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Carbazoles in Optoelectronic Applications†

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The chemistry of carbazoles is well known in optoelectronics. Nowadays, carbazoles are still of significant interest as optoelectronic materials, either as pure carbazoles or as polymeric derivatives. As well as the sustained interest in small carbazole derivatives in applications such as OLEDs and photovoltaic devices, there is also a growing trend towards the use of polymeric compounds in similar applications. In regards to polymeric derivatives, there is also a further shift in research focus from linear conjugated polymers to dendritic forms, as well as branched and hyperbranched systems or molecules featuring star-shaped architectures. Using these dendritic systems, it is possible to achieve defined materials with the same molecular weight as linear polymers.

Keywords: Carbazoles, Organic electronics, OLEDs, Conjugated polymers, Solar cells

INTRODUCTION

In recent years, organic π-conjugated materials with photovoltaic, and/or photo- and electro-luminescent properties have been of interest in numerous studies, due to their potential for use in a wide range of optoelectronic applications such as photovoltaic cells, light-emitting diodes (LED), field-effect

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transistors[1,2] and lasers[3], with the number of possible functions for these materials continually rising. There are numerous benefits to these new organic electronics, including lower cost, improved performance, flexibility, transparency, reliability, and better environmental credentials.

It is for this reason that studies conducted within many research areas are aimed at improving both the performance and design of these systems, while attempting to explain the behaviour of small molecule compounds and polymers, which are the active elements of these systems.

General properties of carbazoles and polycarbazoles for use in optoelectronic applications

The general requirements of compounds found in optoelectronic materials are (but not limited to) high electrical conductivity, defined HOMO-LUMO band gap, and a properly balanced process of introducing charge carriers, which allows for substantial increases in system efficiency. Irrespective of the high demand for such materials, currently no organic compound satisfies all of these requirements, therefore new materials are continually sought.

Small molecule carbazoles are advantageous as optoelectronic materials due to their predictable HOMO-LUMO energy levels (easily tuned through chemical substitution) and high thermal stability,[4] making them suitable for thermal vacuum evaporation. Carbazole-based compounds also are attractive as photoconductors or charge-transporting materials for the following reasons:[5]

- carbazolyl groups quickly form relatively stable radical cations
- some carbazole compounds exhibit relatively high charge carrier mobilities
- different substituents can be easily introduced into the carbazole ring
- carbazole-containing compounds exhibit high thermal and photochemical stability
- carbazole is a cheap raw material, readily available from coal–tar distillation

Conducting polymers (CPs) are also promising derivatives for optoelectronics. CPs are organic polymers containing conjugated double bonds (Fig. 1). CPs are usually insulators or semiconductors in the undoped state, however doping transforms these compounds into useful conductors (Fig. 2). Since the discovery that doped polyacetylene shows significantly greater conductivity than the undoped derivative, conjugated polymers have been intensively studied. Over the past 40 years, a great number of experiments aimed at improving structure and properties have been carried out in order to improve the stability, conductivity or charge storage of CPs, so to push these promising polymers into potential application-based research fields.

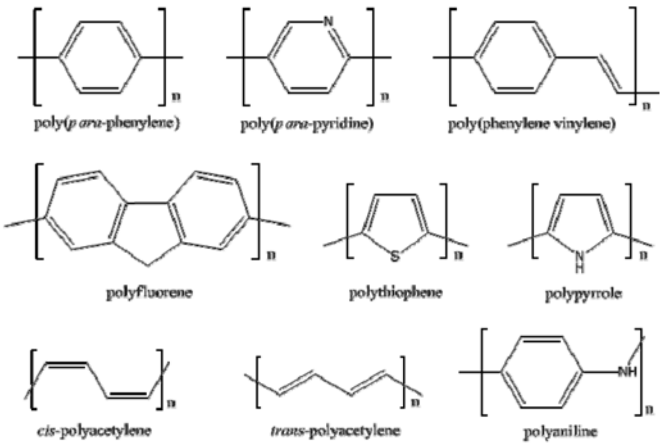

FIGURE 1
Typical conjugated polymer groups

One of the most important properties of conjugated polymers, which determines their usefulness as materials in optoelectronic devices is the value of the HOMO – LUMO band gap. This band gap can be tuned by attaching substituents to the polymer backbone (such as electron-withdrawing or donating substituents) or through the introduction of π-conjugated linkages (including non-conjugated carbon bridges).[6]

