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# A new conducting copolymer bearing electro-active nitroxide groups as organic electrode materials for batteries and pseudosupercapacitors

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Abstract: In order to reduce the amount of conducting additives generally required for polynitroxide based electrodes, we combined a stable radical (TEMPO) with a conductive copolymer backbone constituted by 2,7-bisthiophene carbazole (2,7-BTC), which is characterized by its high intrinsic electronic conductivity. This work deals with the synthesis of this new polymer functionalized by a redox nitroxide. Its fine structural characterization using EPR techniques established that: 1. the nitroxide radicals are properly attached to the radical chain (cw-EPR), 2. the polymer chain has very rigid conformations leading to a set of well-defined distances between first neighbouring pairs of nitroxides (pulsed EPR. The redox group combined with electroactive polymer showed not only a very high electrochemical reversibility but also a perfect match of redox potentials between the de-/doping reaction of bisthiophene carbazole backbone and the redox activity of nitroxide radical. This new organic electrode shows stable capacity (about 60 mAh.g<sup>-1</sup>) and enables to drastically reduce the ratio of carbon additives due to conducting polymer skeleton.

#### Introduction

[b]

Global warming is one the most challenging issue ever faced by mankind. Among solutions aiming at tackling this critical question, the elaboration of devices allowing the storage and use of electrical energy in an environmentally friendly context is a pivotal task.<sup>[1-3]</sup> Following this path, inorganic materials have been deeply investigated.<sup>[4-6]</sup>

Development of organic redox-active materials able to compete with inorganic compounds is a new paradigm in the field of electrochemical storage.<sup>[7-12]</sup> These materials exhibit some key advantages compared to inorganic ones, for example they can be considered as less dependent on natural resources as outlined by Anderson et al.<sup>[13]</sup> They are also more versatile as they can follow two types of electrochemical mechanisms depending if they start

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either by an oxidation (p-type)<sup>[14, 15]</sup> or a reduction (n-type) process.<sup>[16-18]</sup> Pioneered work was made by Nishide et al. based on the reversible and highly stable tetramethyl-piperidinyloxy nitroxide radical (TEMPO). Redox behavior of TEMPO is based on the nitroxide/oxoammonium p-type redox couple. Other organic p-types derivatives (e.g. poly(phenothiazine)...) have also proved their competitive interests.<sup>[19-21]</sup> However TEMPO is highly soluble in organic electrolyte leading to a rapid loss of capacity, so Nishide developed polymer-based TEMPO by integrating TEMPO group on a polymer backbones such as poly(methylmethacrylate). These new redox active polymers have demonstrated interesting performances.<sup>[22, 23]</sup> If the polymer backbone offers a better stability of the TEMPO based electrodes, its insulating character increases the overall electronic resistance. Additionally, the polymer backbone is a dead mass and decreases the specific capacity the material.

Both in batteries and pseudo-supercapacitors, some progresses have therefore to be made in order to satisfy the awaited performance improvements for the next generation of electrochemical energy storage devices.<sup>[24]</sup> It requires the development of improved synthetic methods for TEMPO functionalized polymer through chemical or electrochemical routes.<sup>[25, 26]</sup> For the former, due to the presence of radicals, precursors of the polymers involving a protected amine form of TEMPO have to be prepared before a subsequent oxidation (e.g. using MCPBA) to generate the targeted TEMPO-containing polymers.<sup>[27]</sup> For the later, nitroxide functions can be elegantly introduced within electro-polymerizable monomers (e.g. thiophene<sup>[28, 29]</sup> and pyrrole<sup>[30]</sup> based materials) to obtain targeted materials. Importantly, although results were interesting in both cases, the capacity measured was lower than the theoretical expected one. clearly demonstrating either that the oxidation process is not quantitative or that the (electro)polymerization leads to partly soluble (oligomeric) materials. Indeed, organic and polymer chemistry can provide different nitroxide-containing materials for their anchoring onto capacitive materials or/and to get polymers. J. Luktenhaus et al. and others have shown that architectures like Polythiophene-TEMPO,<sup>[29]</sup> PEDOT-TEMPO<sup>[28,</sup> <sup>31, 32]</sup> Poly(dithieno[3,2-b:2,3-d]pyrrole) bearing TEMPO<sup>[33]</sup> exhibit good conductivity and higher theoretical capacity. This strategy emphasizes the importance to match redox active polymer potentials with those of electroactive groups. A family of polythiophenes bearing nitroxide radical groups, showed that while both species are electrochemically active, there exists an unusual internal electron transfer mechanism that interferes with stabilization of the polymer's fully oxidized form.<sup>[34]</sup>

Conjugated copolymers based on carbazole derivatives are materials which have generated increasing interest in the past

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years for organic electronics applications.<sup>[17, 35-37]</sup> But in our knowledge there is a lack of works dealing with the functionalization of this polymer by a redox group like TEMPO derivatives for electrochemical energy applications.

