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New TBT based conducting polymers functionalized with redox-active tetrazines.

Laetitia Guerret-Legras[a], Pierre Audebert[a], Jean-Frédéric Audibert[a], Claude Niebel[b], Thibaut Jarrosson[b], Françoise Serein-Spirau[b], Jean-Pierre Lère-Porte[b]

[a] *PPSM, ENS Paris-Salay, CNRS, UniverSud, 61 av President Wilson, F-94230 CACHAN, France.*

[b] *Institut Charles-Gerhardt de Montpellier, UMR CNRS 5253, Architectures Moléculaires et Matériaux Nanostructurés, 8 rue de l'école normale, Montpellier, Cedex 5, France*

Corresponding author: Pierre Audebert Tel. + 33 1 47 40 53 39 Fax +33 1 47 40 24 54 audebert@ppsm.ens-cachan.fr.

ABSTRACT

We describe the synthesis of two new polymerizable monomers, and the subsequent polymers functionalized by tetrazine pendant groups, along with their electrochemical behaviour and fluorescence properties. In all cases a very stable conducting polymer is obtained, featuring both the redox activity of the main chain in oxidation and of the tetrazine functional group upon reduction. One of the polymers in addition exhibits an electrofluorochromic behaviour.

Keywords : Conducting polymer, electrochemistry, electrofluorochromism, TBT, tetrazine.

INTRODUCTION.

Although the field of research on multifonctionnal electropolymerizable monomers has reached some maturity, still investigating new multifunctional conducting polymers continues to be of interest, given their potential in several fields such as sensors[1], supercapacitors[2] , light emitting devices,[3] electrochromism[4] or corrosion protection[5]. A recent newcomer in the possibilities opened by this type of organic materials is electrofluorochromism[6], namely the electrochemically induced switching of fluorescence. Therefore, integration of combined optical and redox properties is especially interesting for preparing electrochemically switchable devices. We have shown several times in the past that tetrazine containing materials indeed are very promising ones[7]. Tetrazines are coloured and electroactive heterocycles[8], which own special properties[9]. They possess a very high electron affinity, which permits to reduce them at high potentials (indeed they are the electron poorest C–N heterocycles)[7c]. This allows them to store electrons easily; we have already published one example of functionalized conducting polymers with tetrazine pending groups, showing that the tetrazine properties remained after electropolymerization[10]. However, when included in the polymer chain, the tetrazine appeared to be isolated and in the reduced polymer no delocalization of the negative charge was observed[11]; Therefore we later found out [8] that the tetrazines were more easily addressed as pending groups. This allows some flexibility because of the spacer, which leads to an improved charge transfer. The first electropolymerizable moieties to which we attached tetrazine pending groups, respectively 2,5-bis(2-thienyl)-pyrrole and carbazole, however, were in a few cases difficult to electropolymerize, especially from dilute solutions. On the other hand, the 1,4-bis(thiophen-2-yl)-2,5-bis(2-alkyloxy)benzene core, often abbreviated as TBT (Fig. 1), has long been recognized as a remarkable unit, for efficient electropolymerization, in particular from dilute solutions[12], and also has quite original optical properties[13], and applications in the field of organic lasers[14], solar cells[15] or photoelectrochromic materials[16].

In this article we report the synthesis of two molecules, resp. 1,4-bis(thiophen-2-yl)-2,5-bis(6-hexyl-1-(4-chlorotetrazin-1-yl)benzene (TBTbisTz) and 1,4-bis(thiophen-2-yl)-2-(6-hexyl-1-(4-chlorotetrazin-1-yl)-5-methoxybenzene (TBTmonoTz), which are represented on Fig. 1. We also describe the polymers obtained by electrochemical polymerization of both compounds, along with their original properties. Finally, we present results on the electrofluorochromic behaviour of the polymer issued from TBTbisTz.

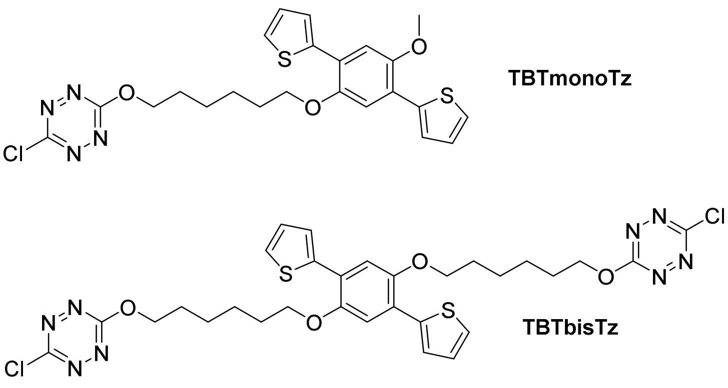


Figure 1 : Structure of the two tetrazine bearing monomers : TBTmonoTz and TBTbisTz

EXPERIMENTAL

1) Synthetic procedure

The synthesis of monomers was performed by reacting the parent alcohol (See Scheme 1) with one or two equivalents of dichlorotetrazine in conditions similar to what reported before.[17] The parent alcohols were prepared as described in the ESI section 2. Spectroscopic characteristics are in accordance with the expected structure and are also given in the ESI. Section).

