Tetrahedron Letters 52 (2011) 6903–6907

Contents lists available at SciVerse ScienceDirect

Tetrahedron Letters

journal homepage: www.elsevier.com/locate/tetlet

Towards hybrid carbazole/pyrrole-based carboxylated monomers: chemical synthesis, characterisation and electro-oxidation properties

Jean-Paul Lellouche[a,*], Zvika Pomerantz[a], Subrata Ghosh[a,b,*]

[a] Department of Chemistry, Nanomaterials Research Center, Institute for Nanotechnology and Advanced Materials, Bar-Ilan University, Ramat-Gan 52900, Israel
[b] School of Basic Sciences, Indian Institute of Technology Mandi, Mandi 175001, India

ARTICLE INFO

Article history:
Received 29 August 2011
Revised 7 October 2011
Accepted 9 October 2011
Available online 14 October 2011

Keywords:
Polycarbazole
Polypyrrole
Hybrid monomers
Electro-polymerisation
Conducting polymers

ABSTRACT

Six novel *hybrid* carbazole (Cbz)–pyrrole (Pyr)-based carboxylated monomers were synthesised and unambiguously characterised using common spectroscopic tools. Clauson-Kaas, amide coupling, LAH (lithium aluminium hydride)-mediated reduction, esterification and debenzylation reactions were used as key chemical reactions towards their multi-step synthesis. The electro-oxidation features of all these six *hybrid* Cbz/Pyr-monomers were investigated for the electro-deposition of corresponding polyCOOH conducting coatings. Quite interestingly, and due to the fact that such electro-oxidisable monomers contain both types of oxidisable heterocycles, that is, Pyr and Cbz species, it was found that the successful electro-polymerisation of these hybrid Cbz/Pyr-monomers was highly dependent on the relative number of Cbz versus Pyr unit(s) present in corresponding monomers. Indeed, a successful electro-deposition of the corresponding conducting polymeric films onto a working Pt electrode was observed only for hybrid monomers characterised by a Cbz/Pyr unit(s) ratio greater than or equal to 1. This result has been validated by systematically tuning the number of oxidisable Cbz and Pyr unit(s) present in monomers through proper chemical design and monomer multi-step synthesis. In that case, cyclic voltammogram analyses readily confirmed the exclusive electro-deposition of *conducting polyCbz-films*.

Electro-polymerisation of carbazole (Cbz) and pyrrole (Pyr) heterocycles is an important chemico-technological tool for the fabrication of corresponding conducting polymer (CP)-modified electrodes as they find wide applications in various fields such as chemical sensing, photoconductive materials, light-emitting diodes, electrochromic materials, etc.[1–19] Furthermore, functionalised CP films are of special interest because of their potential applications in the biosensing field.[20–25] Over the years, various Cbz- and Pyr-based *functional* and *non-functional* oxidisable monomers have been developed through proper chemical design, and their electro-polymerisation towards corresponding conductive coatings has been studied extensively.[26–30] To investigate their mechanism of formation/growth and to understand the potential effect of various added chemical species, such electro-polymerisation processes of Cbz- and Pyr-monomers were studied under different experimental conditions,[31–33] including different solvents and in the presence of some other added interfering chemical entities such as perchloric acid,[4] water,[32] hydrochloric acid,[34] surfactants,[35] pyridine,[36] etc. In addition, it is a well-established fact that the electro-polymerisation of short *N*-hydroxyalkyl or *N*-carboxyalkyl chain-based Pyr-monomers is blocked due to intramolecular trapping of in situ-generated cation radicals by close nucleophilic hydroxyl or acidic hydroxyl groups.[37,38] On the other hand, electrochemical copolymerisation of Pyr- and Cbz-species in the presence of other polymerisable entities such as aniline, furan, styrene, terthiophene, etc. is also a well-studied area of research. Indeed, it enables the easy fabrication of hybrid functional polymers with modified physical properties.[39–45] For example, in order to tailor the surface properties of electro-polymerised conductive films, several hybrid oxidisable monomers based on carbocycle- or heterocycle-attached/fused Cbz- or Pyr-based monomers have been prepared and their electro-oxidation behaviour has been intensively investigated.[6,46–50] Despite numerous efforts invested in this field, to the best of our knowledge, there is no existing report dealing with the synthesis and electro-oxidation properties of hybrid Cbz/-Pyr-based carboxylated monomers.