The present work is focused on the synthesis and the electrochemical characterization of bisthiophene carbazole bearing a redox radical group. The aim is to develop a positive electrode material for application in Lithium batteries. The polymeric material consists of a conducting backbone of 2,7-bisthiophene carbazole (2,7-BTC) with an TEMPO electro-active radical (Figure 1)



Figure 1. Polymer structure of poly(2,7-BTC-TEMPO) on the left and poly(2,7-BTC) on the right.

We present the synthesis of this electro-active conductive redox copolymer poly(BTC-TEMPO), the electrochemical characterization (CV), EPR characterization leading to a structural model of the polymer and battery testing.

## **Results and Discussion**

#### Polymer synthesis

The aim of this work is to synthesize a new polymer composed by a conductive backbone and a reversible redox group with interesting electrochemical characteristics for energy storage systems.<sup>[38]</sup> When designing the polymer structure several considerations were taken into account. First of all, TEMPO was selected as a reversible redox group because polymers with TEMPO groups have shown high oxidation potential (around 3.6 V vs Li\*/Li), a fast reversible redox reaction and good stability over time.<sup>[27]</sup> Second, a bisthiophene carbazole backbone was chosen due to its oxidation potential at ~3.7 V vs Li\*/Li which is close to the redox potential of TEMPO group.[39] Additionally, this conjugated chain presents an electron transfer per repeating unit of 0.5 and a conductivity of 4x10<sup>-3</sup> S.cm<sup>-1</sup>.<sup>[39]</sup> Lastly, the side-chain length linking the TEMPO to the backbone was proved to be well suited to enhance radical pendent interaction and electron migration in polypyrrole moiety.

The procedure followed for the monomer synthesis of 2,7-BTC was based on nucleophilic substitution followed by Suzuki coupling reaction (Figure 2).



Figure 2. Synthesis of BTC and BTC-TEMPO monomer (R=CH3, TEMPO)

This method was easier than the one published by Zotti et *al.* for a very similar monomer structure.<sup>[39]</sup> An extra step was added to the synthesis strategy to obtain 2,7-BTC-TEMPO by insertion of the TEMPO group in the alkyl chain (Figure 3).

Chemical polymerization of 2,7-BTC-TEMPO 2,7-BTC were elaborated in presence of a solution of FeCl<sub>3</sub> The monomer 2,7-BTC-TEMPO (1 g, 1 eq) [ 2,7-BTC (1g, 1eq)] was solubilized in chloroform (10 mL) and a solution of FeCl<sub>3</sub> (1.108 g, 4 eq) [1.561 g, 4 eq] in nitromethane (10 mL) was added dropwise to the reaction volume while vigorous stirring. The reaction proceeds for 24h at 0°C under argon. The obtained solution was added dropwise to methanol and leaved stirring for 24h. Methanol is a non-solvent so the polymer precipitates. After filtration, the precipitate was stirred for 48 hours in aquous solution of NH<sub>4</sub>OH (3.5 mL, 28%) containing EDTA (1.5 g) and washed with water.

Electropolymerization of 2,7-BTC-TEMPO and 2,7-BTC was carried out by cyclic voltammetry. The experiments were performed in a three electrodes cell using as working electrode platinum ITO electrode (see ESI Figure S8 a) and carbon Super P®/PVdF (%w/w=90/10 and 80/20) (see ESI Figure S8b). The counter electrode was platinum and the reference electrode was an Ag wire or an Ag/Ag<sup>+</sup> (silver wire immersed in a solution of 0.01 M AgNO<sub>3</sub>, 0.1 M tetrabutylammonium perchlorate in acetonitrile).



Figure 3. Chemical and Electrochemical polymerization of BTC and BTC TEMPO.

