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Synthesis and characterization of new carbazole-based materials for optoelectronic applications

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ABSTRACT

New triazolo-carbazole derivatives were synthesized by copper-catalyzed azide–alkyne cycloaddition (CuAAC) reactions. The chemical structures of these compounds were confirmed by NMR and FT-IR spectroscopic analysis. The optical properties of the triazolo-carbazoles were investigated by UV–visible absorption and photoluminescence spectroscopy; an emission in the ultraviolet region was observed. The energy levels of these organic materials were determined by cyclic voltammetry and showed a relatively high electronic affinity indicating that they might be good candidates for electron-injection hole-blocking layers in organic light-emitting diodes.

The chemistry of carbazole and its functionalized derivatives dates back nearly to 100 years.[1–6] Historically, the synthetic applications of these compounds have been rooted primarily in the preparation of alkaloids and other natural products.[1–3] However, renewed interest in photophysical properties of carbazole has led to the incorporation of this moiety into the molecular structure of several π-conjugated organic materials for optoelectronic applications.[4–13] The exploitation of carbazole-based compounds as electron-injection hole-blocking layers in multi-layer organic light-emitting diodes (OLEDs) has been widely reported.[14,15] In fact, such compounds are known to have high electron affinity, thereby reducing the interface barriers caused by the band offset between the organic material and the cathode and contributing to the balance of holes and electron transport.[16,17]

Herein, we report a facile synthesis of four new carbazole-based molecules containing the triazole moiety (**TC1**–**TC4**, Fig. 1), using the Cu-catalyzed azide–alkyne cycloaddition (CuAAC) reaction, commonly known as 'click chemistry'.[14,18]

Four carbazole-based azides (**A1–A4**) were prepared as shown in Scheme 1. To ensure good solubility of the final organic π-conjugated materials, we chose to graft a flexible aliphatic chain onto the carbazole unit. Two types of azide were prepared: the first is linear (**A1** and **A3**), whereas the second consists of dendrimer-type structures (**A2** and **A4**). They were obtained by formylation[19] of alkylated carbazole using the Vilsmeier–Haack reaction followed by reduction,[20] chlorination,[21] and azidation[22] (**A1**–**A4**) (Scheme 1).

The triazolo-carbazoles **TC1**–**TC4** were synthesized by a standard CuAAC reaction procedure.[14,16] Sodium ascorbate and aqueous copper sulfate pentahydrate were added to 9-propargylcarbazole and the corresponding azides (**A1**–**A4**) in THF/H_2O (1:1). The mixture was stirred for 24 h at 60 °C. All the triazolo-carbazoles were obtained in good yields after work-up (Scheme 2).[23]

The optical properties of compounds **TC1**–**TC4** were investigated by UV–vis and photoluminescence (PL) spectroscopy in dilute chloroform solution. The absorption spectra showed similar behavior with two maxima between 327 and 340 nm and a shoulder at about 350 nm (Fig. 2, Table 1). A systematic study of these spectra allowed a comparison of materials in pair, that is, **TC1**/**TC3** and **TC2**/**TC4**. Indeed, we noted that compounds **TC1** and **TC3** (linear type) presented quasi-identical spectra. On the other hand, the comparison of **TC2** and **TC4** (dendrimer-type) revealed broadened spectra and a higher absorption-onset for **TC4**. Thus, **TC4** exhibits a more important effective conjugation length which can be related to privileged intramolecular π–π interactions of the conjugated systems. The same behavior of these materials was observed in PL analysis with identical spectra for **TC1** and **TC3** and a slightly broadened **TC4** spectrum compared to **TC2**. The emissions of **TC1**–**TC4** were in the ultraviolet region, with relatively narrow spectra and consisted of two maxima at approximately 358 and 378 nm (Fig. 3, Table 1).