Furthermore, chemically and electrochemically polymerised films show very interesting properties, including very strong fluorescence and electroluminescence (with high intensity and colour purity), while significant changes in polymer struture can lead to changes in the mobility of charge carriers.[7,8] CPs also usually have excellent stability during multiple doping and dedoping cycles as well as a low ionization potential.

Another reason CPs are being developed for electronics is their potential to be used within nanoscale architectures. Conjugated polymers allow for nanoscale deposition control, (in contrast to inorganic semiconductors), and their nanosized building blocks subsequently show various quantum effects compared to their original form.[10] Although the most typical and widely researched CPs are linear macromolecules,[9] recently a new class of these molecules, featuring branched[10] or star-shaped architecture, have also begun to receive attention. This means that depending on the arrangement of the bonds between the arms and the core, these compounds can possess different shapes and hence provide 2D or 3D architecture.[11] Various conjugation orientations therefore allow control over macroscopic and nanoscopic organisation.

Some of the most promising conjugated polymers currently used in optoelectronic applications include polythiophenes,[12,13] polycarbazoles,[14-16]

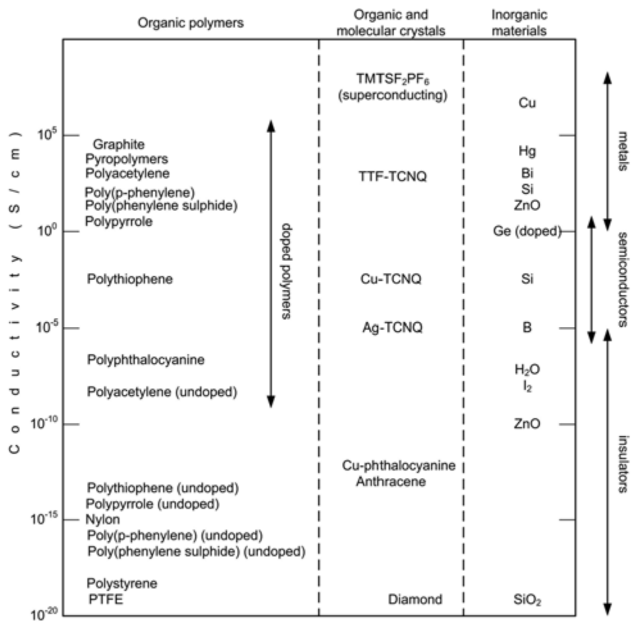

FIGURE 2
Conductivity ranges for polymers (doped and undoped), inorganic materials and molecular crystals.[9]

poly(p-phenylene vinylene)s,[11,17,18] and polyfluorenes.[19,20] Many of these polymers are designed specifically for commercial applications by substitution of the polymer chain with different functional groups, often for improved processability. Polymers based upon carbazoles have become of increasing interest as they also contain many general properties, advantageous to optoelectronic applications. The mechanism of electrochemical carbazole polymerisation and further oxidation of the polymer has been explored and described in detail within literature.[21] Polycarbazole changes colour during oxidation from yellow to green however, despite these unusual optical properties, polycarbazole has no known practical application due to poor stability, attributed to a high HOMO level. To overcome this disadvantage, research efforts have been directed towards modifying the compound's structure through the introduction of different substituents to the ring[14] or substitution of the nitrogen atom.[22,23] These modified polycarbazole derivatives subsequently show excellent thermal and photochemical stability, which can significantly affect their application potential.