2) Electrochemistry

Electrochemical studies were performed using dichloromethane (DCM) (SDS, anhydrous for analysis) as a solvent, with *N,N,N,N*-tetrabutylammonium hexafluorophosphate (TBAFP) (Fluka, puriss.) as the supporting electrolyte. The substrate concentration was *ca.* 1 mM. A home-made 1 mm diameter Pt or glassy carbon electrode was used as the working electrode, along with an AgCl/Ag wire reference electrode and a Pt wire counter electrode. The cell was connected to a CH Instruments 600B potentiostat monitored by a PC computer. The reference electrode was checked *vs.* ferrocene as usually as recommended by IUPAC. In our case, $E°(Fc^+/Fc) = 0.097$ V. Large films (for electrofluorochromism and/or fluorescence data) were prepared in ITO 1cm2 electrode. The transient currents vary as expected with time (sharp decrease, plateau then slow rise) for a conducting polymer deposition and provide additional evidence for the occurrence of a film formation (ESI Fig. 1).

3) Photophysical measurements.

All the spectroscopic experiments on monomers were carried out in dichloromethane (spectroscopic grade, n = 1.424) and at concentrations ca. 1.5 µmol.L^{-1}. UV-vis. absorption spectra were recorded on a double beam Cary 4000 spectrometer from Agilent. Emission spectra were measured on a Fluorolog FL3-221 spectrofluorometer from Horiba Jobin-Yvon in the right angle mode. Fluorescence quantum yields of both monomers TBTmonoTz and TBTbisTz were determined with the following standards: rhodamine 6G in ethanol for the tetrazine quantum yield (λ_{exc}= 520 nm) and quinine sulfate (in 0.5 N sulfuric acid) for the TBT quantum yield ((λ_{exc} = 360 nm).

Optical measurements on grown and dried films were performed on an inverted microscope (Ti Eclipse Nikon) with a x40 (X1.5) NA 0.75 objective in a wide field epi-illumination.

4) Electrofluorochromism experiments.

Set up description

All electrofluorochromism measurements were performed at room temperature using a homemade three-electrode electrochemical cell coupled with an inverted optical microscope[18] . A platinum wire and a Ag/AgCl wire were used as a Counter and Reference Electrode respectively. Transparent ITO (purchased From Solems, 25-35 ohm. , 80 nm thickness) was beforehand washed with isopropanol, then air dried and used as the Working Electrode.

Acquisition procedure

In a first step electropolymerization was carried out with a 2 10^{-4} M solution of TBTbisTz in dichloromethane in addition with tetrabutylammonium hexafluorophosphate (TCI, electrochemical grade) 0.1 M as the supporting electrolyte (chronoamperogram were registered and showed the classical shape featuring an initial rise, a decline and a plateau (ESI Fig. 1). Before the polymerization this solution was purged with argon during 5 minutes to remove dissolved oxygen, then kept flushing at low flow rate during the electrochemical reaction. For the polymerization, ITO potential is stepped up to 1.2 V during 15 s, which accounts for the formation of a thin film of a thickness of c.a. 6 C/cm^2 (det. From the integration of i-t curves). The solution was removed afterwards and the cell rinsed several times with DCM.

Then electrofluorochromism measurements were directly performed after the addition of a TBAFP 0.1 M solution of acetonitrile, this measurements were done under the same purge conditions.

Electrochemical measurements

Substrate potential control and current measurements were performed by a potentiostat (VersaSTAT 4, Ametek) under the VersaStudio software.

Optical measurements.

Optical measurements were performed on an inverted microscope (Ti Eclipse Nikon) with a x40 (X1.5) NA 0.75 objective in a wide field epi-illumination. The tetrazine moiety was excited by the association of a Hg Lamp (Intensilight Nikon) with a band Pass Excitation filter BP 482nm/35nm and a FITC dichroic (506 nm). The emitted light is collected through a long pass emission filter LP 520 nm. In turn, the TBT moiety is excited by the same lamp coupled to a band pass excitation filter BP 380nm and a DAPI dichroic (409nm). In that case the emission filter is a long pass filter LP 410 nm. The chronofluorograms were collected by integration of the wavelengths between 420 and 470 nm for the polyTBT emission, and between 525 and 660 nm for the tetrazines' emission, respectively.

Emission Spectra are recorded with an Ocean Optics spectrometer coupled to the microscope with a UV-VIS (400 µm diameter) Optical Fiber Plus collimator placed in an intermediate image plane, with a 60 µm MFD (Mode Field Diameter) in the sample plane.