Cyclic voltammetry (CV) was employed to estimate the HOMO (highest occupied molecular orbital) and LUMO (lowest unoccupied molecular orbital) energy levels of the triazolo-carbazoles. Knowledge of these energy levels is important to determine the energy barriers and to select cathode and anode materials for

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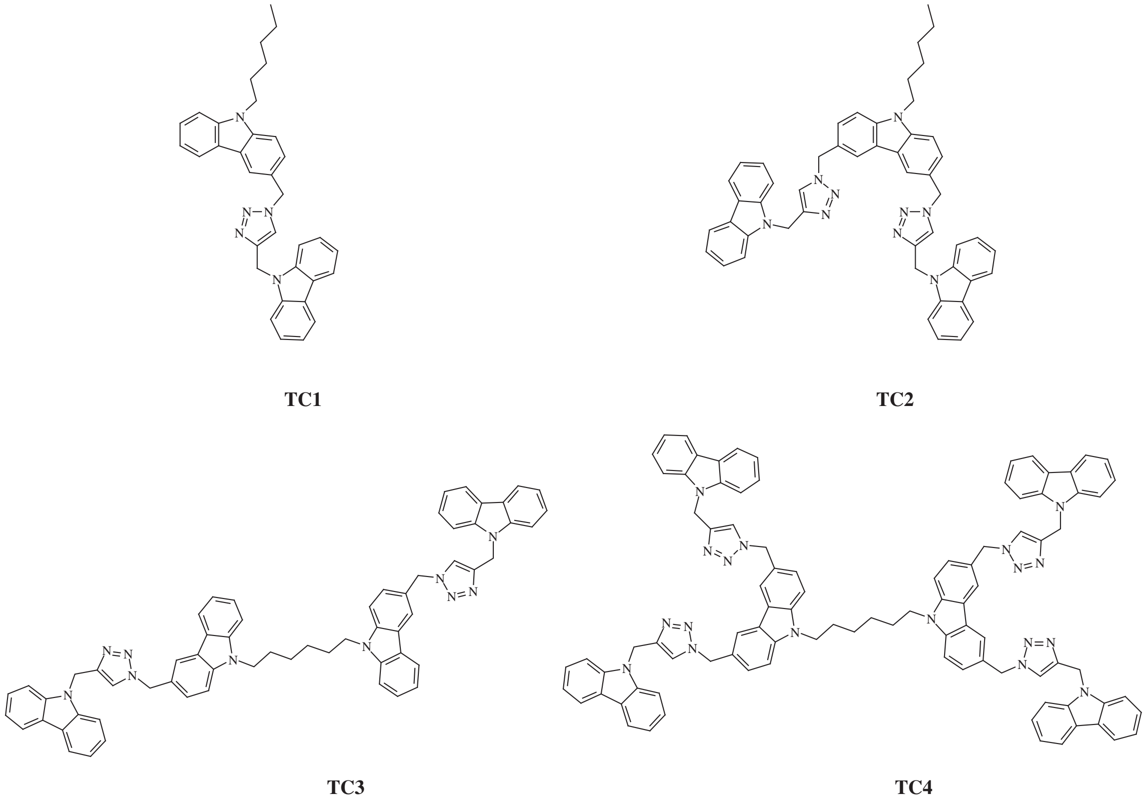
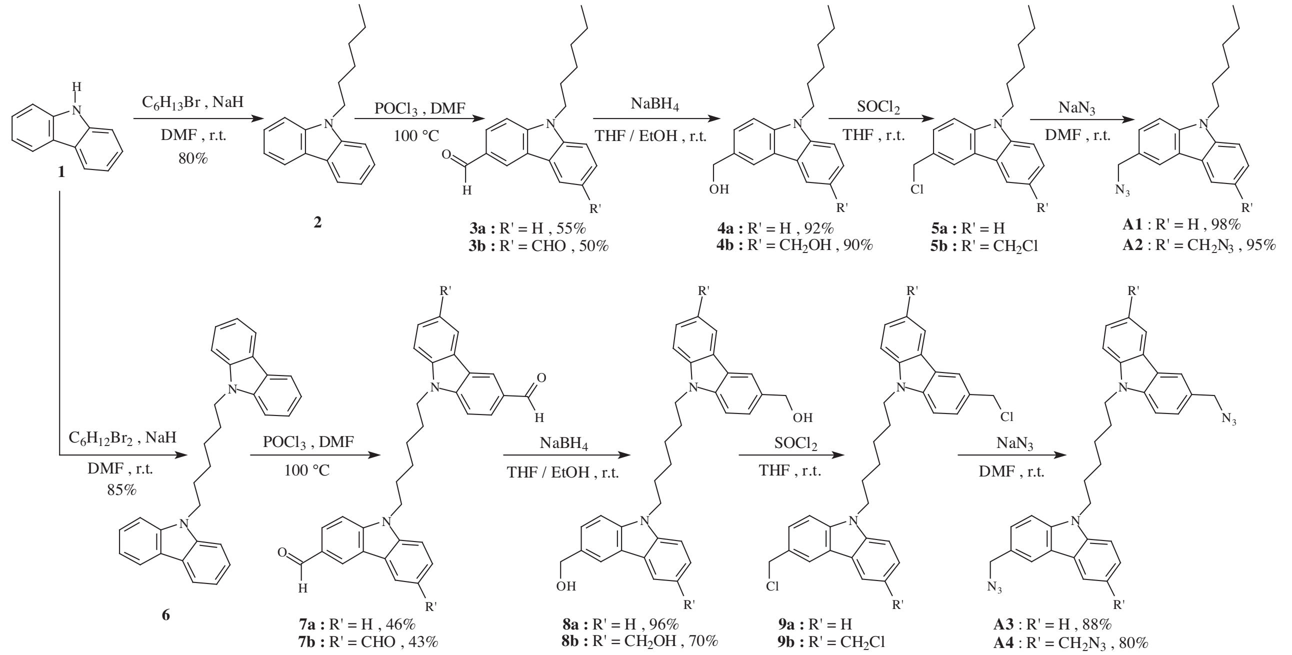