In the present study, we report our own strategy for the incremental synthesis of new and different Cbz/Pyr-based hybrid monomers followed by an investigation into their respective electro-oxidation properties. In order to rationally investigate the electro-polymerisation behaviour of such hybrid Cbz/Pyr-based monomers, the relative ratios of Cbz versus Pyr unit(s) in each monomer were changed systematically through proper chemical design and monomer multi-step synthesis.

To begin our investigation strategy, we initially synthesised two carboxylated hybrid monomers **7** and **8** (Scheme 1). The basic

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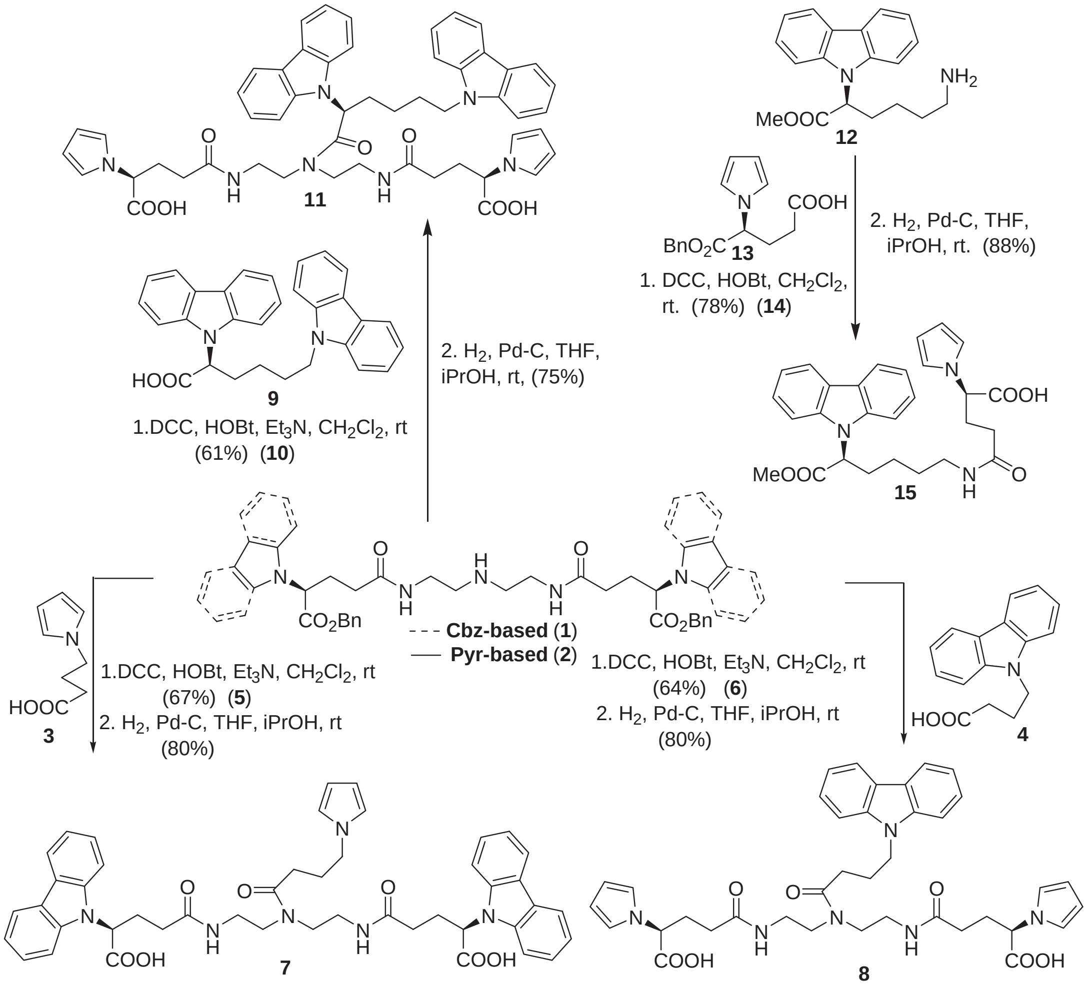
[*] Corresponding authors. Tel.: +972 3 531 8324; fax: +972 3 738 4053 (J.-P.L.); tel.: +91 1905 237926; fax: +91 1905 237924 (S.G.).

