

Carbazole-Functionalised Poly(1-phenyl-1-alkyne)s: Synthesis, Light Emission, and Fluorescent Photopatterning

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Carbazole-containing 1-phenyl-1-alkynes with different spacer lengths [$C_6H_5C\equiv C(CH_2)_mCar$ **1**(*m*) (*m* = 3, 4, 9), Car = 9-carbazolyl] were synthesised in high yields by consecutive substitution and coupling reactions of *n*-chloro-1-alkynes. Polymerisation of the monomers was effected by $NbCl_5$ - and WCl_6 - Ph_4Sn catalysts, furnishing soluble polymers **P1**(*m*) with high molecular weights in high yields. All the polymers were thermally stable, commencing to lose their weights at high temperatures ($\geq 400^\circ C$). Photoexcitation of their THF solutions induced strong blue light emissions with high quantum efficiencies up to 92%. Multilayer electroluminescence devices with configurations of ITO/**P1**(*m*):(PVK)/BCP/Alq₃/LiF/Al were constructed, which gave blue light with maximum luminance and external quantum efficiency of 438 cd m⁻² and 0.63%. UV irradiation of a thin film of **P1**(4) through a mask oxidized and quenched the light emission of the exposed parts, generating a two-dimensional luminescent photopattern.

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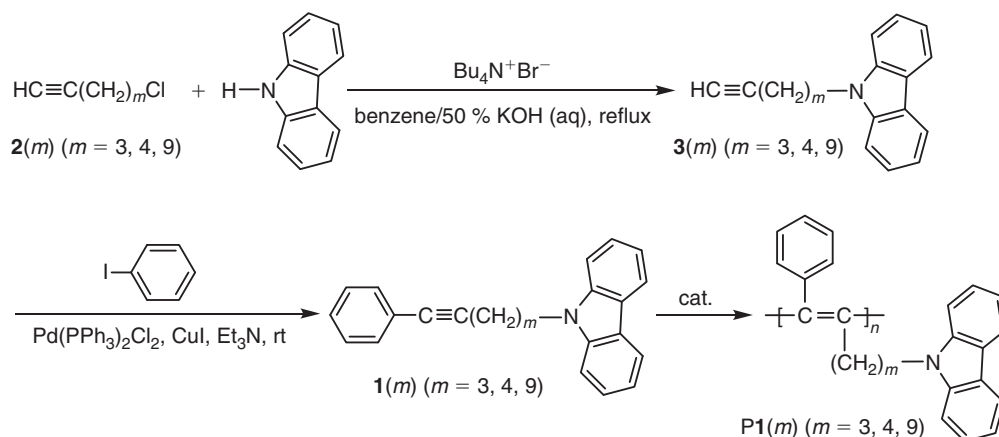
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Introduction

Polyacetylene is a Nobel Prize-winning macromolecule and exhibits a high conductivity upon doping.^[1,2] Its intractability and instability, however, has greatly detracted from its potential for high-technological applications. Replacement of one or two of its hydrogen atoms by appropriate substituent(s) has generated mono- and disubstituted polyacetylenes that show not only better processability and stability but also possess novel properties that are not found in the parent form. Many substituted polyacetylenes prepared so far, however, bear nonpolar alkyl and/or aryl groups.^[3] Introduction of polar functional groups into the polyacetylene structure would further advance polyacetylene research and open up a new avenue in polyacetylene-based speciality materials.^[4]

Carbazole is a well known light-emitting, photoconductive, photorefractive, and hole-transporting material.^[5] Owing to the expectation of generating polymers with unique optoelectronic properties, many groups have attempted to polymerize acetylenes

bearing carbazole moieties.^[6] Most of the efforts, however, have met with only little success. For example, polymerisation of *N*-carbazolylacetylene catalysed by $Fe(acac)_3$ - Et_3Al ^[6a] and 3-(*N*-carbazolyl)-1-propyne in the presence of $Ti(OBu)_4$ - Et_3Al and $WOCl_4$ - Ph_4Sn ^[6b] gave only insoluble polymers and/or oligomers. Masuda found that WCl_6 complexed with *n*- Bu_4Sn worked well for the polymerisation of 3-(9-carbazolyl)-1-propyne^[6c] but the resultant polymer, however, was insoluble. Even when the spacer length in the monomer was lengthened to two or four methylene units, no soluble polymers could be obtained. Because many possible side reactions can be induced by the toxic interaction between the polar nitrogen atom of carbazole and the transition-metal catalysts, synthesis of carbazole-containing polyacetylenes remains largely a challenge.^[7] Our group has also worked on the design and synthesis of polyacetylenes with carbazole pendant groups. Delightfully, when the spacer length in poly[3-(*N*-carbazolyl)-1-propyne] was lengthened to 3 and 9 methylene units, the polymers were readily soluble in common



Scheme 1. Synthesis of carbazole-containing 1-phenyl-1-alkynes and their transformation into polymers.

organic solvents.^[8] We studied their light-emitting properties and found that they emitted intense UV light upon photoexcitation. The polymers were also photoconductive with photosensitivity much better than poly(9-vinylcarbazole), the best-known photoconducting vinyl polymer.^[9] The carbazole-containing polyacetylenes are thus a group of new polymers with novel material properties and further investigation in this area should lead to more fruitful results.

In this paper, we report the synthesis and properties of a group of disubstituted polyacetylenes bearing carbazole appendages of varying spacer lengths [**P1(m)**; Scheme 1]. While **P1(3)** and **P1(9)** are newly prepared, the photo- (PL) and electroluminescence (EL) of **P1(4)** have been briefly discussed in our previous short review.^[10] Details about its preparation and functional properties, however, have not been presented. We would like to give a complete discussion on these, and compare with those of **P1(3)** and **P1(9)** in this paper.

Results and Discussion

Monomer Synthesis

We designed the molecular structures of three chromophore-containing 1-phenyl-1-alkynes and elaborated a two-step reaction route for their synthesis. We first attached carbazole to the acetylene structure through the nitrogen atom by reaction of *n*-chloro-1-alkynes with carbazole, catalysed by tetrabutylammonium bromide (Scheme 1). The obtained products **3(m)** were then further coupled with iodobenzene, giving the desired monomers **1(m)** in high yields (85–97%) after purification by column chromatography. It is noteworthy that **3(m)** could be prepared also by lithiation of carbazole followed by subsequent reaction with *n*-chloro-1-alkynes.^[6c,8] The isolated yields (~70%), however, were much lower than those achieved by the present method, regardless of its more complicated procedure. While **1(3)** and **1(4)** were pale yellow solids, **1(9)** was a yellow viscous liquid. All the monomers were characterised by standard spectroscopic methods and elemental analyses, and all gave satisfactory data corresponding to their structures (see data given in the Experimental Section and spectra provided in the Supplementary Material).