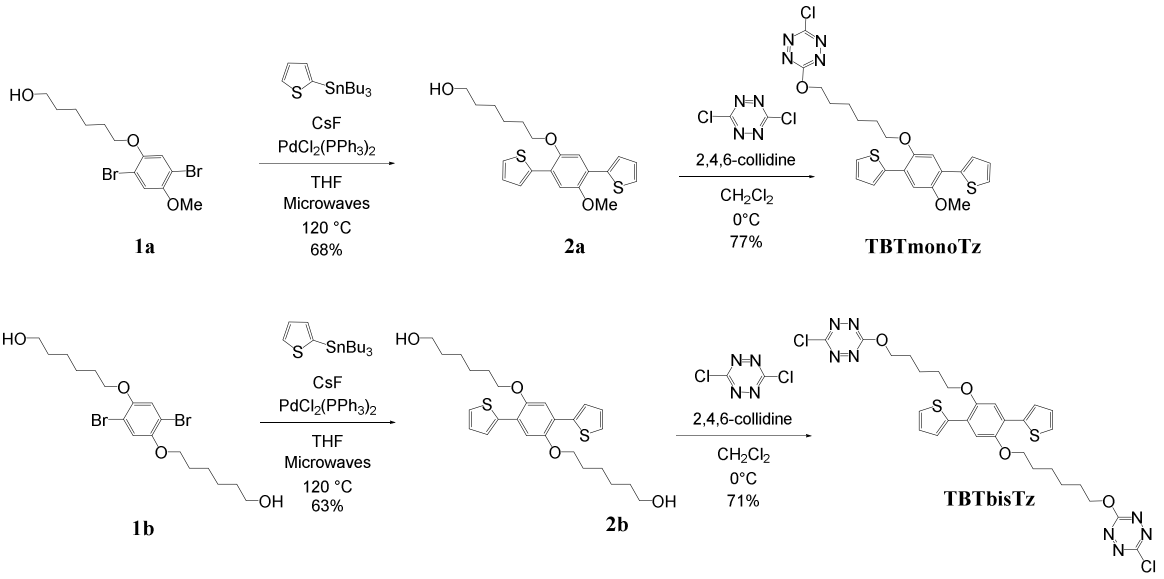
Spectra are corrected from optical chain sensitivity, transmission and blank (residual excitation and autofluorescence of ITO in the solution $TBAF_6$/acetonitrile without potential application).

Fluorescence experiments on as-grown films, in air, were performed with the same set-up, focusing on various parts of the film.

RESULTS AND DISCUSSION

1) Monomer synthesis

The synthesis of both monomers occurs according to the following Scheme 1 below:



Scheme 1 : Synthetic scheme for the preparation of monomers resp. TBTmonoTz and TBTbisTz

The formation of the TBT cores in **2a-b** were both performed by a Stille reaction[13] under microwaves irradiation involving 2-tributyltinthiophene and dibromo aryl **1a-b**.[19] The tetrazine attachment was completed using a procedure we previously described[17] addition of dichlorotetrazine at 0°C to a solution of alcohols **2a** or **2b** in the presence of a base (2,4,6-collidine) provided TBTmonoTz and TBTbisTz in 77 and 71% yield respectively. The non-quantitative yield of this last aromatic substitution is certainly due to a slight sensitivity towards oxidative degradation of the TBT core by dichlorotetrazine, probably because of daylight induced photooxidation by the dichlorotetrazine excited state.

2) Monomers behaviour.

Optical characterization

The absorption spectra of both monomers feature the UV-visible signature of both the electron-rich part (TBT) and the electron-poor part (tetrazine) (Fig. 2). The former moiety absorbs in the near UV region, and the latter both in the UV and the visible. However the proportionally weak UV band of the tetrazine is essentially masked by the TBT broad absorption, while its band in the visible appears clearly, in the usual region for a chloroalkoxytetrazine[17]. The absorptions in the 300-400 nm region (TBT contribution) and in the 500-550 region (tetrazine contribution) roughly scale with the respective numbers of the related units in each molecule.

In both cases a weak fluorescence is recorded, featuring the emission of the TBT core, and the tetrazine, the latter one occurring with an even relative smaller yield. The quantum yields on the monomers have been determined for both wavelengths and have been given in the Table 1 below. The low fluorescence yields are essentially due to mutual quenching, through electron transfer between the two parts (the TBT excited state reduces the tetrazine core, and the tetrazine excited state oxidizes the TBT core) As expected, the TBT fluorescence quenching is stronger when two tetrazines are present on the TBT core.

Quantum yield /%	TBTmonoTz	TBTbisTz
tetrazine	0.26	0.24
TBT	2.13	0.81

Table 1: Emission quantum yields for the wavelengths corresponding respectively to tetrazine core emission (appr. 550-600 nm, upper row) and the TBT core emission (appr. 400-450, lower row)

