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Triaryl-1,4-diamine based polysquaraines: effect of co-solvent and monomer insertion on optoelectronic properties

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A series of N1,N4-didodecyl-N1,N4-diphenylbenzene-1,4-diamine based polysquaraines have been synthesized under micro-wave irradiation in the absence of any catalyst. The effect of solvent of polymerization, on the squaric acid catenation (1,2 and 1,3 linkages), has been studied and polysquaraines integrating linear chain 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 into 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.^{1–8} The first squaric acid based dyes were synthesized in 1965 by A. Treibs and A. Jacob by performing the condensation of squaric acid with pyrrole and phenol derivatives.¹ While the first polysquaraines were also described in this paper, their low solubility hampered their full characterization. The main advantage of using semi-conducting polymers instead of small molecules is their possible formulation as inks, leading to an easy processability through various printing technologies for example and thus decreasing the cost of their optoelectronic devices.^{9,10} By enhancing the

squaric or croconic acids (considered as a stronger acceptor moiety)^{11,12} and benzobisthiazole or benzobisazole were respectively used as withdrawing (acceptor) and donating (donor) moieties.^{13–15} 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.^{16–19} They have then been integrated into various devices to study their optoelectronic preoperties.^{16,20–23} π -conjugated polysquaraines could also be obtained via the condensation of a conjugated monomer with squaric acid.^{19,24,25} 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 same polysquaraines synthesized using Suzuki and Stille cross-coupling reactions.²⁶

In the present work, the polymerization of 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.^{5,27} Notably, polysquaraines incorporating di-functional alcohols as comonomers presented a broad emission and were integrated into OLED, exhibiting a white emission.

The polycondensation was performed between the squaric acid and the N1,N4-dialkyl-N1,N4-diphenyl benzene or triphenyl diamine (TPDA). This monomer was chosen because of an easy alkylation, a 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 2011.²⁸ It was alkylated 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 **SqCl** were allowed to react in a mixture of toluene plus an

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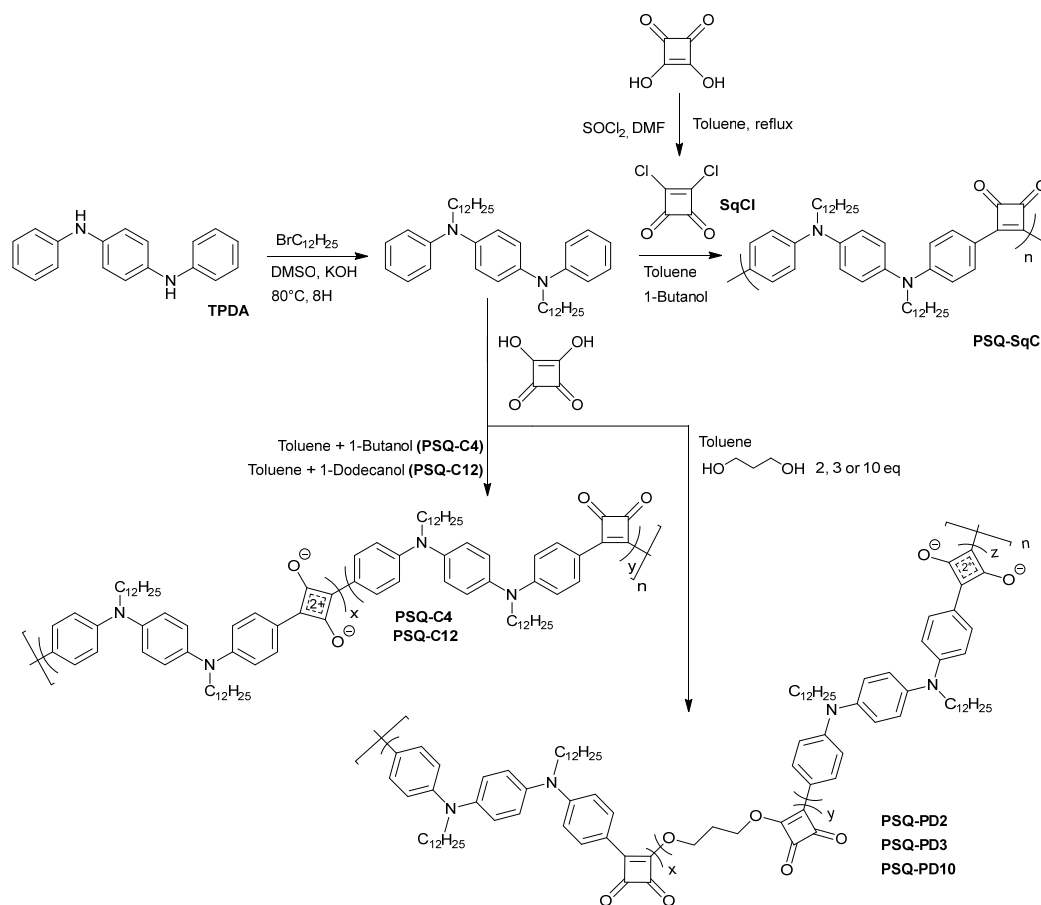
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planarity and electron-donating character of difunctional monomers, Havinga *et al.* synthesized a polysquaraine alternating strong donor and acceptor subunits. In this report,