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#### Structural characterization

After each step of monomer synthesis a <sup>1</sup>H-NMR spectrum was realized to confirm the purity and structural quality of the obtained product (see ESI Figure S7). Complementarily, mass spectroscopy confirmed the successful synthesis of 2,7-BTC and 2,7-BTC-TEMPO monomers. The theoretical and the experimental determined molecular weights (Mw) are summarized in Table 1.

| Table   | 1.  | Molecular  | weights | of | monomers | in | study | obtained | by | Mass |
|---------|-----|------------|---------|----|----------|----|-------|----------|----|------|
| spectro | osc | opy in CH₃ | OH.     |    |          |    |       |          |    |      |

|                   | Monomer<br>theoretical<br>Mw (g/mol) | Monomer<br>experimental<br>Mw (g/mol)<br><b>M</b> | Monomer<br>experimental<br>Mw (g/mol)<br><b>M+H</b> + | Monomer<br>experimental<br>Mw (g/mol)<br>MH+H <sup>+</sup> |
|-------------------|--------------------------------------|---|---|--|
| 2,7-BTC           | 415.61                               | 415.20  | 416.20  | -  |
| 2,7-BTC-<br>TEMPO | 585.82                               | 585.30  | 586.30  | 587.30   |

The presence and structural integrity of the TEMPO radical in 2,7-BTC-TEMPO and in pBTC-TEMPO was investigated by EPR in solution. The EPR spectra of hydroxy-TEMPO and 2,7-BTC-TEMPO (black and red spectra in the inset of Fig 4) both exhibit a main triplet due to nitrogen hyperfine splitting with the same constant (a(N) = 15.4 G). In the case of 2,7-BTC-TEMPO the peak-to-peak height of the feature at the highest magnetic field (centred at 3450.3 G) is clearly lower than for the two other features (at 3419.5 and 3434.9 G). Such a pattern is typical of the slower tumbling of the TEMPO moiety when grafted on a bigger molecule such as 2,7-BTC.<sup>[40]</sup> Despite its poor solubility in most of solvents, pBTC-TEMPO in solution could be prepared by filtration of a dispersion of the polymer in in ortho-dichlorobenzene (see blue EPR spectrum in the inset of Fig 4). The nitrogen hyperfine splitting (a(N) = 15.6 G) is still observed but the corresponding three features are much broader in pBTC-TEMPO than in 2,7-BTC-TEMPO, consistent with the even more restricted mobility of TEMPO moieties when grafted to the polymer.



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Figure 4. Distances distributions measured by DEER experiments (T=60K) in the pBTC-TEMPO polymer. The Tikhonov regularization was performed with different weights ("a" in the legend ) for the second derivative in the regularization process. The sample was obtained by filtration of a dispersion of the pBTC-TEMPO polymer in dichlorobenzene. Inset: room temperature EPR spectra of 4-Hydroxy-TEMPO (dark), BTC-TEMPO (red) 100  $\mu$ M solutions in toluene and same solution of pBTC-TEMPO in dichlorobenzene as for DEER experiments (blue).

DEER (Double Electron-Electron Resonance) experiments were performed for the same pBTC-TEMPO sample (but frozen at T=60K) in order to measure nitroxide-nitroxide distances in the polymer in the [2-6 nm] range. Remarkably, well-resolved distances distribution was obtained after Tikhonov regularization of the DEER signals: two sharp maxima at 2.1 nm and 2.8 nm and two broader features at 3.9 nm and 4.8 nm. The observation of such well-resolved distances distribution with sharp maxima in DEER experiments is exceptional for a polymer grafted with free radicals. It is clearly due to the rigidity of the polymer backbone. The resolution of the distances distribution is comparable to the resolution reported for DEER experiments performed with double strand DNA grafted with nitroxides.<sup>[41, 42]</sup> The 2.1 nm and 2.8 nm distances obtained by this measurement reported here are very intense and in the most reliable domain for DEER measurements, so they were used to build a simple conformational model encompassing two successive monomers in pBTC-TEMPO (see ESI Figure S1 to S6). In this model two successive carbazole moieties can adopt only two conformations (cis and trans) relative to the bis-thiophene moiety. The energy levels of the most stable conformers, compatible with this hypothesis, were computed by DFT (see ESI Figure S1 to S6) and high rotational barriers for local thiophene-thiophene (5.4 kCal/mol) and carbazolethiophene (4.0 kCal/mol) links have been found explaining this strict cis/trans alternation (273 K = 0.5 kCal/mol; see ESI). A second feature of this model is that TEMPO radicals are located on either sides of the local plane defined by two adjacent carbazole groups linked through a dithiophene (which is at least true for the first CH<sub>2</sub> of the alkyl chain linking the carbazole to the TEMPO radical due to possible H ... H contact: cf. Figure S2 right). By using such a model the TEMPO-TEMPO distances shown in the following Figure 5 were derived.