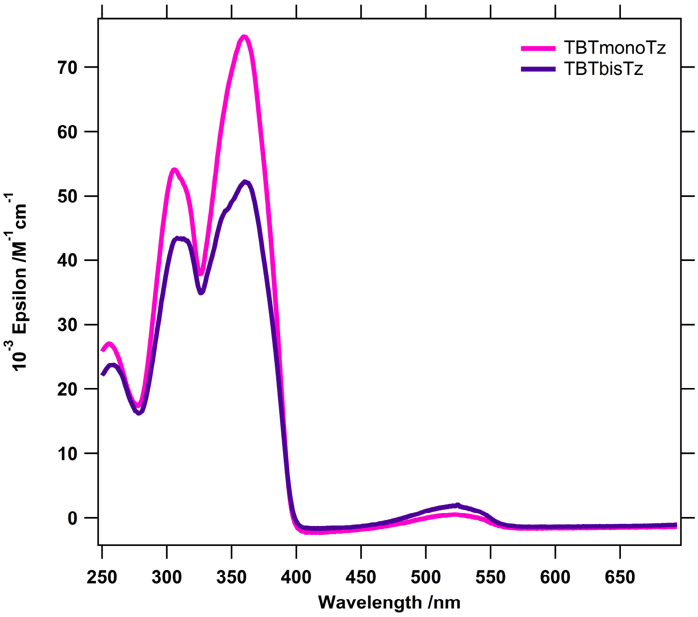


Fig.2: Absorption spectra of both TBTmonoTz (pink, λ_{max1} = 360 nm and λ_{max2} = 522 nm, and TBTbis Tz (purple, λ_{max1} = 360 nm and λ_{max2} = 521 nm. Solutions in DCM, in the μM range, epsilon values in y ordinates.

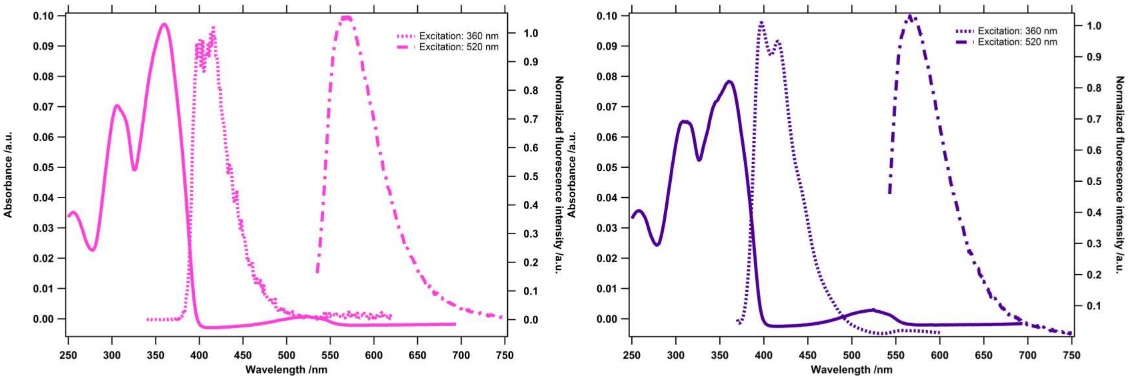


Fig. 3. Absorption (full line) and emission (dashed and dotted line) of TBTmonoTz (left), and TBTbisTz (right) showing both the region of emission of tetrazine (dashed line) and the region of emission of TBT (dotted line) according to the excitation wavelength. Excitation wavelengths were chosen respectively of 530 and 360 nm for each excitation spectrum, to focus on one active moiety (TBT or tetrazine) and exclude absorption of the other partner at the same time.

3) Electrochemistry

a) Monomers behaviour

Both monomers are electroactive in acetonitrile (AN) or dichloromethane (DCM) electrolytes, as represented in Fig. 4, showing both the reversible reduction of the tetrazine moiety and the irreversible oxidation of the polymerizable TBT moiety. The ratio of the peak intensities, as expected, reflects the ratio of the TBT and tetrazine moieties in the molecule. There is only very little mutual influence of the two systems, on each other, as already observed in triphénylamine-tetrazine systems, linked by non-conjugated linkers[20].

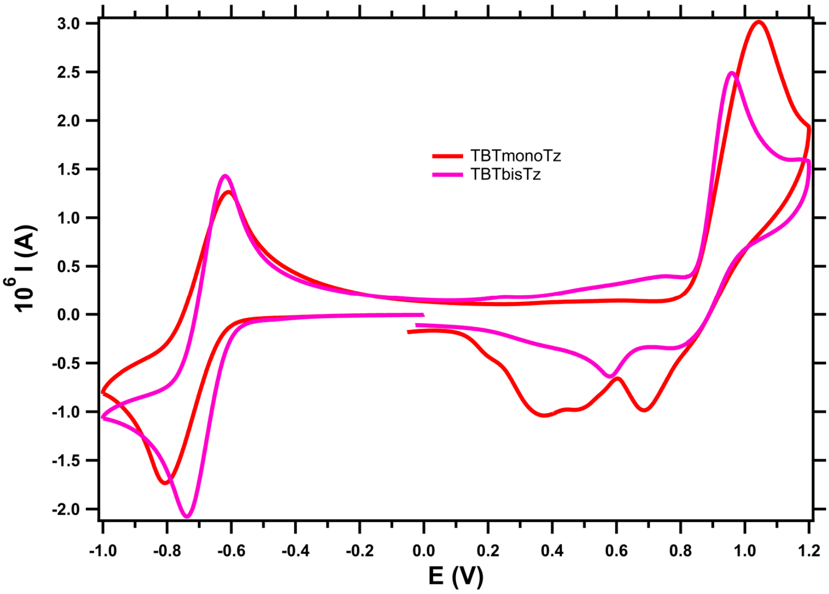


Fig. 4: Cyclic voltammetry at 50 mV/s of TBTmonoTz (3 10^{-3} M) and TBTbisTz (2 10^{-3} M) monomers in both oxidation and reduction. Electrolyte was degassed DCM/TBAFP, with a 1mm diameter C electrode; start in reduction, to avoid electrode modification due to monomer polymerization.