E-mail addresses: lellouj@biu.ac.il (J.-P. Lellouche), subrata@iitmandi.ac.in, sghoshchem2002@iitmandi.ac.in (S. Ghosh).

0040-4039/$ - see front matter © 2011 Elsevier Ltd. All rights reserved.
doi:10.1016/j.tetlet.2011.10.047

difference between these two monomers is the presence of different numbers of Cbz and Pyr unit(s). Monomer **7** contains *one* Pyr unit (Pyr_1) and *two* Cbz units (Cbz_2), whereas monomer **8** contains *one* Cbz unit and *two* Pyr units. The synthetic procedures used for the preparation of these specific monomers are outlined in Scheme 1. The starting C2-symmetrical amino building blocks **1** and **2** were synthesised following a literature procedure.[37] All other Cbz- and Pyr-based building blocks **3**, **4**, **9**, **13**, **16**, **17** and **20** were synthesised by a modified Clauson-Kaas ring closure reaction[37,51–55] using 2,5-dimethoxy-tetrahydrofuran (DMT) and corresponding amino acid derivatives as the key starting materials (amino acid, DMT, NaOAC, AcOH, H_2O, 75 °C, 2 h, 42–76% yields for **3**, **13** and **17**; amino acid, DMT, dioxane, AcOH, HCl, reflux for 3 h and then overnight stirring at rt, 27–30% yields for **4**, **9**, **16** and **20**). The amidation of the amino building blocks **1** and **2** with the carboxyl building blocks **3** and **4** used a combination of dicyclohexyl-carbodiimide (DCC), 1-hydroxybenzotriazole (HOBt) and triethylamine (TEA) as efficient coupling systems affording the corresponding amidated intermediates **5** (67%) and **6** (64%), respectively. The desired carboxylated hybrid monomers Pyr_1/Cbz_2-**7** and Pyr_2/Cbz_1-**8** were synthesised by straightforward debenzylation of intermediates **5** and **6**, respectively (H_2 gas in the presence of a catalytic amount of 10% Pd/C, 80% yields). Next, we investigated the electro-oxidation behaviour of Pyr_1/Cbz_2-**7** and Pyr_2/Cbz_1-**8**. Interestingly, we observed that upon electro-polymerisation (cyclic voltammetry at 50 mV/sec, three electrode-cell, a mixture of 0.2 M n-Bu_4NClO_4 and 0.2 M $LiClO_4$ in a ethylenecarbonate–dimethylcarbonate solution as the background electrolyte; details are available in the following sections), the monomer Pyr_1/Cbz_2-**7** successfully produced a conducting polymeric poly(Pyr_1/Cbz_2-**7**) film on a Pt electrode, but no polymeric film was formed when testing the monomer Pyr_2/Cbz_1-**8**. Interestingly, this experimental result likely indicates that, in the case of hybrid carboxylated Cbz/Pyr-based monomers, their electro-polymerisation may entirely depend on the relative number of Cbz and Pyr unit(s) present in their basic structures. To gain more evidence to support this conclusion, we next synthesised the monomer Pyr_2/Cbz_2-**11,** which contains an equal number of Cbz and Pyr units (*two* Cbz and *two* Pyr units). The monomer Pyr_2/Cbz_2-**11** was also synthesised by coupling both amino building block **2** and dicarbazole-based building block **9**, yielding the intermediate **10** (61%), followed by debenzylation (Scheme 1, 75% yield for Pyr_2/Cbz_2-**11**).