Polymerisation by Metathesis Catalysts

Since NbCl₅- and TaCl₅-Ph₄Sn were effective catalysts for the polymerisation of 1-phenyl-1-alkynes^[11] and 1-(*p*-9-carbazolylphenyl)-2-phenylacetylene,^[6d] we thus tried whether

Table 1. Polymerisation of 5-(9-carbazolyl)-1-phenyl-1-pentyne [**1(3)**]^A

No.	Catalyst	Temp [°C]	Yield [%]	M_w^B	M_w/M_n^B
1	NbCl ₅ -Ph ₄ Sn	60	4.6	16100	2.3
2	TaCl ₅ -Ph ₄ Sn	60	Trace		
3	WCl ₆ -Ph ₄ Sn	rt	8.3	5800	1.9
4	WCl ₆ -Ph ₄ Sn	60	79.3	43000	2.2
5	WCl ₆ -Ph ₄ Sn	80	92.8	40400	3.1
6	MoCl ₅ -Ph ₄ Sn	60	0		

^ACarried out under nitrogen in toluene for 24 h; [M]₀ = 0.2 M, [cat.] = [cocat.] = 10 mM.

^BDetermined by GPC in THF on the basis of a polystyrene calibration.

they were also capable of polymerising **1(3)**. Polymerisation catalysed by NbCl₅-Ph₄Sn in toluene at 60°C, however, gave a polymer in a low yield (Table 1, no. 1). The catalytic activity of TaCl₅-Ph₄Sn was even lower and no polymeric product was isolated at all. Clearly, the catalysts are sensitive to the polar nitrogen atom of the carbazole moiety. Disappointed by the results, we thus checked whether there is any hope for the monomer to be polymerised by early-transition-metal halides. Whereas the reaction with the WCl₆-Ph₄Sn catalyst at room temperature gave a low molecular weight polymer in a low yield, the molecular weight and yield were dramatically boosted when the temperature was raised to 60°C. Further increment of the temperature to 80°C resulted in a much better result: a high molecular weight, yellow powdery polymer was isolated in nearly quantitative yield. In sharp contrast, MoCl₅-Ph₄Sn was inert for the polymerisation.

Similar to the results of **1(3)**, **1(4)** could be polymerised by NbCl₅-Ph₄Sn albeit in a low yield, TaCl₅-Ph₄Sn was again ineffective for the polymerisation (Table 2, no. 1 and 2). Delightfully, WCl₆-Ph₄Sn performed well for the polymerisation at 60°C, producing a polymer with a high molecular weight in over 80% yield. However, polymerisation carried out at 80°C gave a polymer in much lower yield and molecular weight. It should be stressed here that the result for the polymerisation of **1(4)** catalysed by WCl₆-Ph₄Sn is truly amazing. WCl₆-Ph₄Sn had been found to initiate the polymerisation of 6-(9-carbazolyl)-1-hexyne^[6c] and 1-phenyl-1-hexyne,^[11d] a mono-substituted cousin and parent form of **1(4)**, but none of the resultant polymers were soluble. Polymer **P1(4)** prepared by the

Table 2. Polymerisation of 6-(9-carbazolyl)-1-phenyl-1-hexyne **1(4)**^A

No.	Catalyst	Temp [°C]	Yield [%]	M_w^B	M_w/M_n^B
1	NbCl ₅ -Ph ₄ Sn	60	14.2	11200	3.3
2	TaCl ₅ -Ph ₄ Sn	60	Trace		
3	WCl ₆ -Ph ₄ Sn	rt	Trace		
4	WCl ₆ -Ph ₄ Sn	60	81.1	58100	3.3
5	WCl ₆ -Ph ₄ Sn	80	41.6	16500	2.1
6	MoCl ₅ -Ph ₄ Sn	60	0		

^ACarried out under nitrogen in toluene for 24 h; [M]₀ = 0.2 M, [cat.] = [cocat.] = 10 mM.

^BDetermined by GPC in THF on the basis of a polystyrene calibration.

Table 3. Polymerisation of 11-(9-carbazolyl)-1-phenyl-1-undecyne **1(9)**^A

No.	Catalyst	Temp [°C]	Yield [%]	M_w^B	M_w/M_n^B
1	NbCl ₅ -Ph ₄ Sn	60	Trace		
2	TaCl ₅ -Ph ₄ Sn	60	0		
3	WCl ₆ -Ph ₄ Sn	rt	61.5	107200	2.8
4	WCl ₆ -Ph ₄ Sn	60	99.1	181800	5.0
5	WCl ₆ -Ph ₄ Sn	80	82.5	105000	2.8
6	MoCl ₅ -Ph ₄ Sn	60	Trace		

^ACarried out under nitrogen in toluene for 24 h; [M]₀ = 0.2 M, [cat.] = [cocat.] = 10 mM.

^BDetermined by GPC in THF on the basis of a polystyrene calibration.

same catalyst, however, was completely soluble and possessed a high molecular weight, allowing us to investigate its properties by 'wet' spectroscopic methods. Attempts to polymerize **1(4)** by MoCl₅-Ph₄Sn also ended up in disappointment.

Unlike **1(3)** and **1(4)**, **1(9)** underwent sluggish polymerisation in the presence of NbCl₅-Ph₄Sn catalyst (Table 3, no. 1). TaCl₅-Ph₄Sn also failed to polymerise the monomer because **1(9)** shared a common structural feature with **1(3)** and **1(4)**: it possessed a polar functional pendant group. Whereas reactions of **1(3)** and **1(4)** catalysed by WCl₆-Ph₄Sn at room temperature gave only a trace amount of polymeric product, stirring a toluene solution of **1(9)** under the same conditions, surprisingly, produced a high molecular weight polymer in a high yield. The polymerisation proceeded much better at elevated temperatures and the highest molecular weight and yield obtained were $1.8 \times 10^5 \text{ g mol}^{-1}$ and 99%, respectively. MoCl₅-Ph₄Sn, in contrast, failed to produce any polymeric product.

Structural Characterisation by Spectroscopic Methods

The molecular structures of the polymers were characterised by spectroscopic methods with satisfactory results. An example of the ¹H NMR spectra of **P1(9)** and its monomer **1(9)** is given in Fig. 1. The phenyl acetylene protons of **1(9)** absorbed at $\sim\delta$ 7.37 and 7.24, which shifted to δ 6.80 after the polymerisation. The peak was broad because the phenyl protons were attached to a stiff polyacetylene structure, whose motion was limited by the backbone. Similarly, the resonance of the methylene protons next to the triple bond of **1(9)** also became much broader in the polymer. No other unexpected signals were found and all the absorptions peaks could be readily assigned, suggesting that the polymeric product was indeed **P1(9)** with a molecular structure as shown in the inset of Fig. 1b.