b) Polymers behaviour

Actually polymer films can be obtained from the electrochemical oxidation of both monomers, even from low concentration solution, due to the exceptional ability of the TBT core towards electropolymerization; actually, clean polymer films can be grown from DCM solutions at concentrations up the 10^{-4} M range, a rare feature for a functionalized monomer. We show on Fig. 5 the accumulative polymerization of TBTmonoTz. It shows the regular film formation, with the classical growing of the polymer redox response in both oxidation and reduction; polymerization seems more efficient in the case of TBTmonoTz than TBTbisTz, though the reason for this is not obvious. All together the observation of the accumulative syntheses, the visual observation of the ITO electrodes (when uses) and the examination of the transient currents time dependence (ESI Fig.1) allow to conclude unambiguously to the deposition of a conducting film onto the electrode. It cannot be concluded, however, if it is a real polymer, or on the other hand a mixture of shorter oligomers (dimers to pentamers).

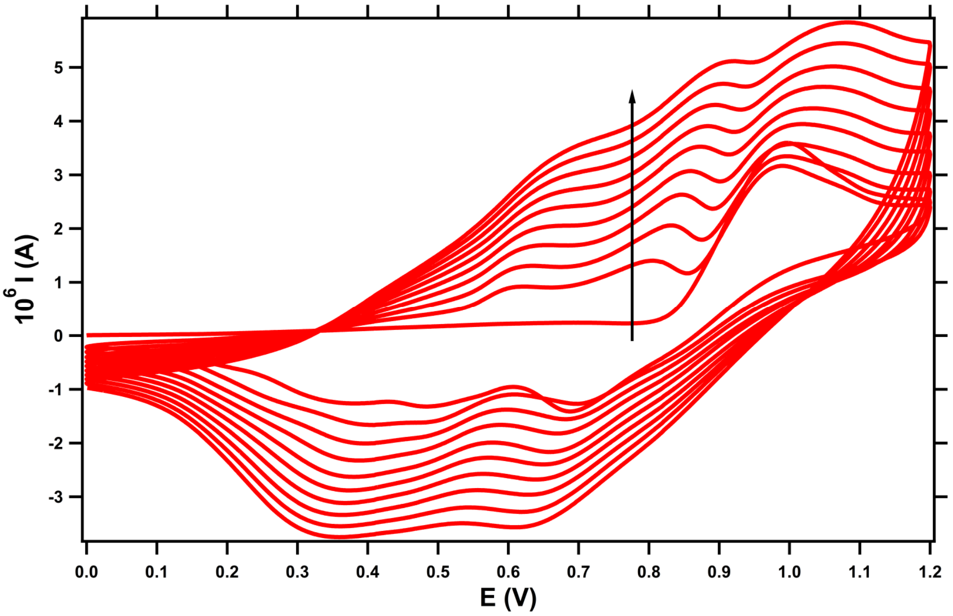


Fig. 5 : Accumulative synthesis of TBTmonoTz (DCM/TBAFP, 3 10^{-3}M) upon repetitive cycling, showing the regular polymer accumulation through increasing of both oxidation and reduction currents on deposed species.

For both monomers, thin films of polymer can therefore be grown from solutions, either by cyclic voltammetry, or by potentiostatic step. The Fig. 6 shows the CV of a thin *TBTbisTz* film, grown by three successive cyclic CV's. It can be observed that, while the CV in oxidation is typical from a standard conducting polymer, on the other hand the CV in reduction displays ideal thin layer behaviour, demonstrating a fast electron exchange at this scan rate.

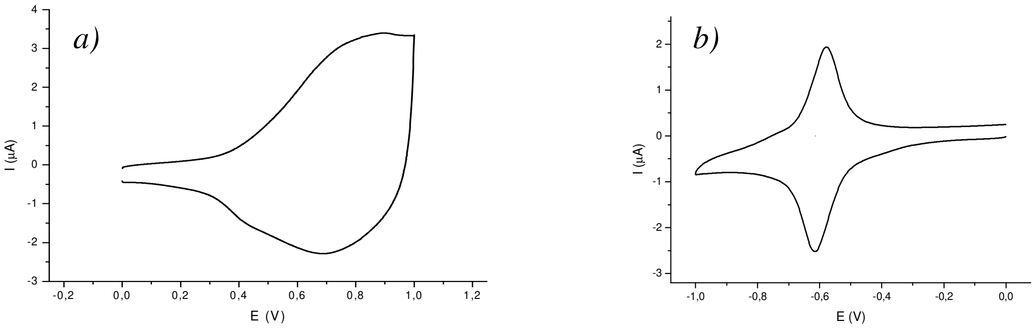


Fig. 6: Cyclic voltametry of a poly(TBTbisTz) film, prepared upon 3 repetitive cycles at 50 mV/s, on a 1 mm diameter Pt electrode into a TBAFP/DCM electrolyte ≈ 10^{-3} M in monomer; a) Polymer in oxidation, and b) Polymer in reduction, scan rate 200 mV/s.