The electro-polymerisation of monomer Pyr_2/Cbz_2-**11** was tested under similar conditions as those stated above, and resulted in the formation of a stable polymeric conducting film on the Pt working electrode. Consequently, to know the fate of a hybrid Cbz/Pyr-monomer containing *one* unit of Cbz and Pyr each, we synthesised the monomer Pyr_1/Cbz_1-**15** (Scheme 1). The starting Cbz-based amino building block **12** was synthesised in two steps following a reported procedure.[55] The coupling of **12** with the carboxylated Pyr-based building block **13** in the presence of DCC and HOBt produced the intermediate **14** (78%), which upon debenzylation yielded the desired hybrid monomer Pyr_1/Cbz_1-**15** (88% yield for **15**). Monomer **15**, upon oxidative electro-polymerisation,

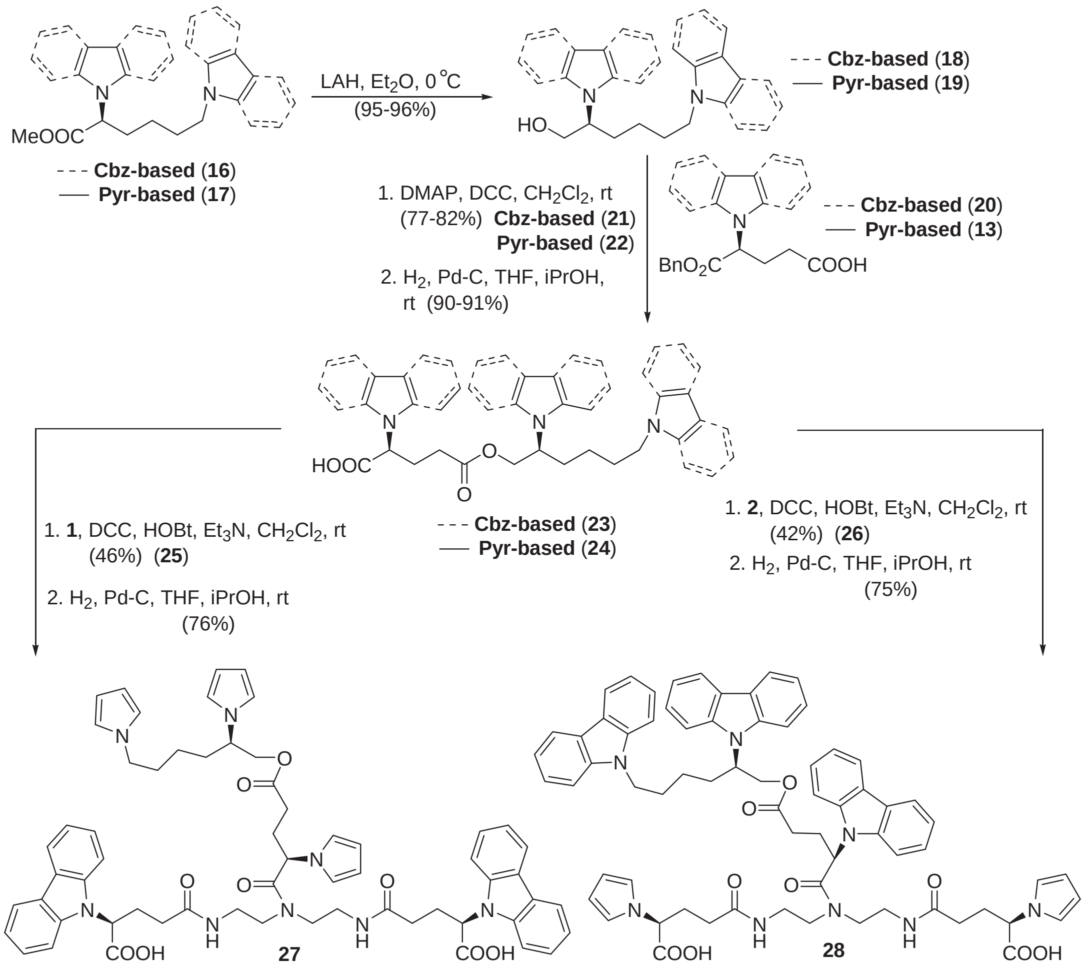


Scheme 1. Synthesis of hybrid carboxylated Cbz/Pyr-based monomers with a Cbz/Pyr ratio of 1:2, 2:1 and 1:1.