Scheme 1. Synthesis of SqCl and TPDA monomers and polysquaraines (PSQ-C4, PSQ-C12, PSQ-SqCl, PSQ-PD2, PSQ-PD3, PSQ-PD10) using different alcohol (i.e. butanol, dodecanol and propanediol) as co-solvent.

alcohol as co-solvent for four hours at 130 °C. Different mixture of solvents (with different alcohol and various ratio between two different solvents) were used allowing a 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 polysquaraines properties (see NMR characterizations in Supporting Information).

Polymer synthesized using **SqCl** (**PSQ-SqCl**) presents only the 1,2 linkages. However, polymer synthesized with squaric acid presents a mixture of 1,2 and 1,3 linkages. Microwave irradiations were preferred to the conventional dean-stark apparatus in order to speed up the polymerization reaction. Indeed, polymers with similar size and dispersities have been obtained after one day with the conventional dean-stark apparatus against only four hours under microwave irradiation. In both case, polymerizations were able to be performed on a gram-scale without impacting the reaction yield or polymer properties. After extraction by soxhlet, respectively in methanol and in chloroform, polymers were characterized by ATR-FTIR spectroscopy. This method allows to estimate the ratio between 1,2 and 1,3 linkages in the polymer backbone.^{29–31}

Physical and structural data of synthesized polysquaraines are reported in table 1.

All samples show comparable size (confirmed by mass spectrometry and NMR, see SI), 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 conversions are close to 100%. It is noteworthy that the shape of chromatograms (see SI) 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. Qualitative percentages of 1,2 additions have been estimated by ATR-FTIR spectroscopy, using the polymer synthesized with **Sq-Cl** monomer as reference with 100% of 1,2 additions. Polymer synthesized using butanol or 1,3-propanediol as co-solvent present a mixture of both linkages with 40% to 65% of 1,2 linkages. However, the use of 1,1,2-dodecanediol 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 polysquaraine PSQ-C4 synthesized using a

Polymer	Co-reagent	Amount of co-reagent	\overline{M}_n^a g.mol ⁻¹	\overline{M}_w^a g.mol ⁻¹	\overline{D}^a	T _d ^b °C	1,2 addition ^c (%)
PSQ-C4	Butanol	Co-solvent	2800	6700	2.4	427	50%
PSQ-C12	Dodecanol	Co-solvent	2400	7200	3	388	< 10%
PSQ-SqCl	Butanol	Co-solvent	2500	6800	2.7	429	100%
PSQ-PD2	1,3-propanediol	2 eq	2200	4500	2.0	367-459	40%
PSQ-PD3	1,3-propanediol	3 eq	3700	12700	3.4	367-425	50%
PSQ-PD10	1,3-propanediol	10 eq	1800	8100	4.5	372	65%

Table 1: Characteristics of polysquaraines. ^aMeasured by SEC in CHCl₃ at 30 °C, relative to PS standards. Values between brackets have been estimated by mass spectrometry FD-TOF. ^bDegradation temperature obtained by TGA under N₂ at 10 °C min⁻¹. ^cEstimated from ATR-FTIR spectra (see Supporting Information)