Fig. 2 shows the ¹³C NMR spectra of **1(9)** and **P1(9)** in CDCl₃. The spectrum of **P1(9)** displayed no acetylene carbon resonances of **1(9)** at δ 90.4 and 80.6. It also exhibited no phenyl and methylene acetylene carbon absorptions due to their transformations to the styrene and allylic structures in the polymer. The olefin backbone absorptions, however, were hard to distinguish, possibly due to overlap with the carbon resonances of the carbazole pendant.

Thermal Stability and Electronic Absorption

As stated in the introduction, unsubstituted polyacetylene has found little technological applications owing to its low thermal stability. Its derivatives with appropriate substituents, however, are thermally much more stable. For example, the 5% weight loss for poly(1-phenyl-1-propyne) occurs at 330°C.^[12] As shown in Fig. 3, our polymers showed greater thermal stability in the thermogravimetric analysis, with higher degradation temperatures ($\geq 400^\circ\text{C}$). Clearly, this is due to the presence of the carbazole pendant, which may wrap the polyacetylene backbone and thus protect it from thermal degradation.^[13] Polymers with longer spacer lengths degraded readily at lower temperatures. This is understandable because of the plasticising effect of the alkyl spacer, which allows the polymers to melt at relatively low temperatures.

The absorption spectrum of **P1(3)** in THF is shown in Fig. 4. Whereas **1(3)** absorbed no photons with wavelengths longer than 340 nm, the spectrum of **P1(3)** was well extended to the visible spectral region. Certainly, the absorptions at the longer wavelengths are obviously from the double-bond backbone of the polymer. The spacer length had little effect on the ground-state electronic transitions: the UV spectra of **P1(4)** and **P1(9)** were almost identical to that of **P1(3)**.

Photoluminescence

Previous studies show that the PL properties of polyacetylenes were sensitive to their molecular structures.^[14,15] For example, poly(phenylacetylene)s were incapable of emitting light but their disubstituted cousins such as poly(1-phenyl-1-alkyne)s (PPAs) and poly(diphenylacetylene)s were strong emitters. Being derivatives of PPAs, **P1(m)** were also anticipated to emit intensely upon photoexcitation. Fig. 5a shows the PL spectra of **P1(m)** in THF. When the THF solution of **P1(3)** was UV-irradiated, it emitted a strong blue light of 448 nm, whose intensity was more than three-fold higher than that of poly(1-phenyl-1-octyne) (PPO) under the same measurable conditions. The fluorescence quantum efficiency ($\Phi_F = 80\%$) calculated using 9,10-diphenylanthracene ($\Phi_F = 90\%$ in cyclohexane) as standard was also much higher than that of PPO ($\Phi_F = 43\%$), revealing that the optical properties of polyacetylenes can be readily manipulated by molecular engineering, and the incorporation of chromophoric units into the PAA structure has resulted in polymers with stronger and more efficient emissions. The bulky carbazole pendant may have better alleviated the interaction between the polymer chains. The excitons are thus likely to be confined in the isolated polymer chain and their chances to recombine radiatively are increased. Moreover, as the PL spectrum of carbazole overlaps with the absorption spectrum of the polyacetylene backbone, the light emitted by the former at ~ 370 nm is absorbed by the latter, which pumps it to its excited state. When the excitons decay back to their ground state, a strong, blue light is emitted from the polymer chain. Polymers **P1(4)** and **P1(9)** emitted at similar wavelengths with

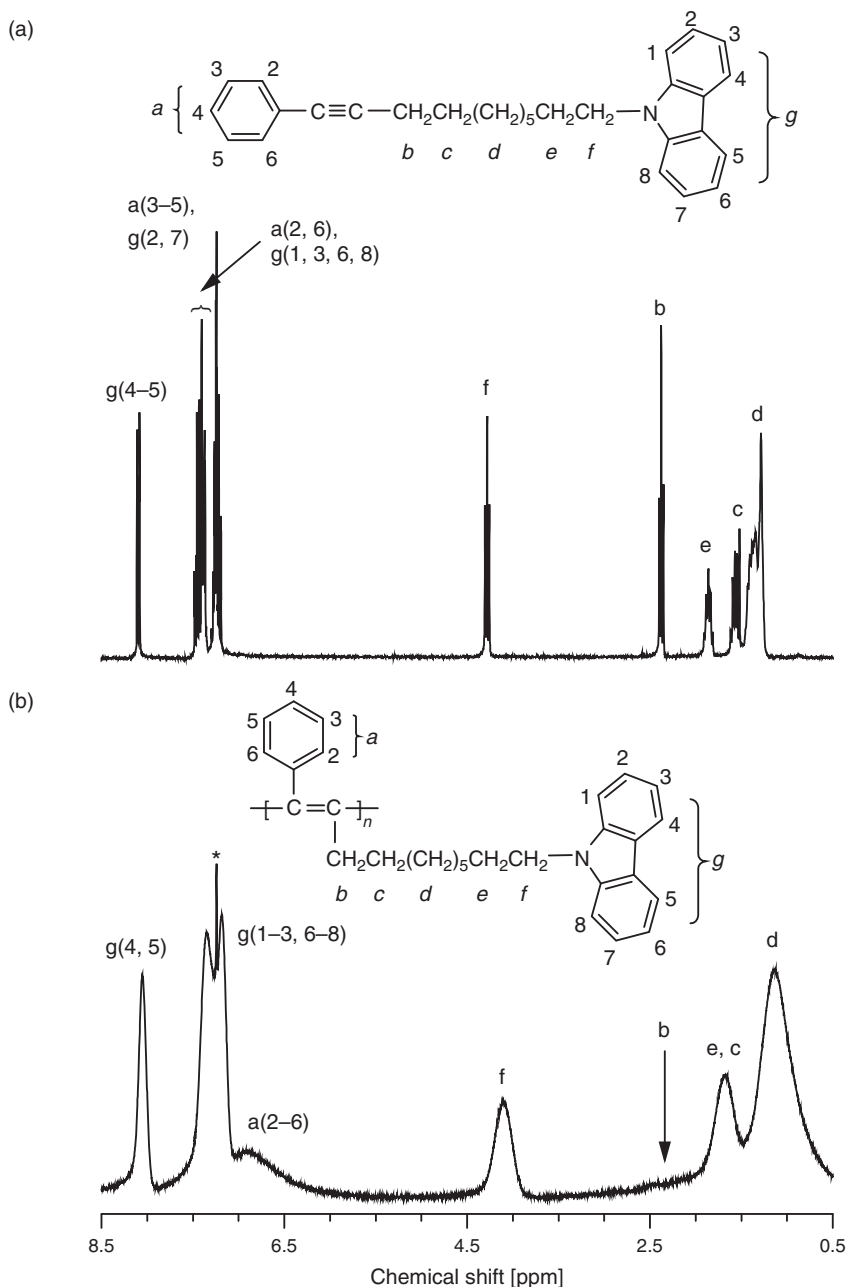


Fig. 1. ¹H NMR spectra of CDCl₃ solutions of (a) **1(9)** and (b) its polymer **P1(9)** (sample from Table 3, no. 4). The solvent peak is marked with an asterisk.

higher Φ_F values, in agreement with the previous observations that longer spacer length favours stronger PL and EL in PPAs.^[16]

Electroluminescence

Electroluminescence from PPO have been studied in the late 90s but only light of low luminance (0.5 cd m^{-2}) and efficiency (0.01 %) was observed.^[16a,16c] Since **P1(m)** are stronger PL emitters than PPO, they were expected to show better device performance. Since there is better efficiency in multilayer devices compared with single-layer devices, we studied the EL of **P1(m)** by fabrication of multilayer devices with a configuration of ITO/**P1(m)**/BCP/Alq₃/LiF/Al. All the polymers emitted blue EL of 488 nm (Fig. 5b). The spectral patterns resembled

those of the PL spectra, confirming that the EL emissions were truly from the polymer emitting layer and that the excimer emissions were unlikely involved in the EL process.