successfully produced a stable conductive poly(Pyr_1/Cbz_1-**15)** film. From the electro-polymerisation results of these four carboxylated hybrid Cbz/Pyr-monomers Pyr_1/Cbz_2-**7**, Pyr_2/Cbz_1-**8**, Pyr_2/Cbz_2-**11** and Pyr_1/Cbz_1-**15**, one can readily conclude that successful electro-polymerisation/conducting film growth can be expected only for carboxylated hybrid Cbz/Pyr-monomers for which the Cbz to Pyr unit(s) ratio is greater than or equal to 1. Finally, and in order to reinforce such an attractive conclusion, we decided to synthesise one additional pair of hybrid Cbz/Pyr-monomers containing different and higher numbers of Cbz and Pyr units. For this purpose, we synthesised monomers Pyr_3/Cbz_2-**27** and Pyr_2/Cbz_3-**28** following the reaction procedures outlined in Scheme 2. Both starting diCbz- and diPyr-based esters **16** and **17** were synthesised from the readily available (commercial source) material L-lysine methyl ester using a modified Clauson-Kaas ring closure reaction.[37,51–55] The $LiAlH_4$-mediated reduction of these esters produced the corresponding alcohols **18** and **19** (95% and 96% yields, respectively) which on further esterification with Cbz and Pyr-based building blocks (*S*)-**20**/**13** in the presence of a combination of DCC and dimethylaminopyridine (DMAP) produced both intermediates **21** and **22** (82% and 77% yields). The building blocks **13** and **20** were similarly synthesised from a protected L-glutamic acid derivative (benzylated H-Glu-*Z*) according to known procedures.[37,55] A catalytic amount of 10% Pd/C was used as the debenzylating catalytic agent to convert ester intermediates **21** and **22** to the corresponding acid intermediates **23** and **24** (91% and 90% yields, respectively), which on further amidation with C2-symmetrical building blocks **1** and **2** produced the final amide intermediates **25** and **26** (46% and 42% yields). Finally, the debenzylation of **25** and **26** yielded the final targeted dicarboxylated hybrid monomers Pyr_3/Cbz_2-**27** and Pyr_2/Cbz_3-**28** (76% and 75% yields). Monomer **27** contains *three* Pyr and *two* Cbz units, whereas monomer **28** contains *three* Cbz and *two* Pyr units. Next, and quite similarly, we investigated the electro-oxidation behaviour of both compounds Pyr_3/Cbz_2-**27** and Pyr_2/Cbz_3-**28**. The electro-polymerisation results fully agreed with our previously drawn conclusion. While monomer Cbz_3/Pyr_2-**28** with a Cbz/Pyr ratio >1 produced a stable conductive film upon electro-polymerisation, no such film was formed upon electro-polymerisation of monomer Cbz_2/Pyr_3-**27** which possesses a Cbz/Pyr ratio <1.

The final carboxylated hybrid monomers were foamy in nature. No column purification was necessary in the final debenzylation step since a simple washing of the crude products with suitable solvents (see Supplementary data section for details) yielded spectroscopic grade final products. Common spectroscopic tools such as $^{1}H/^{13}C$ NMR (300 and 75 MHz, respectively), mass spectrometry analyses, etc. were used for the unambiguous characterisation of all intermediates and final compounds.