The dependence of the peak currents with the scan rate in reduction, however, changes when scan rates reach the 1 V/s range, from a thin layer to a diffusive behaviour, even with thin films. This is attested by the dependence shown in ESI Fig. 2. The deviation from linearity may derive from the variable stability of the films upon cycling in the tetrazine reduction range; The ESI fig. 3 shows that the films of poly(TBTmonoTz) can passivate completely after only about 10 slow scans in reduction[1], on the other hand poly(TBTbisTz) films can reach a stable signal after some film “breaking”.

We have checked that both monomers feature essentially similar electrochemical responses, at the difference that the tetrazine signal is enhanced with TBTbisTz, as it could be expected from the relative higher tetrazine content. However, the polymer response is unusual in the case of the poly(TBTmonoTz) thin films (Fig. 4). In thick films, the reduction peak is multiple (this may stem from oligomers formation). In the case of thin films, the separation between the so-called faradic and capacitive currents is extremely well defined (Fig. 7), a feature almost never observed in electrochemically prepared conducting polymers, outside from nanodots[21]. This may also be the consequence of the fact that the deposit consists in short-chain oligomers rather than a polymer We have nevertheless checked that the behavior of the deposits was as expected for an adsorbed species, since both currents (capacitive plateau and faradic peak) scale linearly with the scan rate, which is indicative of a thin layer behavior (ESI Fig. 5).

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[1] Trials in different solvents did not allow to distinguish if this comes from redissolution of the films, degradation of the tetrazines, or both.

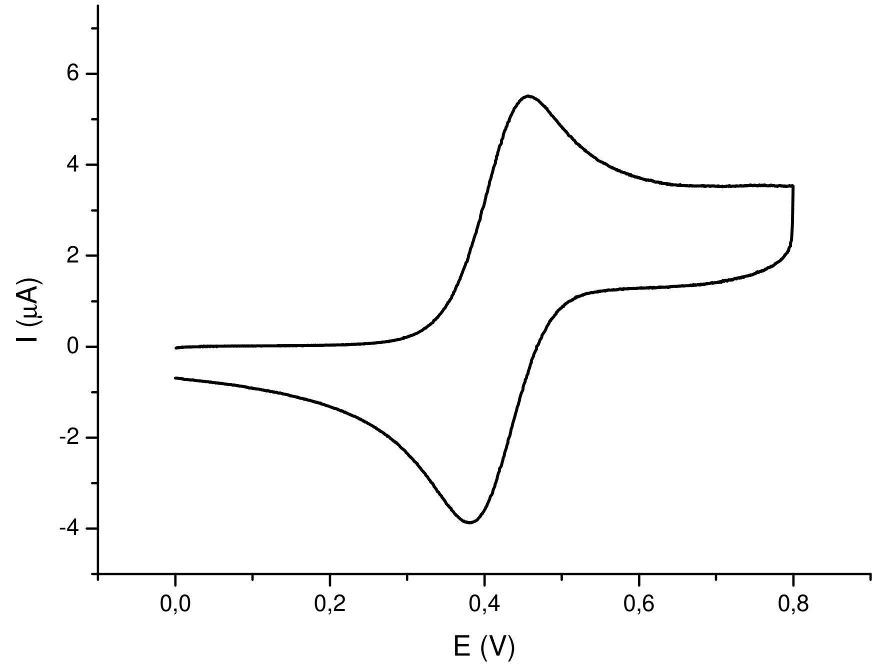


Fig. 7: Cyclic voltammogram of a thin poly(TBTmonoTz) film obtained after only two oxidative scans at 50 mV/s from a 10^{-3} M monomer solution (for polymer alone scan rate 200 mV/s, electrolyte ACN/TEAFP)

4) Fluorescence.

We have prepared several films of each monomer on ITO plates, reduced them at 0V afterwards for about 30 s, and analysed the tetrazines fluorescence response in dependence with the films' thicknesses. The results are represented and gathered on Fig. 8. It can be seen that the fluorescence of the tetrazines, although weak, can still be registered and increases roughly with the film thicknesses for both monomers; this stands of course for relatively thin films (less than a minute growth).