The change in the current density with the applied voltage of the EL devices is shown in Fig. 6a. The current flowing through the EL device of **P1(3)** was low until its turn-on voltage (13 V) was reached. Afterwards, it increased exponentially. Unlike in **P1(3)**, the current density in the EL devices of **P1(4)** and **P1(9)** remained low even at high voltage, presumably due to the lower mobility of the charge carriers in their longer, insulating alkyl chains. The light emitted from **P1(3)** was also weak at low voltage but became stronger when the voltage exceeded 19 V (Fig. 6b). The luminance reached its maximum value of 438 cd m^{-2} at 26 V, which was bright enough for a flat panel

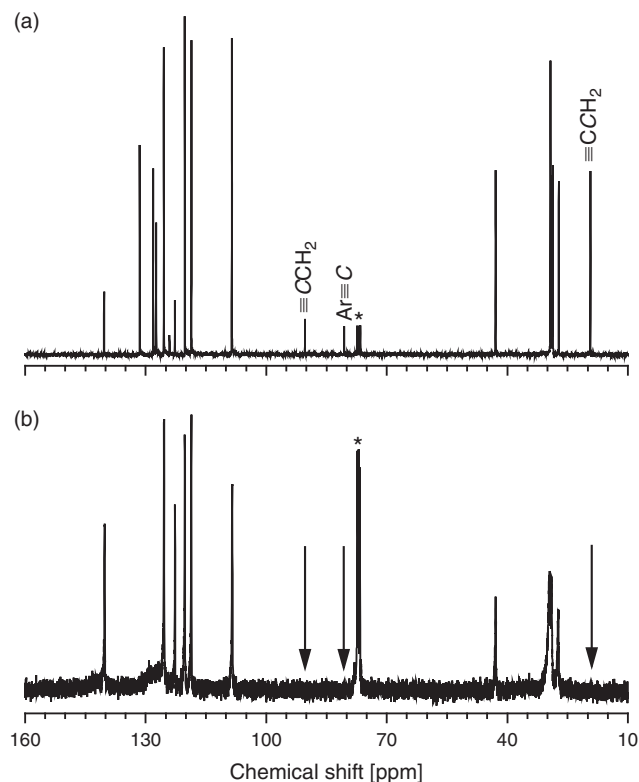


Fig. 2. ^{13}C NMR spectra of CDCl_3 solutions of (a) **1(9)** and (b) its polymer **P1(9)** (sample from Table 3, no. 4). The solvent peaks are marked with asterisks.

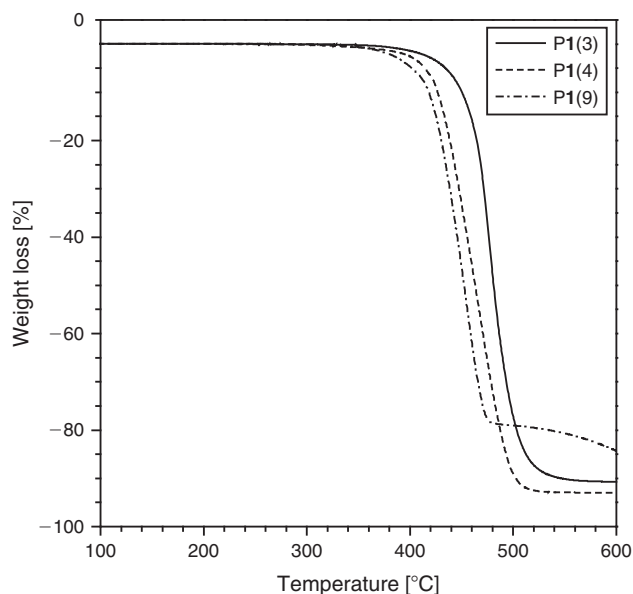


Fig. 3. TGA thermograms of **P1(3)** (sample from Table 1, no. 4), **P1(4)** (Table 2, no. 4), and **P1(9)** (Table 3, no. 4) recorded under nitrogen at a heating rate of $20^{\circ}\text{C min}^{-1}$.

display. Since no light was emitted from PPO using the same device configuration, the strong EL intensity observed in **P1(3)** was probably due to its unique molecular structure, which well matched the band gaps of the electrodes. The luminance, however, decreased upon further increment of the applied voltage because of the destruction of the EL device by the large

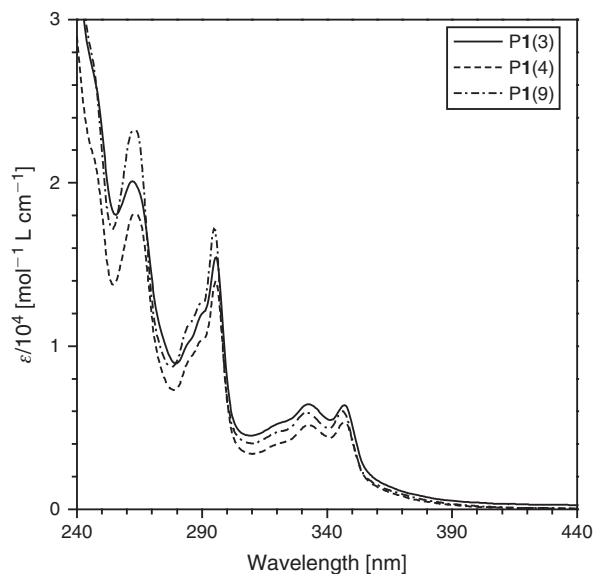


Fig. 4. UV spectra of THF solutions of **P1(3)** (sample from Table 1, no. 4), **P1(4)** (Table 2, no. 4), and **P1(9)** (Table 3, no. 4).