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Figure 5. : First- and second-neighbour predicted distances (in nm)

The shortest expected distance in this model is 1.5 nm. It corresponds to the DFT computed N-N distance between two carbazole groups. Such a short distance is not accessible by DEER experiments due to limited microwave excitation power and limited cavity bandwidth. In addition to 2.1 and 2.8 nm, this model predicts distances at 3.1, 3.4, 3.9 and 4.1 nm between nitroxides separated by one or two BTC moieties. These predicted values are in good agreement with the shoulders (3.1-3.4 nm) and the maximum (3.9 nm) observed in the measured distance distribution. In this particular experiment all measured distances longer than 3.0 nm should be considered with caution, because of their limited weight in the computed distribution and because of limited S/N. However, the non-zero probability of distances in the 3.0-3.5 nm and 3.8-4.7 nm ranges can be considered as reliable and are in good agreement with the second neighbour distances predicted by our model. This very good agreement is a clear evidence that polymer chains remain very rigid and planar in solution with only discrete and planar conformations accessible. Moreover despite the intrinsic flexibility of the hexyl linkers, the nitroxide radicals are also located at precise positions corresponding each to an extended linker chains slightly tilted from the plane of the carbazole moiety.

Chemical polymerization of both poly(2,7-BTC) and poly(2,7-BTC-TEMPO) was confirmed by UV-Vis (Figure 6).





Both monomers displayed a maximum peak absorption at 355 nm while both polymers showed an absorption peak at 429 nm, attributed to the  $\pi$ - $\pi^*$  electron transition. The observed red-shift from 355 nm to 429 nm is an indication of the extended electron delocalization and the improved electron transportation in the polymer. At this extremely low concentration, the spectra of 2,7-BTC-TEMPO and poly(2,7-BTC-TEMPO) display a very intense main absorption band at 350 nm and 430 nm. At this scale (normalized spectra) due to the extremely low molar absorption coefficient ( $\epsilon$ ) of TEMPO group (around 100 M<sup>-1</sup>cm<sup>-1</sup>) it is not possible to observes its characteristic signature at 466 nm. The calculated  $\epsilon$  of monomer 2,7-BTC was 1.11x10<sup>4</sup> M<sup>-1</sup>cm<sup>-1</sup>. The radical nature of TEMPO derivatives inhibits NMR characterization. Due to low solubility it was not possible to obtain the degree of polymerization by Gel Permeation Chromatography.

#### **Electrochemical Characterization**

#### Platinum working electrode

Poly(2,7-BTC) and poly(2,7-BTC-TEMPO) were studied using cycling voltammetry (CV) first on platinum (Pt) working electrode. Sequential scans of monomer in solution exhibited increasing current which is characteristic of electrochemical polymerization with deposition of polymer on the electrode surface (Figure 7a) and Figure 7c). To identify the redox couples and evaluate the reversibility of the redox reaction on the deposited polymers, CV was further performed in acetonitrile containing  $Bu_4NPF_6$  (0.1 M) at different scan rates.

Figure 7d shows the CV profile of poly(2,7-BTC-TEMPO) on which the polymer electrode exhibits a couple of anodic and cathodic peaks at about 0.40V and 0.32V versus Fc\*/Fc, respectively, with a potential separation of about 0.08 V. These peaks are assigned to the reversible oxidation of nitroxide radicals to the corresponding oxoammonium cations in the polymer associated with anion charge compensation. Poly(2,7-BTC) was prepared to make sure that the oxidation peak observed comes from the oxidation of TEMPO. Indeed, this polymer did not show any redox response in this range, meaning that the redox response observed is due to the nitroxide group (Figure 7b). Furthermore, the capacitive response of the conductive backbone is observed in the same potential range for both polymers.

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**Figure 7.** (a) Electro-polymerization by cyclic voltammetry of BTC 3 mM at 50 mV/s, with the first cycle highlighted in red; (b) Cyclic voltammetry of pBTC at 10 mV/s; (c) Electro-polymerization by cyclic voltammetry of 1,5 mM BTC-TEMPO at 50 mV/s (10 cycles), with the first cycle highlighted in red; (d) Cyclic voltammetry of pBTC at 50 mV/s (50 cycles); (e) Cyclic voltammetry of pBTC at different scan rates (5 cycles each); (f) Oxidation peak current versus scan rate. All experiments were performed in acetonitrile containing  $Bu_4NPF_6$  (0.1 M) using Pt as working electrode. Note Fc\*/Fc electrode has a value of 3.22 V versus Li/Li\*.