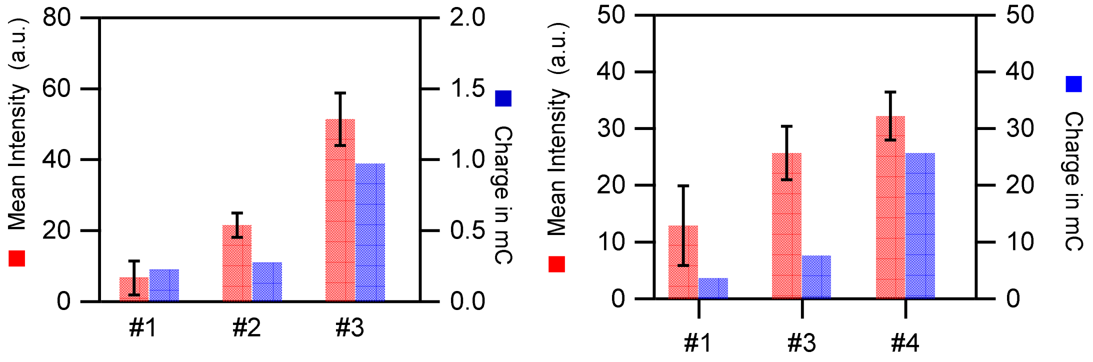
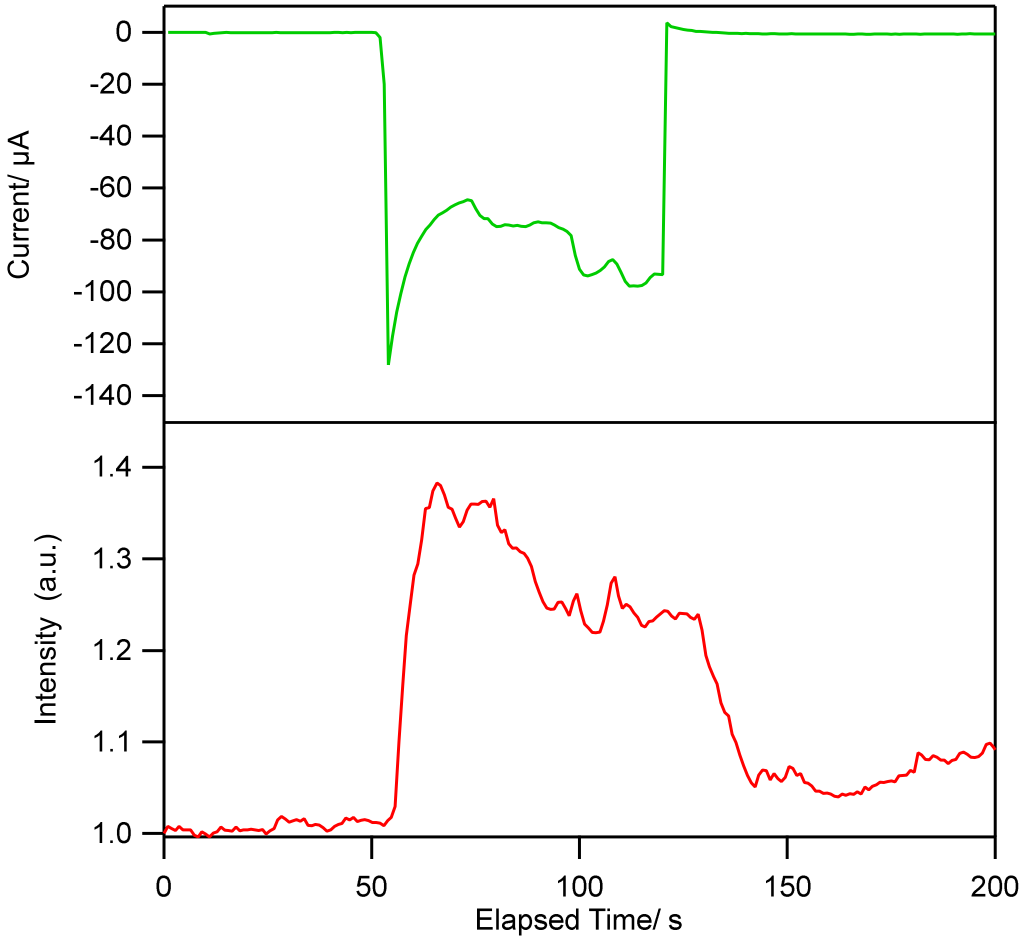


Fig. 8 : Correlation of the fluorescence intensity with the charge passed for dry thin films of poly(TBTmonoTz) (left) and poly(TBTbisTz) (right) (ITO substrate)

5) Electrofluorochromism.

We have investigated the electrofluorochromic behaviour of the polymer issue for TBTbisTz, because we expected an enhanced response from the tetrazine moieties. We analysed respectively the response to the tetrazine reduction of the TBT fluorescence, and the response to the TBT oxidation of the tetrazine fluorescence. In the monomer case, both the TBT moiety and the tetrazine moiety fluorescence emissions were quenched through electron transfer to their counterparts (the oxidizing neutral tetrazine oxidizes the emitting TBT excited state, which is a good electron donor, and the reducing neutral TBT reduces the emitting tetrazine excited state, which is conversely a good electron acceptor).