Figure 1. Molecular structures of **TC1–TC4**.



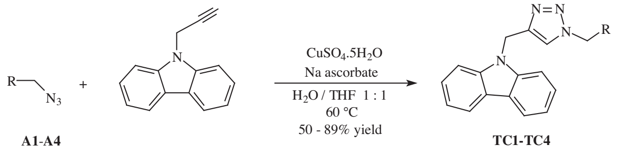
Scheme 1. Synthetic route to **A1–A4**.

OLEDs.[24,25] CV analysis is reliable, as the electrochemical processes are similar to those involved in charge injection and transport processes in such electronic devices.[26,27]

The organic films were drop-coated onto indium-tin oxide (ITO) glass substrates and scanned both at positive and negative potentials in 0.1 M $(n\text{-Bu})_4NBF_4$/acetonitrile solution at a scan rate of 50 mV s^{-1}. According to an empirical method, and by assuming that the energy level of ferrocene/ferrocenium is 4.8 eV below the vacuum level, the HOMO and LUMO energy levels and the electrochemical gap ($E_{\text{g-el}}$) can be calculated as follows:[28,29]

$$E_{\text{HOMO}}\ (\text{IP; ionization potential}) = -(V_{\text{onset-ox}} - V_{\text{FOC}} + 4.8)\ \text{eV}$$

$$E_{\text{LUMO}}\ (\text{EA; electron affinity}) = -(V_{\text{onset-red}} - V_{\text{FOC}} + 4.8)\ \text{eV}$$



Scheme 2. Copper-catalyzed click reactions of azides **A1–A4** with 9-propargylcarbazole.

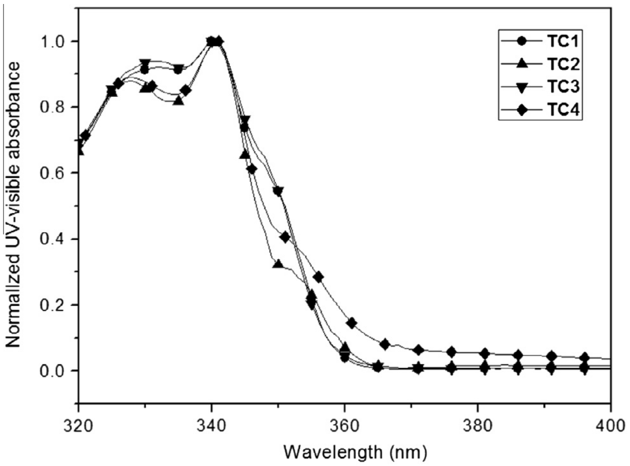


Figure 2. Normalized UV–vis absorption spectra of **TC1–TC4** in dilute chloroform solution (5×10^{-5} mol L^{-1}).

where, V_{FOC} is 0.73 V, the ferrocene half-wave potential measured versus Ag/AgCl, $V_{onset\text{-}ox}$ is the material oxidation onset and $V_{onset\text{-}red}$ is the material reduction onset.