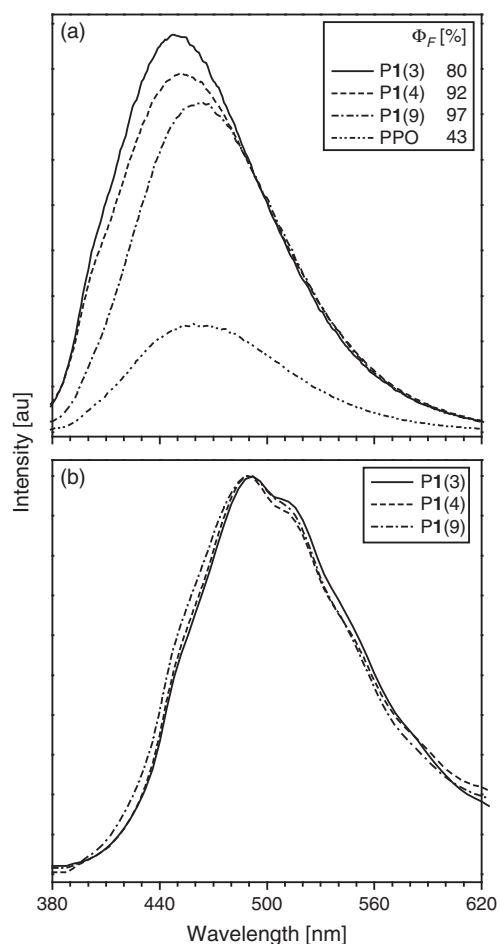


Fig. 5. (a) PL spectra of THF solutions of **P1(3)** (sample from Table 1, no. 4), **P1(4)** (Table 2, no. 4), **P1(9)** (Table 3, no. 4), and poly(1-phenyl-1-octyne) (PPO). Concentration: 0.05 mM, excitation wavelengths (nm): 370 [**P1(3)**, **P1(4)**, and **P1(9)**] and 355 (PPO). (b) EL spectra of multilayer devices of **P1(3)** (sample from Table 1, no. 4), **P1(4)** (Table 2, no. 4), and **P1(9)** (Table 3, no. 4). Device configuration: ITO/**P1(m)**/BCP (20 nm)/Alq₃ (30 nm)/LiF (0.8 nm)/Al.

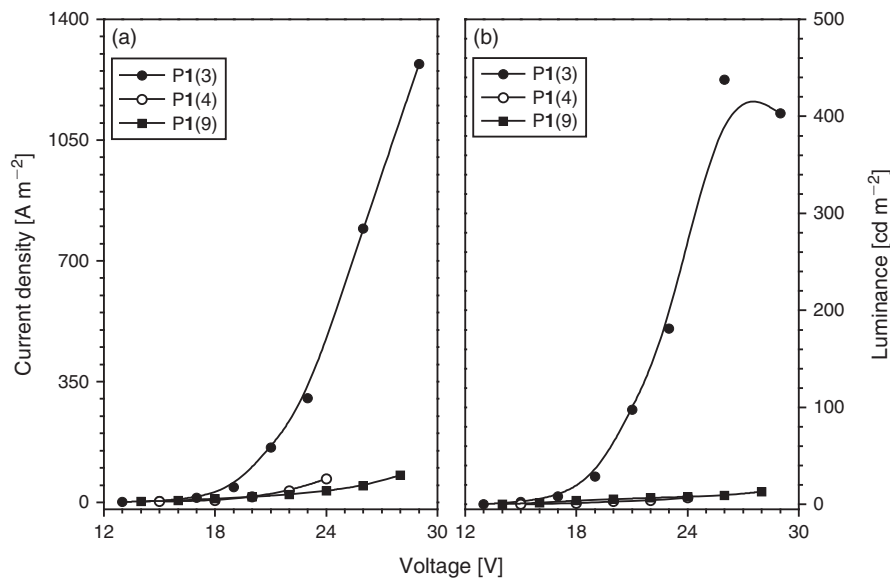


Fig. 6. (a) Current density and (b) luminance versus voltage curves in multilayer EL devices of $\text{P1}(m)$ with a device configuration of ITO/ $\text{P1}(m)$ /BCP (20 nm)/ Alq_3 (30 nm)/LiF (0.8 nm)/Al.

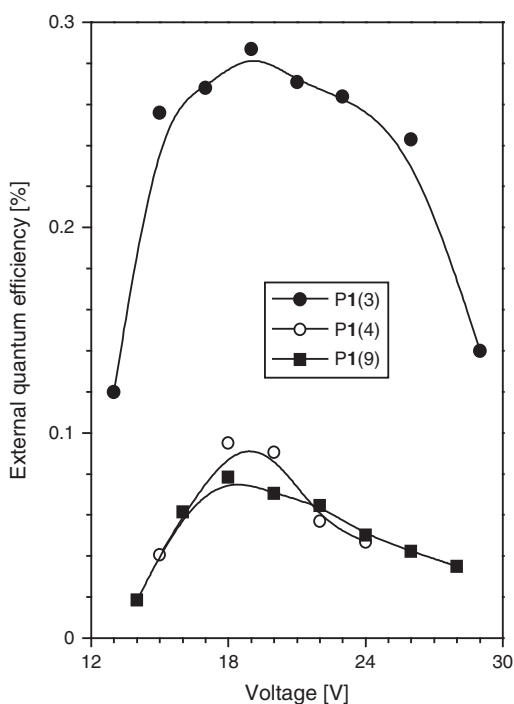


Fig. 7. External quantum efficiency versus voltage curves in multilayer EL devices of $\text{P1}(m)$ with a device configuration of ITO/ $\text{P1}(m)$ /BCP (20 nm)/ Alq_3 (30 nm)/LiF (0.8 nm)/Al.

injection current. The low current density in the EL devices of $\text{P1}(4)$ and $\text{P1}(9)$ also resulted in weak EL emissions: the luminance from $\text{P1}(4)$ and $\text{P1}(9)$ was merely 7 and 13 cd m^{-2} , respectively.

Fig. 7 shows the external quantum efficiency versus voltage curves in EL devices of the polymers. The external quantum efficiency of the $\text{P1}(3)$ -based device increased with increasing applied voltage and reached its maximum value of 0.29% at 19 V. When the voltage was further increased, the efficiency, however, became lower. Lengthening the spacer length in the

polymer led to poorer device performance: the EL efficiencies of $\text{P1}(4)$ and $\text{P1}(9)$ were 2.9 and 1.7-folds lower than that of $\text{P1}(3)$.

The device performances of $\text{P1}(m)$ are clearly better than the previous results but there is still much room for improvement. In our recent study, we found that the EL efficiency of chromophore-containing PPAs could be largely enhanced by doping with poly(9-vinylcarbazole) (PVK).^[17] Would similar EL enhancement be observed in $\text{P1}(m)$? To address this question, we constructed three new EL devices using blends of $\text{P1}(m)$ and PVK at weight ratio of 1 : 4 as the emitting layers.^[17a]

Table 4 summarises the device performances of the polymer blends. All the EL devices started to emit at lower voltages. Clearly, the addition of PVK improved hole transportation, which in turn enhanced the recombination of holes and electrons. The EL efficiency of polymers $\text{P1}(3)$ and $\text{P1}(4)$ was greatly enhanced, whereas $\text{P1}(9)$ remained constant. The external quantum efficiency of an EL device of doped $\text{P1}(3)$ was 0.63%, which was more than two-fold higher than the undoped one. The extent of enhancement was even higher in $\text{P1}(4)$, with the external quantum efficiency of the polymer blend being four times higher than the pure polymer. It is noteworthy that the emissions from the PVK-doped polymers were all 20 nm blue-shifted from those of the pure polymers (Fig. 8). The exact reason remains unclear at present but as the EL spectrum of PVK is peaked at 440 nm, the electronic perturbation of PVK on the optical properties of $\text{P1}(m)$ should be, in most cases, responsible for such phenomenon.