The peaks' symmetry in Figure 7d suggests a good electrochemical reversibility of the redox mechanism in the polymer and the narrow gap between the peaks implies large electrode reaction rates, which is important to reach high power rates during charge/discharge process of the battery. Nevertheless, the 50 cycles curves displayed in Figure 7b do not completely overlap with each other as for a TEMPO group in solution, indicating a small instability over time. The CV study of poly (2,7-BTC-TEMPO) at various scan rates shows that the peak current is linearly proportional to the scan rate, which means that the current is controlled by the electrochemical reaction of the TEMPO and not by diffusion of counter ions in the electrolyte.<sup>[33]</sup> The oxidation potential shift to higher potentials during measurements and the same behavior was previously reported for a polythiophene bearing TEMPO.<sup>[43]</sup>

#### Carbon composite based working electrode

Electro-polymerizations of 2,7-BTC and 2,7-BTC-TEMPO were also performed on carbon based composite electrodes (carbon Super P/Polyvinylfluoridene [PVdF] 80/20 and 90/10 % w/w coated on aluminum foil) (Figure 8). As observed in the case of Pt based electrode, there is a current increase for each one of the 10 cycles. The electro-polymerization of 2,7-BTC-TEMPO on carbon 80/20 shows in the first cycle two redox peaks at 0.25 V and 0.20 V corresponding to the TEMPO oxidation and reduction, and one peak at 0.57 V for the monomer oxidation. However, contrary to what is observed in Pt, these peaks are progressively hidden by the redox feature of the polymer on carbon.



**Figure 8.** Electropolymerization of 2,7-BTC-TEMPO on carbon 80/20 composite by cyclic voltammetry of 1,5mM BTC-TEMPO at 50mV/s (10 cycles), with the first cycle highlighted in red. Note that Ag/Ag<sup>+</sup> electrode has a value of 3.3 V versus Li/Li<sup>+</sup>.

The CV response of the electrode was studied before and after polymerization in order to compare charge capacity.<sup>[43]</sup>

# Comparison of electrochemical performance as electrode material of lithium batteries

Poly(2,7-BTC) and Poly(2,7-BTC-TEMPO) have been implemented into composite based electrodes constituted by 40% wt of active materials, 40% wt of carbon and 20% wt of PvdF binder. Electrochemical performances have been evaluated by galvanostatic cycling at various C-rate in half cell (i.e. using lithium metal as negative electrode) with classical electrolytes for lithium battery (1 M LiPF<sub>6</sub> in a 1/1 mixture of ethylene carbonate [EC] / dimethylcarbonate [DMC]). As shown in Figure 9, after few cycles in which the observed capacity decreases due to the partial dissolution of the active materials, some very stable specific capacities are then obtained at 1C-rate in both cases with 30 mAh.g<sup>-1</sup> and 50 mAh.g<sup>-1</sup> for Poly(2,7-BTC) and Poly(2,7-BTC-TEMPO) respectively. This last value is in good agreement with the theoretical value calculated for Poly(2,7-BTC-TEMPO) of 53 mAh.g<sup>-1</sup> taking into account one electron exchange per monomer unit. The cycling tests show high coulombic efficiency (98% and 97%) and capacity retention (95% and 93% considering the 6th cycle as reference) and confirm that our polymerization strategy is efficient to prevent active materials from dissolution into electrolytes. Moreover if the contribution of nitroxide group to the global redox activity clearly appears at low C-rate (1 C to 5 C), it is even more significant at very high power (10 C to 50 C) and can be explained by its remarkably faster redox kinetics compared to de/doping mechanism of BTC backbone.

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**Figure 9.** Electrochemical performances of the electrodes materials at various C-rate between 3.0V and 4.0V vs Li<sup>+</sup>/Li. : a) 40%pBTC, 40% Super P, 20% PVdF, c) 40% pBTC-TEMPO, 40% Super P, 20% PVdF, e) 50%pBTC-TEMPO, 30% Super P, 20% PVdF, f) 60% pBTC-TEMPO, 20% Super P, 20% PVdF. Charge and discharge profile for electrodes materials: b) 40%pBTC, 40% Super P, 20% PVdF, d) 40% pBTC-TEMPO, 40% Super P, and 20% PVdF.

#### Reduction of carbon content in organic electrodes

Even if the presented work could not reach higher capacity and power-rates than previous publications,<sup>[41, 42]</sup> we were able to dramatically reduce the ratio of carbon additives in organic radical electrodes. Indeed, generally comprised between 60 and 40%wt, this new TEMPO grafted conductive polymer shows similar electrochemical performances with only 20%wt carbon until 5C.

#### Conclusions

This work describes the synthesis and the characterization of the 2,7-BTC, 2,7-BTC-TEMPO monomers and of the poly(2,7-BTC-TEMPO). We have successfully designed and synthesized a poly(bisthiophene carabazole) bearing pendent TEMPO radicals for the first time.