A



B

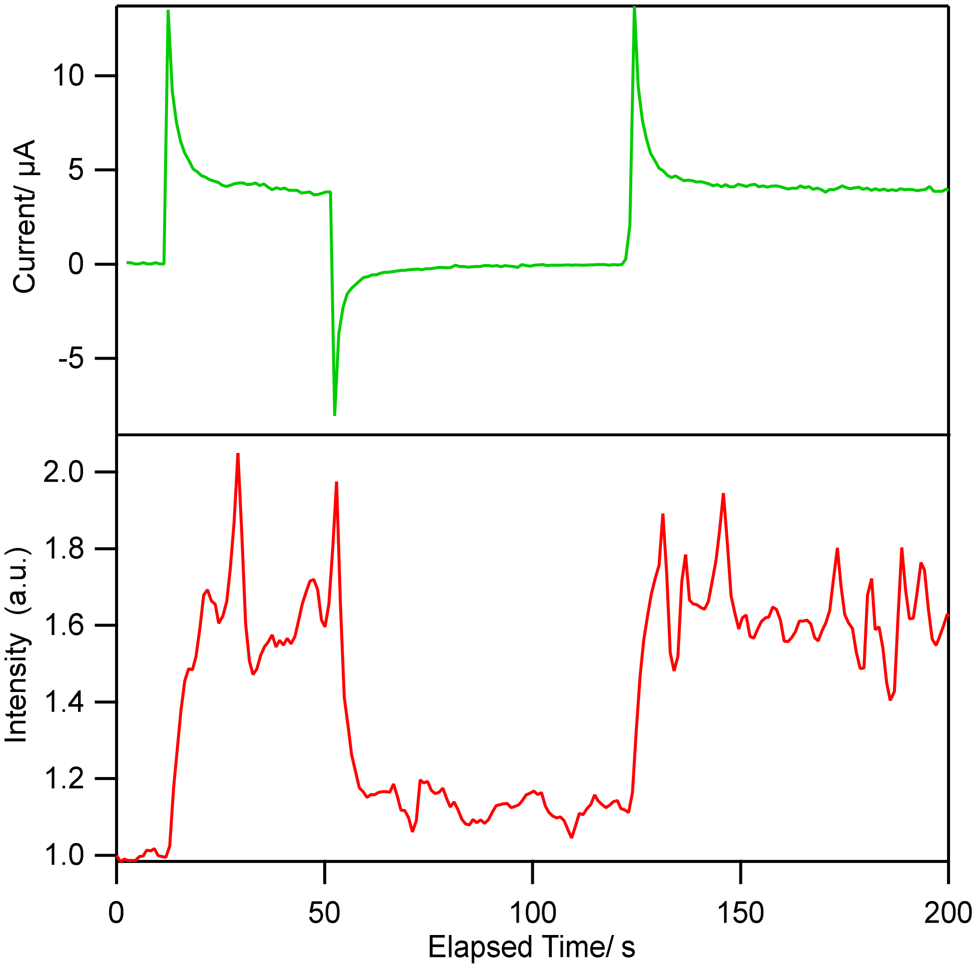


Fig. 9 : A: Bottom (red) : Fluorescence of the TBT recorded in function of the potential applied to the polymer; Top (green) reduction currents (linked to tetrazines reduction).Potential steps between -0.2V(start) and -1.2V (step) and return to the initial -0.2V potential.

B: Bottom (red) : Fluorescence of the tetrazine recorded in function of the potential applied to the polymer; Top (green) oxidation and reduction currents (linked to TBT oxidation and subsequent reduction). Potential steps between -0.2V (start) and +1.2V (step) then back to the initial -0.2V potential, followed by a second oxidation step at +1.2V.

Contrariwise to the monomer state where the TBT cation-radical is not stable, in the polymer both the oxidized state of the (polyTBT) and the reduced state of the tetrazine are expected to be stable, and we envisaged to restore fluorescence, by switching them. Actually, this is what can be seen on the chronofluorograms presented on Fig. 9, A. It can be seen clearly that the fluorescence of the polyTBT appears again when the tetrazines are reduced. However, this phenomenon is not reversible, probably because the tetrazines are destroyed at the reduction process (no occurrence of reoxidation current).

Similarly, the tetrazines' fluorescence, which can be recorded in native oxidized films (Fig. 9, B) disappears when the polymer is reduced, and appears again when the polymer is reset in its oxidized state; this time the process is reversible and can be observed a few times

(Fig. 9, A). However, and despite it is not possible to measure a QY in these conditions, the emission remains weak in these cases, and the observed fluorescence is weaker than for standard chloroalkoxy tetrazine solutions. The changes of the spectra with the time, from which the chronofluorograms have been extracted, are displayed in the ESI section, Fig. 5 and 6.

Actually the most representative experiments have been performed with thin films; experiments with thicker films indeed show that the emission of the tetrazines saturates and even starts to slightly decrease upon increasing the film thickness. This might be due to diffusion losses, and/or absorption in the polymer bipolaronic band (this observation is similar to the one made with dry films, cf sect. 4).

Conclusion

We have reported in this communication the first examples of polymerizable monomers and derived polymer containing tetrazine pendant groups. While the carbazole moiety allows the formation of a poorly stable polymer film, on the other hand the 1,4-bis(thiophen-2-yl)-2,5-bis(2-alkyloxy)benzene (TBT) moiety allows the deposition of well-defined films of controlled thicknesses. In addition, dual electrofluorochromism could have been observed, both on the polymer and the pending tetrazine emission. The anti-corrosion properties of these films will be the subject of further investigations.

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