Star-shaped monomers based on carbazoles and their branched polymers have also been identified as potential materials optoelectronic applications. Photophysical and electrical properties of branched polymers based on star-shaped monomers could be controlled more efficiently than linear polymers, due to their highly branched and well-defined structures. Such materials are expected to be less aggregated,[24] with the potential to form more uniform amorphous layers, required for pure colour output in OLED devices. Furthermore, the HOMO energy levels of carbazole-based structures makes them promising materials as donors in high-efficiency bulk heterojunction cells with fullerenes.

Carbazoles and polycarbazoles in OLED devices

One of the largest fields within the optoelectronic research is the development of organic-light emitting diodes (OLEDs). This is due to their immense potential in commercial applications such as in lighting, smart phones and flat panel displays.[25] Although the idea of OLEDs was proposed as early as the 1980s,[26] it was only upon the mechanistic understanding of how to harvest the 75% of triplet excitons[27,28] formed upon electrical stimulation, that all organic LEDs became a lucrative and commercial success.

Within this field, carbazole derivatives have played an imperative role, not only as materials for hole transporting layers, (utilizing their good charge mobility), but also in the development of OLED emitting materials. Small molecule donor(s)-acceptor (D-A) materials, based upon carbazole donors have been extensively used as emitting materials within OLED devices. Although the synthesis, photophysical and light output of such carbazole containing devices can be found in numerous reviews,[25,29] significant emphasis should be placed upon the role of D-A based carbazole derivatives in the synthesis of blue emitting OLEDs,[30-34] (Fig. 3) specifically required to replace blue emitting phosphorescent LEDs, whose instability renders them unsuitable for use in long term commercial applications. These small molecule containing carbazole derivatives have now been used as emitting materials to produce OLEDs with an external quantum efficiency (%EQE) of above 20%,[31,35,36] (Fig. 4), luminance above 1000 cd/m^2 at acceptable voltages, and low turn-on voltages.[37]

The use of carbazole in such small molecule emitting layers stems from its electron-donating properties, used to stimulate charge-transfer character

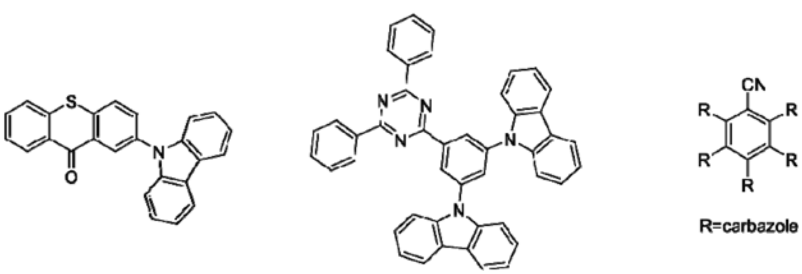

FIGURE 3
Examples of small molecule OLED emitting materials containing carbazole.[32,34,38]

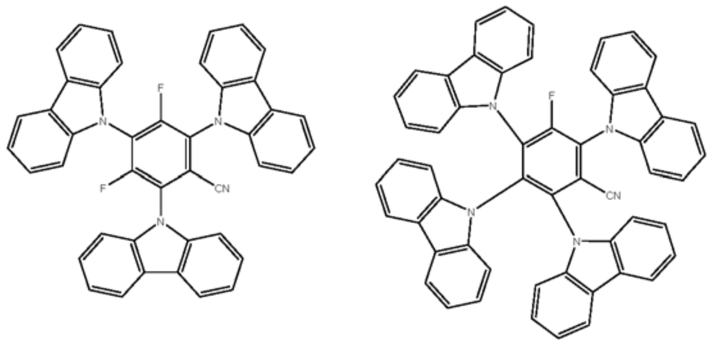

FIGURE 4
Small molecule carbazoles 3CzFCN and 4CzFCN with %EQEs above 20%[31]

when bonded to an effective acceptor moiety. Furthermore, carbazoles contain a predictable local triplet level (required for efficient coupling to the singlet state in thermally activated delayed fluorescence (TADF), or for upconversion to the singlet state *via* triplet-triplet annihilation (TTA)), synthetic flexibility (the ability to bond to numerous acceptor units) and acceptable electromobility, all of which will see small carbazoles used within OLEDs long into the future.