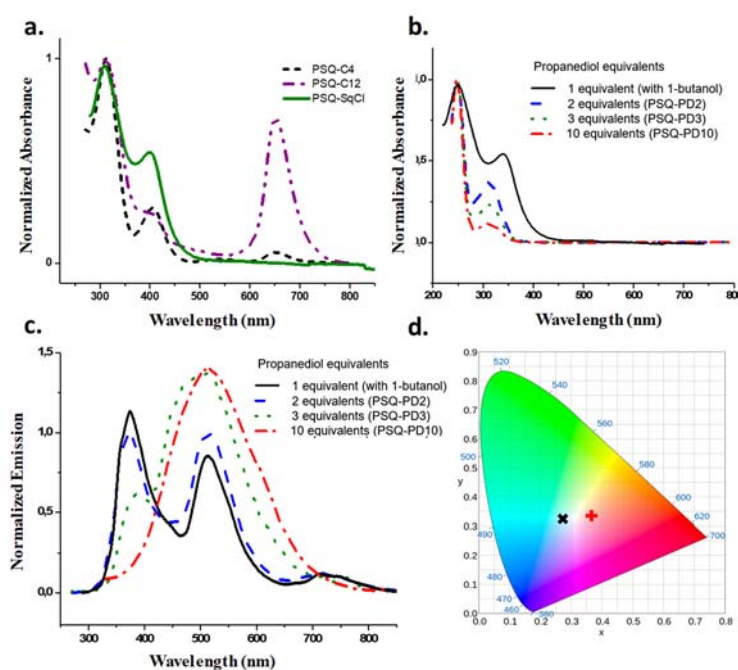


Figure 1: a. Absorption spectra of polysquaraines synthesized using various amounts of 1,3 propanediol and 1-butanol as co-solvent. b. and c. Absorption (b.) and emission (c.) spectra of polysquaraines PSQ-PD in function of 1,3-propanediol insertion in the chain (in film on a quartz substrate, excitation at 250 nm). d. CIE 1931 chromaticity diagram for the solution of the PSQ-PD10 polymer (black x) and the corresponding OLED made thereafter (red cross)

classical mixture of toluene and 1-butanol as solvent,³² presents three absorption bands, respectively peaking at 300, 400 and 650 nm (Figure 1-a). 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.^{25–27} When dodecanol is used as co-solvent (**PSQ-C12**), the intensity ratio of these absorption peaks changes (Figure 1-a). Indeed, the intensity of the absorption at 650 nm, corresponding to 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 co-monomer (**PSQ-SqCl**). The latter was synthesized in one step from squaric acid in 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 co-solvent (dodecanol)

could favor the kinetic addition, leading to the formation of 1,3 linkages, as confirmed by ATR-FTIR and absorption spectroscopies, which allow us to tune the optical properties (Figure 1-a and Supporting Information).

In addition, as the squaric acid can react with alcohol, the polymerization reaction was performed with difunctional alcohol such as 1,3-propanediol to study the impact of alcohol insertion on polymer properties (polymers PSQ-PD). The reaction was performed in toluene with different ratio 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 chain in the polymer it's difficult to estimate the amount of 1,3-propanediol present in the chain (see ATR-FTIR and NMR spectra in Supporting Information). It is noteworthy that the reaction with only 1 equivalent of propanediol doesn't allow obtaining a polymer due to monomers solubility issue. The absorption and emission spectra of this polymer are presented in Figures 1b and 1c respectively. As the number of propanediol equivalents is increasing, a decrease of the absorption peak at 310 nm is observed, as well as a decrease of 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 700nm, 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 Figure 1d, the x and y coordinates are respectively 0.27 and 0.32, which correspond 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 Figure S35 in Supporting Information).

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 the polysquaraine formed the emissive layer, and Calcium was used as the cathode, covered by Aluminum to protect Calcium from oxidation. As schematic representation of the OLEDs structure along with the corresponding energy diagram are provided in Figure S36 in Supporting Information. 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 OLEDs 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 6V and stay on above 30V (see Figure S37 in supporting informations). The power efficiency is of the order of 10^{-5} lm/W. 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.³³

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) (Figure 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 higher (if not the highest) reported for a single-polymer based white OLED.³⁴

In this work, new squaraine based conjugated polymers and random co-polymers have been synthesized *via* metal-free polycondensation. By modifying the 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 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 Stoke-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.

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