The proposed synthetic pathway was relatively simple and leads to good reaction yields. EPR and DEER characterization demonstrated the structural stability of the TEMPO group in the polymer and revealed its spatial distribution. In a second part, electropolymerization on Pt substrates were successfully performed and both TEMPO groups and conductive backbone exhibited an electrochemical response. Furthermore, it was proved that it is possible to electropolymerize 2,7-BTC and 2,7-BTC-TEMPO on carbon composite electrodes which improves their electrochemical performances.

Poly(2,7-BTC-TEMPO) is a suitable active material for positive electrodes of lithium batteries and good pseudosupercapacitors.

This redox and electroactive polymer shows stable cycling behaviour and, even if its specific capacity is moderate, very high electrochemical performances is maintained at high C-rate, and carbon content could be dramatically reduced in comparison with previously reported polynitroxides. This copolymer Poly(2,7-BTC-TEMPO) exhibits a loss of only 20% between 10 C and C and 40% between 20 C and C which is a remarkable experimental result. However, further tests should be realized with higher number of cycles at high current density but also with lower amount of carbon additives. So far, the battery results are very promising and if the initial loss of capacity could be avoided, outstanding characteristics would be reached, with high potential for industrial application.

### **Experimental Section**

#### Materials

2,7-Dibromocarbazole (98%), 4-hydroxy-2,2,6,6-tetramethyl-piperidine-1oxvl free radical (4-hydroxyl-TEMPO, 98%) and Tetrakis (triphenylphosphine)-palladium(0) (P(PPh<sub>3</sub>)<sub>4</sub>, 97%) were purchased from TCI Europe. Thiophene-2-boronic acid pinacol ester (98%), 1-Bromohexane (98%), Sodium hydride (NaH, 60% dispersion in mineral oil), Hexanes (97%), Ethyl acetate (99.5%), Toluene anhydrous (99.7%), and Ethylenediamine tetracetic acid disodium salt dehydrate (EDTA, 99+%) were supplied by Sigma-Aldrich. Dimethylformamide (DMF, 99.8%, extra dry) and 1,6-Dibromohexane (98%) were supplied by Acros, potassium chloride (KCl, 99.5%) was purchased from Prolabo. Sodium sulfate (Na<sub>2</sub>SO<sub>4</sub>, 99%) and silica seeds Geduran ® Si 60 (0.063-0.200 mm) were supplied by Merck KGaA. Dichlorometane (CH2Cl2, 99.9%) and Sodium Carbonate (Na<sub>2</sub>CO<sub>3</sub>, 99.5%) were purchased from Carlo Erba reagents. All reagents and solvents were used as received. Experimental Details.

#### Synthesis of N-(6-Bromo hexyl)-2,7-dibromo carbazole (1)

Product (1) was synthetized as shown in Figure 2.<sup>[17]</sup> In a typical procedure, 2.0 g (1 eq) of 2,7-Dibromocarbazole was solubilized in dry DMF (dimethylformamide) at 0°C under argon and then 0.344 g of sodium 30 minutes, then 5 ml (5.3 eq) of 1,6-dibromo hexane were added dropwise and the reaction proceeded at 70°C for 24 h. Finally the solution was washed with a saturated solution of NaCl (2 x 400 mL), dried with Na<sub>2</sub>SO<sub>4</sub> and filtered. The obtained oily product was purified by silica-packed column chromatography (eluent: ethyl acetate/hexane 1/50). A white powder was collected and recrystallized by dissolution in hexane at 70°C. A thin white powder was obtained (70% yield). 1H NMR (200 MHz, CDCl<sub>3</sub>, 25°C see Fig S7).

#### Synthesis of N-(4-hydroxyTEMPO Hexyl)- 2,7- dibromo carbazole (2)

In a typical procedure, 0.48 g (1.15 eq) of 4-Hydroxy TEMPO were introduced in a three necked flask equipped with an argon inlet and magnetic stirrer. The dry DMF (10 ml) as solvent reaction was added at 0 °C under argon atmosphere. After sodium hydride (0.145 g, 1.3 eq) was added slowly and the reaction mixture was stirred at 0°C under argon for 1 h. Then a solution of (1) (1,18 g, 1eq) in DMF (10 ml) was added dropwise. The reaction proceeds overnight at 0°C under argon atmosphere. The reaction mixture was washed with a saturated solution of NaCl (2 x 400 mL) dried with Na<sub>2</sub>SO<sub>4</sub> and filtered. The solid product was subsequently purified by silica-packed column chromatography (eluent:

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ethyl acetate/hexane from 1:50 to 1:10). An orange powder was obtained (70% yield): <sup>1</sup>H NMR (200 MHz, CDCl<sub>3</sub>, 25  $^{\circ}$ C, see Fig S7).

