co-solvent for four hours at 130 °C. Different mixtures of solvents (with different alcohols and various ratios between two different solvents) were used allowing the tuning of polymers’ structure and more specifically, the ratio between 1,2 and 1,3 linkages on the squaric acid subunit. 1,3-Propanediol was used to study its insertion into the polymer chain and the impact on polysquaraine properties (see the NMR characterization in the ESI†).

The polymer synthesized using $\text{SqCl}$ ($\text{PSQ-SqCl}$) presents only the 1,2 linkages. However, the polymer synthesized with squaric acid presents a mixture of 1,2 and 1,3 linkages. Microwave irradiation was preferred to the conventional Dean–Stark apparatus in order to speed up the polymerization reaction. Indeed, polymers with similar sizes and dispersities have been obtained after one day with the conventional Dean–Stark apparatus against only four hours under microwave irradiation. In both cases, polymerizations were able to be performed on a gram-scale without impacting the reaction yield or polymer properties. After extraction using a Soxhlet extractor in methanol and in chloroform, respectively, the polymers were characterized by ATR-FTIR spectroscopy. This method allows the estimation of the ratio between 1,2 and 1,3 linkages in the polymer backbone.$^{29-31}$ The physical and structural data of the synthesized polysquaraines are reported in Table 1.

All samples show comparable size (confirmed by mass spectrometry and NMR, see the ESI†), from 3500 to 3700 g mol$^{-1}$ with dispersity ranging between 2.0 and 3.0, the latter values being quite coherent with a step-growth polymerization mechanism, considering that the conversions are close to 100%. It is noteworthy that the shape of the chromatograms (see the ESI†) is also in agreement with a polycondensation process where a series of oligomers can be distinguished. The thermogravimetric (TGA) and differential scanning calorimetry (DSC) analyses showed good thermal stability with decomposition temperatures ranging from 430 to 450 °C. The qualitative percentages of 1,2 additions have been estimated by ATR-FTIR spectroscopy, using the polymer synthesized with the $\text{Sq-Cl}$ monomer as a reference with 100% of 1,2 additions. The polymers synthesized using butanol or 1,3-propanediol as a co-solvent present a mixture of both linkages with 40% to 65% of 1,2 linkages. However, the use of 1-dodecanol leads to more than 90% of 1,3 linkages. The UV-vis absorption and fluorescence spectra of the different polysquaraines synthesized herein were recorded in order to evaluate their optical properties. Concerning UV-vis absorption, the spectrum of the polysquarine PSQ-C4 synthesized using a classical mixture of toluene and 1-butanol as a solvent$^{32}$ presents three absorption bands peaking at 300, 400 and 650 nm (Fig. 1a). These peaks are due to the presence of a mixture of different linkages in
this polymer. The peak at 400 nm corresponds to 1,3 linkages. When dodecanol is used as a co-solvent (PSQ-C12), the intensity ratio of these absorption peaks changes (Fig. 1a). Indeed, the intensity of the absorption at 650 nm, corresponding to the 1,3 linkages, is enhanced compared to the one corresponding to the 1,2 linkages (at 400 nm). A reference model polymer, only composed of 1,2 linkages, was synthesized using dichlorosquaric acid as a co-monomer (PSQ-SqCl). The latter was synthesized in one step from squaric acid in the presence of thionyl chloride in toluene and purified by sublimation (Scheme 1). This model polymer allowed us to confirm the discrimination between 1,2 and 1,3 linkages since it does not show any absorption band at 650 nm characteristic of 1,3 linkages, as previously discussed.

Moreover, the use of a longer alcohol as a co-solvent (dodecanol) could favor the kinetic addition, leading to the formation of 1,3 linkages, as confirmed by ATR-FTIR and absorption spectroscopy, which allows us to tune the optical properties (Fig. 1a and the ESI†).