The obtained cyclic voltammogram of **TC4** is shown in Figure 4 as an example, and the estimated E_{HOMO} and E_{LUMO} values of all the products are summarized in Table 2.

A comparison of these compounds revealed that the HOMO energy levels were almost identical (Fig. 5). However, a higher electron affinity was observed for **TC1**. The LUMO levels of these compounds were comparable with that of bathocuproine (BCP). BCP is widely used as an electron-injection hole-blocking layer in OLEDs.[30,31] It prohibits excitons diffusing toward the Al electrode where they would otherwise be quenched.[32] However, it is known that BCP crystallizes quickly, which results in degradation of the device performance.[33,34] For this reason, it is desirable to replace BCP by other materials in such devices. In fact, the fused triazolo-carbazoles **TC1–TC4** might be good replacements for BCP and for the elaboration of multilayer devices.

In summary, we have successfully employed the Cu-catalyzed azide–alkyne cycloaddition (CuAAC) reaction to generate fused triazolo-carbazole derivatives. The structures of the products were confirmed through spectral analysis. Investigations of the optical properties in dilute chloroform solution showed emissions in the ultraviolet region for all products. These new materials show relatively high electron affinity and would appear to be good candidates for electron-injection hole-blocking layers. Work is

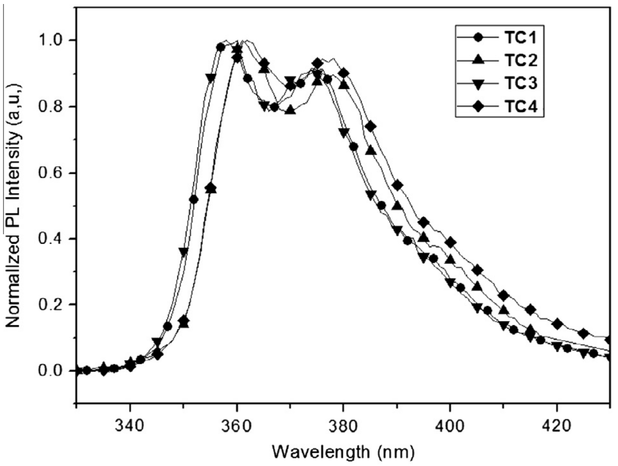


Figure 3. Photoluminescence spectra of **TC1–TC4** in dilute chloroform solution (2×10^{-7} mol L^{-1}).

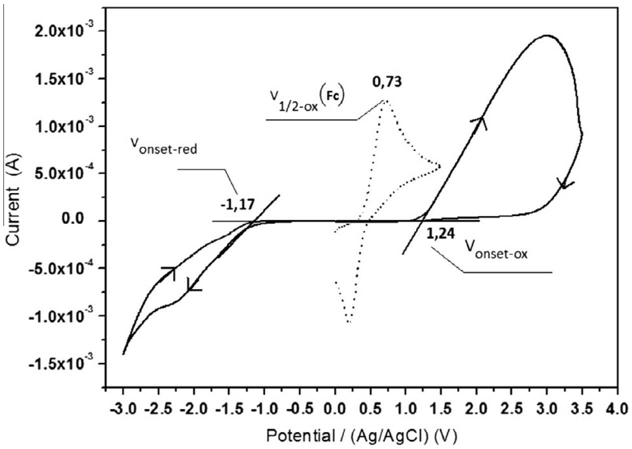


Figure 4. Cyclic voltammogram of **TC4** film coated on an ITO electrode in 0.1 M $(n\text{-Bu})_4NBF_4$/acetonitrile at a scanning rate of 50 mV s^{-1}.