# Synthesis of N-(4-hydroxyTEMPO Hexyl)- 2,7-bisthiophene carbazole (3)

The synthesis is shown in Figure 2. In a typical procedure 0.8g, (1eq) of (2) and 1.16 g (4 eq) of thiophene-2-boronic acid pinacol ester were dissolved in toluene (20 ml). Then 2M Na<sub>2</sub>CO<sub>3</sub> aqueous solution (2 ml) and Pd(PPh<sub>3</sub>)<sub>4</sub> (0.128 g, 8% mol) were added. The reaction mixture was stirred under argon at 90 °C for 24 h. Then the solution was washed with a saturated solution of NaCl (2 x 400 mL) dried with Na2SO4 and filtered. The product was purified by silica-packed column chromatography (eluent: ethyl acetate/hexane from 1:20 to 1:4). A light orange powder was obtained (50% yield): 'H NMR (200 MHz, CDCl<sub>3</sub>, 25 °C). MS (EI): calculated for C<sub>35</sub>H<sub>41</sub>N<sub>2</sub>O<sub>2</sub>S<sub>2</sub> m/z: 586, found 585.

#### Synthesis of N-Hexyl-2,7-bisthiophene carbazole (5)

The synthesis of is shown in Figure 2. Synthesis was carried out starting from commercial 2,7-dibromo carbazole.1H NMR (200 MHz, CDCl<sub>3</sub>, 25 °C). MS (EI): calculated for C<sub>26</sub>H<sub>25</sub>NS<sub>2</sub> m/z: 415, found 416. This procedure and the NMR characterization was previously described in the paper of Zotti et Al<sup>[39]</sup> and Reynolds et Al.<sup>[37]</sup>

#### Synthesis of pBTC-TEMPO and pBTC

pBTC-TEMPO synthesis is shown in Figure 3 and pBTC synthesis in Figure 3. For pBTC-TEMPO synthesis, in a typical procedure 1 g (1 eq) of 2,7-BTC-TEMPO was solubilized in chloroform (10 mL) and a solution of FeCl<sub>3</sub> (1.108 g, 4 eq) in nitromethane (10 mL) was added dropwise to the reaction volume while vigorous stirring. The reaction proceeds for 24h at 0°C under argon. The obtained solution was added dropwise to methanol and leaved stirring for 24 h. Methanol is a non-solvent so the polymer precipitates. After filtration, the precipitate was stirred for 48 hours in aqueous solution of NH<sub>4</sub>OH (3.5 mL, 28%) containing EDTA (1.5 g) and washed with water.

#### UV-Visible and EPR analysis

UV-Visible spectra were recorded using a Bio-Tek instruments UVIKON XS spectrometer. Room temperature Continuous wave EPR spectra were recorded with a Bruker EMX spectrometer operating at X-band (9.65 GHz) frequency combined with an ER-4116 dual mode cavity. DEER (Double Electron Electron Resonance) measurements were performed at 60 K at X-band by using a Bruker Elexsys 580 spectrometer equipped with a 5 mm dielectric-ring resonator. The four-pulse DEER sequence was used with pulse lengths of 16 and 32 ns for the  $\pi/2$  and  $\pi$  pulses, respectively. Background echo decay was corrected by using a homogeneous one-dimensional spin distribution. The corrected dipolar evolution was fitted by using Tikhonov regularization, as implemented in the DEER Analysis 2013 package.<sup>[44]</sup>

#### **DFT calculations**

DFT calculations have been performed with the ADF (Amsterdam Density Functional) code developed by E. J. Baerends and co-workers.<sup>[45]</sup> Triplezeta basis sets have been used throughout. All geometry optimization have been performed in vacuo relying on the Generalized Gradient Approximation (GGA) VBP exchange-correlation (XC) potential (VWN + BP: Vosko,<sup>[46]</sup> Wilk & Nusair + corrective terms by Becke<sup>[47]</sup> for the exchange, and Perdew<sup>[48]</sup> for the correlation).