Fluorescent Photopatterning

When PPAs are irradiated by UV light in air, their emissions are quenched due to photooxidation of the polymer chains. Since our polymers are also light-emissive, we thus explored their potential use in PL imaging. The polymers can form uniform, tough films by solution spin-coating. UV irradiation of a thin film of $\text{P1}(4)$ through a copper mask bleached the exposed regions, while the unexposed parts remained emissive. A photopattern was thus generated without performing the development process (Fig. 9).

Table 4. Performances of EL devices of pure and PVK-doped P1(*m*)^A

Polymer ^B	λ_{\max} [nm]	V_{on} [V]	L_{\max} [cd m^{-2}]	CE_{\max} [cd A^{-1}]	PW_{\max} [lm W^{-1}]	QE_{\max} [%]
P1(3)	492	13	438	0.65	0.12	0.29
P1(4)	488	15	7	0.21	0.04	0.10
P1(9)	492	14	13	0.37	0.06	0.17
P1(3):PVK	460	9	72	0.76	0.23	0.63
P1(4):PVK	468	11	314	0.49	0.14	0.40
P1(9):PVK	468	10	219	0.20	0.06	0.18

^ADevice configuration: ITO/P1(*m*):PVK/BCP (20 nm)/Alq₃ (30 nm)/LiF (0.8 nm)/Al. Abbreviation: λ_{\max} = emission maximum, V_{on} = turn-on voltage, L_{\max} = maximum luminance, CE_{\max} = maximum current efficiency, PW_{\max} = maximum power efficiency, QE_{\max} = maximum external quantum efficiency.

^BPure P1(*m*) or their blends with PVK (1 : 4 by weight) were used as emitting layers.

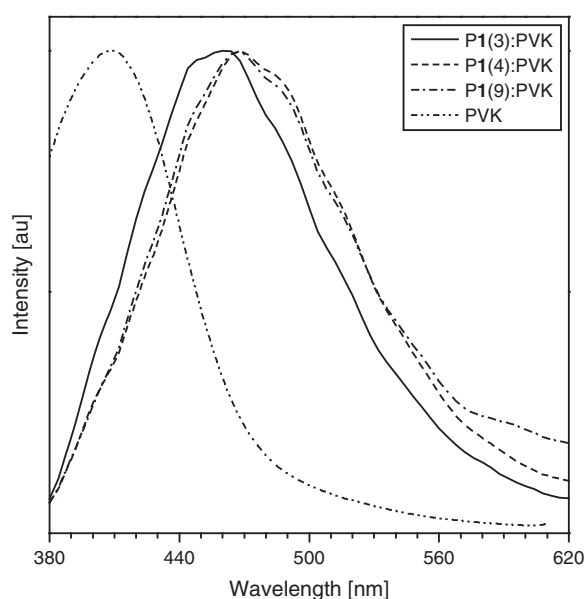


Fig. 8. EL spectra of PVK and multilayer devices of PVK-doped P1(3) (sample from Table 1, no. 4), P1(4) (Table 2, no. 4), and P1(9) (Table 3, no. 4). Device configuration: ITO/P1(*m*):PVK/BCP (20 nm)/Alq₃ (30 nm)/LiF (0.8 nm)/Al.

Conclusions

In this work, carbazole-containing PPAs with different spacer lengths were synthesised and the effect of the chromophoric unit on the optical properties of the polymers was investigated. The findings can be summarised as follows: (1) The monomers were prepared in high yields by consecutive substitution and coupling reactions of *n*-chloro-1-alkynes. Their polymerisation was effected by NbCl₅- and WCl₆-Ph₄Sn, giving high molecular weight (M_w up to 1.8×10^5) polymers in high yields (isolation yield up to 99%). (2) All the polymers possessed high thermal stability and degraded at high temperatures ($\geq 400^\circ\text{C}$), due to the protective jacket effect contributed by the phenyl and carbazole pendants. (3) The polymers emitted strong blue light of ~ 450 nm in THF solutions with high quantum efficiencies up to 92%. (4) Multilayer EL devices with configurations of ITO/P1(*m*):PVK/BCP/Alq₃/LiF/Al were constructed, which gave blue light with maximum luminance and external quantum efficiency of 438 cd m^{-2} and 0.63%. (5) The polymers were photosensitive and UV irradiation of their thin films through copper masks oxidized and quenched the light emission of the exposed parts, generating two-dimensional luminescent photopatterns.

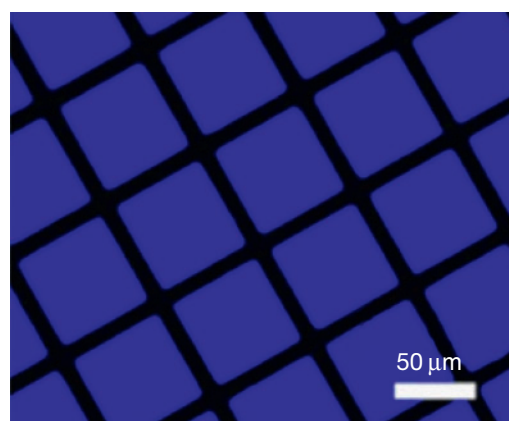


Fig. 9. Two-dimensional photopattern generated by photooxidation of P1(4) film in air at room temperature for 5 min. The photograph was taken under UV illumination.

Poly(*p*-phenylene),^[18] poly(alkylfluorene),^[19] and poly(*p*-phenylene vinylene) derivatives^[20] are well known blue light-emitting polymers. Although intense blue PL has been observed in PPO, it, however, shows an inferior EL performance. Our work presented here shows that by engineering of the molecular structures of the polymers and optimization of the EL configurations, disubstituted polyacetylenes can emit strong EL in high efficiency and are promising light-emitting materials.

Experimental

Materials

Toluene (BDH) was pre-dried over 4 Å molecular sieves and distilled from sodium benzophenone ketyl immediately before use. Dichlorobis(triphenylphosphine)palladium(II), copper(I) iodide, carbazole, 5-chloro-1-pentyne **2** ($m = 3$), 6-chloro-1-hexyne **2** ($m = 4$), iodobenzene, tungsten(VI) chloride, tantalum(V) chloride, niobium(V) chloride, tetraphenyltin, poly(9-vinylcarbazole) (PVK), tris(8-hydroxyquinolinolato) aluminium (Alq₃), and 2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline were purchased from Aldrich and used without further purification. Molybdenum(V) chloride was purchased from Acros. Acetylene 11-chloro-1-undecyne **2** ($m = 9$) was prepared by reaction of 11-undecyn-1-ol with thionyl chloride.