CPs can be simultaneously addressed for use as active materials in both OLEDs and solar cells. This is due to that fact that photovoltaic and LED materials work upon the same principles: fluorescence, charge occurrence and exciton formation by charge injection and photoexcitation. An important feature of CPs for OLED purposes is the generation of high electroluminescence efficiency. As with small molecule derivatives, it is also important to obtain polymer LEDs that emit light in the blue part of the electromagnetic spectrum, as there are few such examples of blue emitting polymers, which simultaneously work with the appropriate stability. Moreover, blue light can be transformed into red and green by internal or external color conversion.[39]

OLEDs based on conductive polymers require that a balanced distribution of entering charge carriers, positive (holes) and negative (electrons), is maintained. This ensures the effective recombination of these individuals and consequently significantly improves OLED performance. However, a large energy gap, high ionization potential, or low electron affinity, often lead to disruption of the desired equilibrium. The control over this process can be achieved by influencing the effective conjugation length as well as the introduction of electron donating or electron accepting substituents to the chromophore.[40] It is here that a move towards dendritic derivatives,[10] or molecules featuring star-shaped architecture[41,42] may have the greatest impact.

Polymeric carbazoles have been researched as OLED materials. The first groups of conjugated polymers, which gave a photovoltaic response also func-

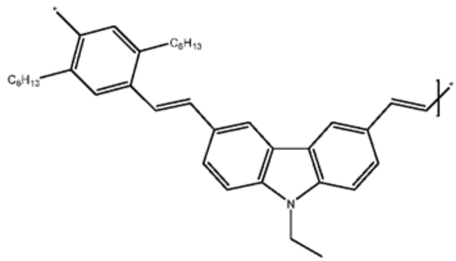

FIGURE 5
Organic polymer containing dialkylphenylene vinylene and N-ethylcarbazole units used in LED devices.[44]

tioned as a LED. Single-layer poly(9-vinylcarbazole) (PVK) LEDs, with the structure ITO/PVK/Al emitted blue light, but with unsatisfactory working time.[44] A single-layer LED, in which a layer of light-emitting polymers poly(1,4-dihexyl-2,6-phenylenevinylene-alt-N-ethyl-3,6-carbazolevinylene) and poly(1-methyl-4-(2-ethylhexyl)phenylenevinylene-alt-N-ethyl-3,6-carbazolevinylene) were used, emitted intense light at 460 and 490 nm when only a few volts were applied (Fig. 5).[44] In contrast inorganic LEDs typically require several volts in order to obtain light output. By electropolymerisation, very stable statistical copolymers with different compositions of EDOT and 3,6bis(3,4-ethylendioxythiophene)-N-methyl carbazole have also been obtained. These polymers absorbed light ranging from 424 to 580 nm, which gave the compound a colour from violet to green, achieved by changing the composition ratio of the copolymer films.[45] Blends of poly(N-vinyl carbazole) and blue-emitting fluorene derivatives with 9-ethyl-N,N′-diphenyl-N,N′-dipyren-1-yl-9H-carbazole-3,6-diamine have also been synthesised, emitting an orange or red colour, with different compositions.[46]

Carbazoles and polycarbazoles in solar cells and photovoltaic cells

Due to the growing environmental concern surrounding the use of fossil fuels and non-renewable energy sources, there has been considerable research concerning materials for use in light harvesting and solar cells. Concerning these materials, polymer sources have attracted much attention due to their ability to be deposited on flexible substrates at low cost,[47] while being synthesized from non toxic materials.[48] Additionally, the extremely high optical absorption coefficient of organic small molecule and polymeric semiconductors (of order 107 cm^{-1}) offers the possibility for production of very thin organic solar cells (100–150 nm) and therefore, only tiny amounts of these materials are required to be fabricated in order to generate a photovoltaic cell.[49]