#### Mass spectrometry analysis

The mass spectra were recorded on a LXQ type THERMO SCIENTIFIC spectrometer, equipped with an electrospray ionization source and linear-trap detector. Solutions were injected in the spectrometer at 10  $\mu$ L min<sup>-1</sup> flow rate. Ionization voltage and capillary temperature were set at about 6 kV and 250°C, respectively. The data were acquired in positive mode with an injection time of 5-200 ms. The LXQ calibration (m/z 50-2000) was achieved according to the standard calibration procedure from the manufacturer (mixture of caffeine, MRFA and Ultramark 1621).

#### **Cyclic Voltammetry**

The cyclic voltammetry tests were performed with an Autolab PGSTAT 302 N potentiostat in a three electrodes cell containing a 0.1 M tetraethyl ammonium perchlorate acetonitrile electrolytic solution. The working electrode was a Pt disk. A Pt wire was used as counter electrode and a silver wire was used as pseudo-reference. The reference was calibrated after each experiment against ferrocene /ferrocenium couple.

#### Electrode preparation and batteries performances

Composite electrodes for the electrochemical characterization were prepared by mixing the polymer, Super P® (SP; Imerys) and poly(vinylidene difluoride) (PVdF, 5130; Solvay) in N-methyl-2-pyrrolidone (NMP; Sigma-Aldrich). The overall weight ratio was 40/40/20, 50/30/20 or 60/20/20. All slurries were coated on aluminum foil, serving as current collector, and after pre-drying disk-shaped electrodes were punched, having an average active material mass loading of about 1 mg cm<sup>-2</sup> for pBTC/SP/PVdF and electrodes were subsequently pressed at 10 t for 10 s before all the electrodes were dried at 80 °C for 48 h under vacuum.

Coin cell assembly was carried out in an argon-filled MBraun glove box using metallic lithium foil as counter and reference electrodes and Celgard® 2400 and Viledon® (Freudenberg) as separator, the latter soaked with a 1M solution of LiPF<sub>6</sub> in a 1:1:1 volume mixture of ethylene carbonate (EC) and dimethyl carbonate (DMC) (UBE), serving as electrolyte. Cyclic voltammetry (CV; scan rate: 0.01 mV s<sup>-1</sup>) and galvanostatic cycling were performed using a multichannel VMP3 potentiostat (Biologic) and an Arbin BT-2000, respectively. With respect to a maximum theoretical capacity of 60 mAh g<sup>-1</sup>, assuming a one-electron transfer per unit, a C rate of 1C is defined as a specific current of 60 mA g<sup>-1</sup>. As lithium foil served as counter and reference electrode, all potential values given herein refer to the Li<sup>+</sup>/Li redox couple (Ag/Ag<sup>+</sup> reference electrode has a value of 3.3 V versus Li/Li<sup>+</sup>)

#### **Batteries performances**

During charge and discharge, the reached capacity (C), the same is to say the number of charges transferred in the battery, is obtained by integrating the current of the cell with respect to charge/discharge time ( $\Delta t$ ).

$$C(Ah/Kg) = \frac{\int_0^{\Delta t_I} dt}{M} \qquad \text{or} \qquad C(Ah/L) = \frac{\int_0^{\Delta t_I} dt}{Vol} \qquad (\text{eq.3})$$

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Normalizing this value by the mass of the two electrodes or the mass of the positive working electrode gives the gravimetric capacity of the battery and the electrode, respectively (in mAh/g, shown in eq.4). Normalizing the integral with respect to the volume will consequently yield the volumetric capacity of the battery (or electrode) in mAh mL<sup>-1</sup>. On the other hand, theoretical capacity (C\_theoretical) is given in eq. 2 where n is the number of transferred electrons for every repeating unit, F is the Faraday constant (96,487 C mol<sup>-1</sup>) and Mw is the molecular mass of the polymer repeating unit.

$$C_{theoretical} (mAh/g) = \frac{n \times F(C/mol)}{M_{w}(g/mol)}$$
(eq.4)

The energy density (E) and power density (P) are then derived from the capacity values:

$$E(Wh/Kg) = C.\Delta V$$
 (eq.5)

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 $P(W/Kg) = \frac{C \Delta V}{\Delta t}$ 

(eq.5)

Considering the formula for the theoretical capacity, there are two ways to improve this value: by generating multiple redox reactions per repeating unit and/or by reducing the molecular weight of the repeating unit.

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**Keywords:** Organic redox batteries• conducting polymers • DEER characterization • TEMPO derivatives• Electrochemical energy storage. Pseudosupercapacitors

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L. Assumma, Y. Kervella, J.-M. Mouesca , M. Mendez, V. Maurel, L. Dubois, T. Gutel\*, S. Sadki\*

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A new conducting copolymer bearing electro-active nitroxide groups as organic electrode materials for batteries and pseudosupercapacitors

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