Instruments

The mass spectra were recorded on a Finnigan TSQ 7000 triple quadrupole mass spectrometer operating in a chemical ionization (CI) mode using methane as carrier gas. Elemental analysis

was performed on a ThermoFinnigan Flash EA1112. The molecular weights of the polymers were estimated by a Waters Associates GPC system using a set of monodisperse polystyrene standards for the molecular weight calibration. The ^1H and ^{13}C NMR spectra were measured on a Bruker ARX 300 NMR spectrometer. The thermal stability of the polymers was evaluated on a Perkin Elmer TGA 7 under dry nitrogen at a heating rate of $20^\circ\text{C min}^{-1}$. The UV spectra were measured on a Milton Roy Spectronic 3000 Array spectrophotometer. The PL spectra of the polymers in THF were recorded on a Perkin-Elmer LC 5 luminescence spectrofluorometer. EL spectra were obtained on a Kollmorgen Instrument PR650 photo-spectrometer. The luminescence area was 12.6 mm^2 . Current-voltage characteristics were obtained using a Hewlett-Packard HP4145B Semiconductor Analyzer.

PL Quantum Yield

The PL quantum yields of the polymers in THF solutions were estimated by the literature method^[21] using 9,10-diphenylanthracene as reference.

Fabrication of EL Devices

Multilayer EL devices were prepared by spin-coating toluene solutions of **P1(m)** or their blends with PVK (1 : 4 by weight) onto ITO glass.^[17a] The thickness of thin films of **P1(3)**, **P1(4)**, and **P1(9)** were 75, 65, and 66 nm, respectively while those of the PVK-doped films were all 60 nm. BCP (hole-block layer; 20 nm), Alq_3 (electron-transport layer; 30 nm), LiF (electron-injection layer; 0.8 nm), and Al were in turn deposited under vacuum (2×10^{-6} Torr).

Photopatterning

Photooxidation of the film of **P1(4)** was conducted in air at room temperature using 365 nm light obtained from a Spectroline ENF-280C/F UV lamp (diameter = 5 cm) at a distance of 1 cm as light source. The intensity of the incident light was $\sim 18.5\text{ mW cm}^{-2}$. The film was prepared by spin coating the polymer solution (5 mg mL^{-1} in 1,2-dichloroethane) at 1000 rpm for 1 min on a silicon wafer, and was dried under vacuum at 40°C for 1 h. The photopattern was then generated using procedures as described in our previous paper.^[17c]

Monomer Synthesis

The carbazole-containing 1-phenyl-1-alkynes **1(m)** were prepared by substitution and coupling reactions of *n*-chloro-1-alkynes. Typical procedures for the synthesis of the monomers are as follows:

5-(9-Carbazolyl)-1-Pentyne [**3(3)**]

To a mixture of carbazole (2.0 g, 12.0 mmol) and a catalytic amount of tetrabutylammonium bromide in 30 mL of benzene and 30 mL of 50% aqueous KOH, was added 5-chloro-1-pentyne (1.0 g, 9.8 mmol). The reaction mixture was refluxed for 12 h. The crude product was extracted with chloroform and purified by silica-gel column chromatography using hexane/chloroform mixture (4 : 1 by volume) as eluent. A pale yellow solid was isolated in 88.0% yield (2.0 g). 6-(9-Carbazolyl)-1-hexyne [**3(4)**] and 11-(9-carbazolyl)-1-undecyne [**3(9)**] were prepared in a similar fashion and obtained as yellow solids in 84.7 and 93.7% yields, respectively.

5-(9-Carbazolyl)-1-Phenyl-1-Pentyne [**1(3)**]

Compound **1(3)** was prepared by Pd-catalysed coupling of **3(3)** (1.7 g, 7.2 mmol) with iodobenzene (1.8 g, 8.9 mmol) in the presence of $\text{Pd}(\text{PPh}_3)_2\text{Cl}_2$ (0.1 g, 0.14 mmol), CuI (0.1 mg, 0.1 mmol) and PPh_3 (0.2 mg, 0.1 mmol) in triethylamine (50 mL) under nitrogen. The procedures were similar to those of previously published paper.^[13a] Monomer **1(4)** and **1(9)** were prepared by similar procedures and their characterisation data are given below.

Characterisation Data of **1(3)**

Pale yellow solid; yield 96.9%. (Found: C 88.90, H 6.22, N 4.60. $\text{C}_{23}\text{H}_{19}\text{N}$ requires C 89.28, H 6.19, N 4.53%). ^1H NMR (300 MHz, CDCl_3), δ (ppm): 8.10 (d, $J = 7.2$ Hz, 2H, Carazole (Car)-H at 4 and 5 positions), 7.48 (m, 6H, Car-H at 1, 3, 6, and 8 positions and Ar-H ortho to $\text{C}\equiv\text{C}$), 7.32 (m, 3H, Ar-H para and meta to $\text{C}\equiv\text{C}$), 7.24 (m, 2H, Car-H at 2 and 7 positions), 4.50 (t, $J = 6.8$ Hz, 2H, NCH_2), 2.44 (t, $J = 6.8$ Hz, 2H, $\equiv\text{CCH}_2$), 2.19 (m, 2H, $\equiv\text{CCH}_2\text{CH}_2$). ^{13}C NMR (75 MHz, CDCl_3), δ (ppm): 140.4, 131.5 (aromatic carbons ortho to $\text{C}\equiv\text{C}$), 128.3 (aromatic carbons meta to $\text{C}\equiv\text{C}$), 127.8 (aromatic carbon para to $\text{C}\equiv\text{C}$), 125.6, 123.6 (aromatic carbon linked with $\text{C}\equiv\text{C}$), 122.8, 120.3, 118.9, 108.6, 89.0 ($\equiv\text{CCH}_2$), 81.6 (ArC \equiv), 41.5 (NCH_2), 27.8 ($\equiv\text{CCH}_2\text{CH}_2$), 17.0 ($\equiv\text{CCH}_2$). m/z (CI) 310.1 [$\text{M}+\text{H}$]⁺ requires 310.1.