In addition, as squaric acid can react with alcohol, the polymerization reaction was performed with a difunctional alcohol such as 1,3-propanediol to study the impact of alcohol insertion on the polymer properties (polymers PSQ-PD). The reaction was performed in toluene with different ratios of 1,3-propanediol. Unfortunately, due to the presence of a mixture of 1,2 and 1,3 linkages and the presence of randomly inserted alcohol chains in the polymer, it is difficult to estimate the amount of 1,3-propanediol present in the chain (see the ATR-FTIR and NMR spectra in the ESI†). It is noteworthy that the reaction with only 1 equivalent of propanediol does not allow obtaining a polymer due to monomers’ solubility issue. The absorption and emission spectra of this polymer are presented in Fig. 1b and c, respectively. As the number of propanediol equivalents increases, a decrease in the absorption
peak at 310 nm is observed, as well as a decrease in the emission signal at 350 nm. At the same time, the emission peak at 500 nm is increased and broadened. This can be explained by a break in the polymer conjugation, forming independent chromophore units that emit at different wavelengths. In fact, the broad emission of the polymers synthesized with 3 and 10 equivalents covers the whole visible spectrum, from 350 to 700 nm, which is particularly interesting since it could suggest a white emission of these two products. The emission spectrum, the CIE chromaticity coordinates and the absolute fluorescence quantum yield of the 10-equivalent polymer that exhibits the broader emission were measured in solution, using an integration sphere. According to the CIE diagram presented in Fig. 1d, the x and y coordinates are respectively 0.27 and 0.32, which corresponds to a white emission in solution, with a quantum yield of 18%.

Prior to its integration into devices, the HOMO and LUMO levels of the PSQ-PD10 polysquaraine were measured by cyclic voltammetry and determined at −5.16 eV and −2.81 eV, respectively, giving an electron gap of 2.35 eV (see Fig. S35 in the ESI†).

This polymer was then integrated into a simple OLED device with the following architecture: glass/ITO/PEDOT:PSS/PSQ-PD10/Ca/Al. Glass/ITO has been used as the transparent anode, PEDOT:PSS as the hole transport material, a 50 nm thick layer of polysquaraine formed the emissive layer, and calcium was used as the cathode, covered with aluminum to protect calcium from oxidation. A schematic representation of the OLED structure along with the corresponding energy diagram is provided in Fig. S36 in the ESI†. Note that this simple architecture was chosen in order to demonstrate the potential of polysquaraines as promising emissive materials. No device engineering or optimization has been attempted, since the scope of this work lies on the synthesis of the material and not on the optimization of the devices made thereafter.

The OLED performance was measured using the integration sphere of the external quantum efficiency measurement system of Hamamatsu.

The PSQ-PD10 OLEDs switch on at a voltage of 6 V and stay on above 30 V (see Fig. S37 in the ESI†). The power efficiency is of the order of 10−3 lm W−1. This low value is attributed to the fact that the devices have not been appropriately engineered to increase performance; the thicknesses of the participating layers have not been optimized, while only a standard hole transport layer has been incorporated to facilitate charge injection in the emissive layer. Additionally, thickness irregularities can be spotted on the OLED surface (note that the device area is 0.4 cm2), deteriorating device performance. Moreover, the thickness of the different layers being small, the low efficiency could be due to losses, mainly due to the formation of surface plasmons.13

Besides the low power efficiency, it is important to note that the average emission of the PSQ-PD10 OLEDs that have been tested is white, slightly reddish. The best OLED obtained in terms of color exhibits an almost pure white emission as verified by the chromaticity CIE coordinates (0.359, 0.340) (Fig. 1d). The dominant wavelength at maximum brightness is 566 nm. Finally, the color rendering index (CRI) value is as high as 93 (versus a maximum of 100). This value is among the highest reported for a single-polymer-based white OLED.14

In this work, new squaraine-based conjugated polymers and random co-polymers have been synthesized via metal-free polycondensation. By modifying squaric acid, a reference model was synthesized in order to quantify the ratio between 1,2 and 1,3 linkages on the squaraine unit, allowing a better understanding of the structure–properties relationship. This ratio could also be modified by changing the co-solvent used during the polymerization, leading to polymers presenting an absorption peak in the near-IR region. Thus, by using difunctional alcohol as a co-solvent, statistic copolymers were synthesized. They showed an absorption at low wavelength (250 nm) and a white emission centered around 500 nm in solution which means that they present a large Stokes shift. These copolymers exhibit a very broad emission from 350 nm to 650 nm, which covers almost the whole visible range and renders them attractive for white OLED applications. Therefore, the most promising co-polymer was successfully integrated into simple OLED devices. Preliminary studies verified the fabrication of OLEDs with a white emission and a high CRI.

Conflicts of interest

There are no conflicts to declare.

Notes and references