The electrochemical studies dealing with this entire set of potentially oxidisable hybrid Cbz/Pyr-molecules consisted of two discrete steps. The first step dealt with the tentative electro-polymerisation of hybrid Cbz/Pyr-based monomers previously synthesised on a Pt working electrode. In the second step, the resulting modified electrodes were washed intensively using CH_3CN and were immersed in a *monomer-free* electrolyte solution (a mixture of 0.2 M *n*-Bu_4NClO_4 and 0.2 M $LiClO_4$ in an ethylenecarbonate–



Scheme 2. Synthesis of higher order carboxylated hybrids Cbz/Pyr-based monomers with a Cbz/Pyr ratio of 2:3 and 3:2, respectively.

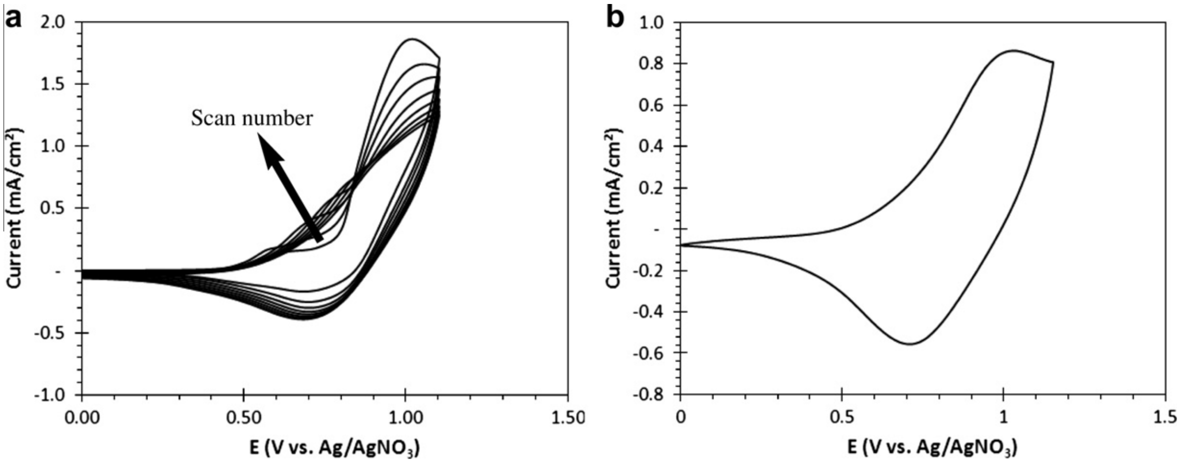


Figure 1. (a) Oxidative electro-polymerisation of hybrid monomer Pyr$_1$/Cbz$_2$-**7**. (b) Cyclic voltammogram of the resulting conducting poly(Pyr$_1$/Cbz$_2$-**7**) film.

Table 1
Summary of electro-polymerisation results for all hybrid monomers

Monomers	Cbz unit(s)	Pyr unit(s)	Cbz/Pyr ratio	Polymerisation result	
				Pyr window	Cbz window
7	2	1	>1	Negative	Positive
8	1	2	<1	”	Negative
11	2	2	1	”	Positive
15	1	1	1	”	”
27	2	3	<1	”	Negative
28	3	2	>1	”	Positive

dimethylcarbonate solution (1:2 molar ratio)) to study the voltammetric responses of the resulting conducting films.

Accordingly, the electro-polymerisation of all hybrid Cbz/Pyr-monomers was investigated by cyclic voltammetry (50 mV/sec) on a 1 mm diameter Pt working electrode using a three-electrode cell (Pt ribbon counter-electrode, Ag/AgNO$_3$ reference electrode) operated 10 times between 0 and 1.1 V (for Cbz polymerisations), -1.0 and 0.8 V (for Pyr polymerisations), or between -1.0 and 1.1 V for potential copolymerisations. The background electrolyte consisted of a mixture of 0.2 M n-Bu$_4$NClO$_4$ and 0.2 M LiClO$_4$ in an ethylenecarbonate–dimethylcarbonate solution (1:2 molar ratio) in which the monomer concentrations were adjusted to 5 mM. All the electrochemistry experiments were performed under a glove box atmosphere (dry Ar containing less than, 1 ppm H_2O and O_2).