Table 2
Electrochemical data for **TC1–TC4**

	$V_{onset\text{-}ox}$ (V)	$V_{onset\text{-}red}$ (V)	E_{HOMO} (eV)	E_{LUMO} (eV)
TC1	1.19	−1.10	5.26	2.97
TC2	1.16	−1.26	5.23	2.81
TC3	1.15	−1.30	5.22	2.77
TC4	1.24	−1.17	5.31	2.90

Table 1
Optical data for **TC1–TC4** in dilute chloroform solution

	Absorption				Photoluminescence		
	λ_{max} (nm)	ε_{max} (10^4 M^{-1} cm^{-1})	λ_{onset} (nm)	$E_{g\text{-}op}$ (eV)	λ_{max} (nm)	FWHM[b] (nm)	Stokes shift (nm)
TC1	331; 340; 348[a]	0.59; 0.65	358	3.46	358; 374	34.6	18
TC2	327; 340; 352[a]	0.63; 0.74	362	3.42	361; 377	35.8	21
TC3	332; 340; 348[a]	0.98; 1.06	359	3.45	359; 375	36.4	19
TC4	328; 340; 352[a]	2.34; 2.73	366	3.39	362; 378	37.9	22

[a] Shoulder.
[b] Spectrum full width half maximum.

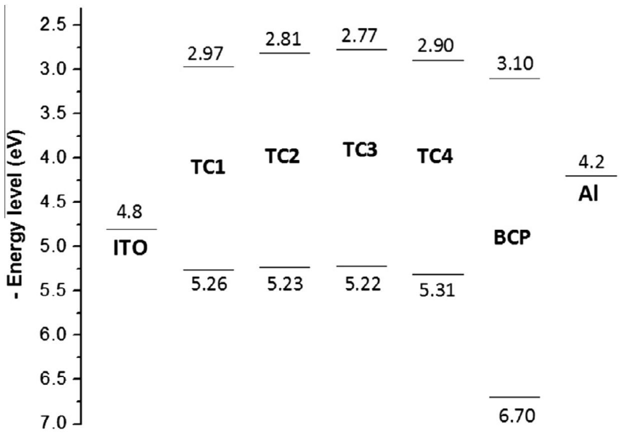


Figure 5. Comparison of the HOMO–LUMO energy levels of **TC1**–**TC4** and those of BCP, ITO, and aluminum.

currently under way toward the application of these materials in multilayer devices.

Acknowledgments

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Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.tetlet.2013.05.091.

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23. *General method for the preparation of triazolo-carbazoles derivatives (**TC1–TC4**):* Sodium ascorbate (0.51 mmol) and $CuSO_4 \cdot 5H_2O$ aqueous solution (0.24 mmol) were added to 9-propargylcarbazole (0.62 mmol equivalent of azido groups) and azide (**A1**–**A4**) (0.62 mmol) in THF (10 mL)/H_2O (10 mL). The mixture was stirred for 24 h at 60 °C. After cooling to room temperature, the solvent was evaporated in vacuo and the residue was diluted with CH_2Cl_2, washed with water and brine, dried over $MgSO_4$ and concentrated. The residue was purified by recrystallization from EtOAc.
*9,9′-Hexane-1,6-diylbis(3,6-bis{[4-(9H-carbazol-9-ylmethyl)-1H-1,2,3-triazol-1-yl]methyl}-9H-carbazole) (**TC4**):* (50%); obtained as a yellow solid; mp: 240 ± 2 °C (EtOAc); ^1H NMR (300 MHz, DMSO-d_6): δ 1.18 (m, H16,16′), 1.55 (m, H15,15′), 4.20 (t, H14,14′, J = 6.9 Hz), 5.61 (s, H10), 5.62 (s, H13), 7.17 (t, H3′,6′, J = 7.2 Hz), 7.32–7.44 (m, H1,8,2,7,2′,7′), 7.72 (d, H1′,8′, J = 8.1 Hz), 8.00 (s, H4,5), 8.06 (s, H11), 8.11 (d, H4′,5′, J = 7.5 Hz); ^{13}C NMR (300 MHz, DMSO-d_6): δ 25.8 (C16,16′), 28.1 (C15,15′), 37.5 (C13), 42.1 (C14,14′), 53.2 (C10), 109.5–143.3 (Caromat.); HRMS Calcd for $C_{94}H_{76}N_{18}$: 1457.6579 $[M+H]^+$; found: 1457.6580 $[M+H]^+$; IR (KBr) cm^{-1}: 745, 1321, 1460, 1481, 2845, 2929, 3051, 3134.
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