Crucial to the charge carrier separation yield and overall efficiency of the photovoltaic cell is an alignment of the energy levels of the component materials as well as of the electrodes. The HOMO energy levels for carbazole based polymers are typically in the -5.2 to -5.8 eV range that is necessary for donors in high-efficiency bulk heterojunction in organic photovoltaic devices.

Many all polymer solar cells synthesised with carbazoles have taken advantage of the small molecule's synthetic flexibility, bonding groups in both the 3,6 and 2,7 positions of the carbazole moieties (Fig. 6) Most carbazole polymers are synthesized as co-polymers containing thiophene moieties in order to achieve the required charge separation. In one example, Park *et. al.*, synthesised a poly[*N*-9''-hepta-decanyl-2,7-carbazole-alt-5,5-(4',7'-di-2-thienyl-2',1',3'-benzothiadiazole) compound resulting in an internal quantum efficiency of almost 100%, meaning that every photon absorbed resulted in a separated pair of charges, collected at the electrode.[51] Other similar thiophene/carbazole base co-polymers report promising solar cell properties such as acceptable hole mobilities and charge migration.[16,48,52] Blouin *et. al.* also states in their combined theoretical and synthetic study that it is the carbzole within these compounds that most often dictates the position of the polymer's HOMO and thus its hole mobility capacity.[53] A carbazole-polymer derivative has already been shown to provide a 6% power conversion, which is good grounds for the design of further polycarbazoles, as efficiencies close to 10% are required for commercial applications. This makes carbazole-based polymers and copolymers most promising materials for obtaining high efficiency organic solar cells in the future.[50]

Small molecule carbazole-based solar cell materials have also been investigated. These have included carbazole/ thiophene derivatives similar to known polymer moieties, obtaining short circuit photocurrent densities of 11.0 $mAcm^{-2}$.[54] More recent examples have used BODIPY dyes extended with conjugated carbazole groups, in order to study energy transfer and photocurrent losses.[55]

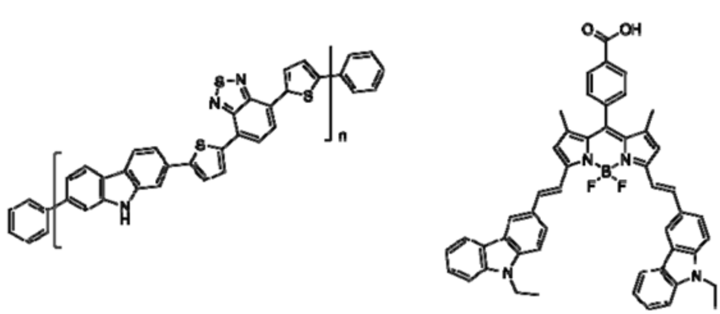

FIGURE 6
Examples of carbazole containing co-polymer (left), and small molecule[55] (right) materials used in solar cells.

CONCLUSIONS

Researchers worldwide are in an extensive search of new materials for organic electronics with emphasis upon performance and stability. The primary requirement of optoelectronics is the ability to prepare a well-defined material, featuring desirable electronic properties, while also being durable and preferably soluble in common organic solvents. In this respect, carbazole derivatives are potential candidates, as they can be easily oligo- or polymerised to produce materials that have proven suitable for optoelectronic and photovoltaic applications. These materials have already been encountered in prototypical, or even commercial, chemical sensors, photovoltaic cells, OLEDs and other optoelectronic devices. While a great amount research is still required to improve the structure and properties both small molecule and conjugated carbazole polymers, the outlook appears promising for the use of these electroactive molecules in future commercial applications.

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