Characterisation Data of 6-(9-Carbazolyl)-1-Phenyl-1-Hexyne [**1(4)**]

Pale yellow solid; yield 86.9%. (Found: C 88.74, H 6.64, N 4.47. $\text{C}_{24}\text{H}_{21}\text{N}$ requires C 89.12, H 6.54, N 4.33%). ^1H NMR (300 MHz, CDCl_3), δ (ppm): 8.10 (d, $J = 7.6$ Hz, 2H, Car-H at 4 and 5 positions), 7.44 (m, 4H, Car-H at 1, 3, 6 and 8 positions), 7.34 (m, 2H, Ar-H ortho to $\text{C}\equiv\text{C}$), 7.24 (m, 5H, Ar-H para and meta to $\text{C}\equiv\text{C}$ and Car-H at 2 and 7 positions), 4.30 (t, $J = 7.2$ Hz, 2H, NCH_2), 2.44 (t, $J = 7.2$ Hz, 2H, $\equiv\text{CCH}_2$), 2.07 (m, 2H, NCH_2CH_2), 1.66 (m, 2H, $\equiv\text{CCH}_2\text{CH}_2$). ^{13}C NMR (75 MHz, CDCl_3), δ (ppm): 140.3, 131.5 (aromatic carbons ortho to $\text{C}\equiv\text{C}$), 128.2 (aromatic carbons meta to $\text{C}\equiv\text{C}$), 127.6 (aromatic carbon para to $\text{C}\equiv\text{C}$), 125.6, 123.7 (aromatic carbon linked with $\text{C}\equiv\text{C}$), 122.8, 120.3, 118.7, 108.6, 89.3 ($\equiv\text{CCH}_2$), 81.3 (ArC \equiv), 42.4 (NCH_2), 27.9, 26.0, 19.0 ($\equiv\text{CCH}_2$). m/z (CI) 324.1 [$\text{M}+\text{H}$]⁺ requires 324.1.

Characterisation Data of 11-(9-Carbazolyl)-1-Phenyl-1-Undecyne [**1(9)**]

Pale yellow liquid; 90.2%. (Found: C 88.23, H 8.15, N 3.68. $\text{C}_{29}\text{H}_{31}\text{N}$ requires C 88.50, H 7.94, N 3.56%). ^1H NMR (300 MHz, CDCl_3), δ (ppm): 8.11 (d, $J = 7.6$ Hz, 2H, Car-H at 4 and 5 positions), 7.43 (m, 6H, Car-H at 1, 3, 6 and 8 positions and Ar-H ortho to $\text{C}\equiv\text{C}$), 7.24 (m, 5H, Ar-H para and meta to $\text{C}\equiv\text{C}$ and Car-H at 2 and 7 positions), 4.28 (t, $J = 7.2$ Hz, 2H, NCH_2), 2.38 (t, $J = 7.2$ Hz, 2H, $\equiv\text{CCH}_2$), 1.84 (m, 2H, NCH_2CH_2), 1.57 (m, 2H, $\equiv\text{CCH}_2\text{CH}_2$), 1.43–1.29 [m, 10H, $(\text{CH}_2)_5$]. ^{13}C NMR (75 MHz, CDCl_3), δ (ppm): 140.4, 131.5 (aromatic carbons ortho to $\text{C}\equiv\text{C}$), 128.1 (aromatic carbons meta to $\text{C}\equiv\text{C}$), 127.4 (aromatic carbon para to $\text{C}\equiv\text{C}$), 125.5, 124.1 (aromatic carbon linked with $\text{C}\equiv\text{C}$), 122.8, 120.3, 118.6, 108.6, 90.4 ($\equiv\text{CCH}_2$), 80.6 (ArC \equiv), 42.9 (NCH_2), 29.3, 29.0, 28.8, 28.9, 28.8, 28.6, 27.2, 19.3 ($\equiv\text{CCH}_2$). m/z (CI) 394.1 [$\text{M}+\text{H}$]⁺ requires 394.1.

Polymerisation

The polymerisation reactions and manipulations of **1**(*m*) were carried out under nitrogen using Schlenk techniques in a vacuum line system or an inert-atmosphere glovebox (Vacuum Atmospheres), except for the purification of the polymers, which was done in an open atmosphere. Typical experimental procedures for the polymerisation can be found in our previous publications.^[17]

Characterisation Data of Poly[5-(9-Carbazolyl)-1-Phenyl-1-Pentyne] [P1(3)]

Yellow powdery solid; yield 79.3%. M_w 43000; M_w/M_n 2.2 (GPC; Table 1, no. 4). ¹H NMR (300 MHz, CDCl₃), δ (ppm): 8.08 (br, Car-H at 4 and 5 positions), 7.23 (br, Car-H at 1–3 and 6–8 positions), 3.60 (NCH₂), 1.64 (=CCH₂ and =CCH₂CH₂). ¹³C NMR (75 MHz, CDCl₃), δ (ppm): 139.7, 125.5, 122.5, 120.2, 118.5, 108.6, 41.2, 27.0. UV (THF, 4.5×10^{-5} mol L⁻¹), $\lambda_{\max}/\epsilon_{\max}$: 296 nm/1.5 $\times 10^4$ mol⁻¹ L cm⁻¹.

Characterisation Data of Poly[6-(9-Carbazolyl)-1-Phenyl-1-Hexyne] [P1(4)]

Yellow powdery solid; yield 81.1%. M_w 58100; M_w/M_n 3.3 (GPC; Table 2, no. 4). ¹H NMR (300 MHz, CDCl₃), δ (ppm): 8.05 (br, Car-H at 4 and 5 positions), 7.17 (br, Car-Hx at 1–3 and 6–8 positions), 3.65 (NCH₂), 0.91 (=CCH₂, NCH₂CH₂ and =CCH₂CH₂). ¹³C NMR (75 MHz, CDCl₃), δ (ppm): 139.7, 125.3, 122.6, 120.2, 118.7, 108.4, 41.5, 29.6. UV (THF, 3.0×10^{-5} mol L⁻¹), $\lambda_{\max}/\epsilon_{\max}$: 295 nm/1.3 $\times 10^4$ mol⁻¹ L cm⁻¹.

Characterisation Data of Poly[11-(9-Carbazolyl)-1-Phenyl-1-Undecyne] [P1(9)]

Pale green powdery solid; yield 99.1%. M_w 181800; M_w/M_n 5.0 (GPC; Table 3, no. 4). ¹H NMR (300 MHz, CDCl₃), δ (ppm): 8.02 (br, Car-H at 4 and 5 positions), 7.30, 7.21 and 7.16 (br, Car-H at 1–3 and 6–8 positions), 6.80 (br, Ar-H ortho, para and meta to C=C), 4.08 (NCH₂), 1.66 (NCH₂CH₂ and =CCH₂CH₂), 1.13 [(CH₂)₅]. ¹³C NMR (75 MHz, CDCl₃), δ (ppm): 140.2, 125.4, 122.7, 120.3, 118.6, 108.5, 42.9, 29.5, 29.0, 27.3. UV (THF, 1.9×10^{-5} mol L⁻¹), $\lambda_{\max}/\epsilon_{\max}$: 295 nm/1.7 $\times 10^4$ mol⁻¹ L cm⁻¹.

Supplementary Material

¹H and ¹³C NMR spectra of the monomers **1**(*m*) are available on the Journal's website.

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