An illustrative cyclic voltammogram of the electro-polymerisation process of monomer Pyr$_1$/Cbz$_2$-**7** and its typical electrochemical behaviour are reported above in Figure 1. The observed current increase during polymerisation process testing from one scan to another indicates the successful growth of a conducting polymer phase. The subsequent voltammogram analysis was mainly based on previous conclusions relating to (i) the electro-polymerisation of a typical dicarbazole-based monomer (namely 2,6-bis-carbazole-9-yl-hexanoic acid pentafluorophenyl ester)[56,57] and to (ii) the electro-chemical characterisation of the corresponding poly-DiCbz-polymer. In brief, we noted two main peaks in the polymerisation voltammogram appearing at ca. 0.6 V and at ca. 0.9 V. The first peak may be assigned to the oxidation of the deposited conducting polymer (doping process) and the latter to the oxidation of hybrid Cbz/Pyr-monomers to produce the corresponding conducting polymers.[56,58] We noticed that the lower potential peak appeared only on the second scan, while the higher potential peak appeared on the first scan. Moreover, the current of the first peak increased much faster from one scan to another than the current of the second peak. These differences rather emphasized the fact that these two observed peaks arose from different electrochemical processes: oxidation of the deposited polymer (at ca. 0.6 V) and oxidation of the monomers to produce the polymer (at ca. 0.9 V).[56,57] The film characterisation in monomer-free solutions (typical CV, Fig. 1b) strongly resembled the polymerisation voltammograms. This assay showed one broad peak appearing at ca. 0.9 V reflecting the polymer insulator to conductor transformation via a well-known polaron–bipolaron mechanism.[57,59]

Quite interestingly, not all the hybrid Cbz/Pyr-monomers presented the same response during the electro-polymerisation processes according to tested Cbz/Pyr-electro-oxidation windows. When the hybrid monomers Pyr$_1$/Cbz$_2$-**7**, Pyr$_2$/Cbz$_1$-**8**, Pyr$_2$/Cbz$_2$-**11**, Pyr$_1$/Cbz$_1$-**15**, Pyr$_3$/Cbz$_2$-**27** and Pyr$_2$/Cbz$_3$-**28** were subjected to electro-polymerisation individually under a wide electrochemical window covering both the Cbz and Pyr-heterocycle oxidation potential ranges (i.e., -1.0 to 1.1 V), we did not observe any copolymerisation of Pyr and Cbz species in any of the hybrid monomers. The electro-polymerisation features of all Cbz/Pyr-based hybrid monomers are summarised in Table 1.

In conclusion, we have synthesised six novel carboxylated hybrid Cbz/Pyr-based monomers in which the number of Cbz and Pyr unit(s) in each monomer has been tuned systematically for testing their electro-chemical behaviours. All these monomers have been characterised spectroscopically. When these monomers were subjected to electro-polymerisation, we observed that the monomer(s) containing a Cbz-unit/Pyr-unit ratio $\geqslant 1$ successfully produced electro-conductive film(s) on a working Pt electrode. Although the mechanism is not clear to us, it seems that nucleophilic Pyr has a terminating effect on the growth of the corresponding polyCbz conducting film and complete termination/chain growth interruption solely depends on the Cbz-unit/Pyr-unit ratio parameter.

Acknowledgment

This work was funded by the VIth European Framework NACBO project (NMP3-2004-500802-2).

Supplementary data

Supplementary data (synthetic procedures for Cbz- and Pyr-based building blocks/intermediates, characterisation data for all new compounds/intermediates, cyclic voltammograms for the electro-polymerisation of monomers **8**, **11**, **15**, **27** and **28** (1 mm Ø Pt electrode) that include corresponding voltammetric responses of the resulting conducting films in supporting electrolyte (without monomer) and scanned copies of ^{1}H NMR and ^{13}C NMR spectra of all new compounds including intermediates) associated with this article can be found, in the online version, at doi:10.1016/j.tetlet.2011.10.047.

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