Electroluminescent polymeric materials

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Synthesis of organometallic polymers represents an important area of research in material science. For synthetic chemists, an equally challenging endeavour is to develop methodologies suitable for preparation of polymeric materials with precision and purity. This review briefly summarizes the current interest in electroluminescent polymeric materials with particular reference to the use of organometallic reactions in synthesis of such polymers.

Introduction

THE last two decades were marked by tremendous advances in the area of electronics and telecommunication. This includes semiconductors, solar cells, high-density batteries and especially materials of optoelectronic interest like electroluminescent and nonlinear optical materials[1]. The light emitting diode (LED) could be a new generation of alternative flat panel display to the cathode ray tubes and liquid crystal displays. Though the story of LED goes back to 1907 (ref. 2), the studies were limited to the use of inorganic semiconductors such as GaN, ZnS and ZnSe. However, large area display technologies by LED have not been practicable due to problems in fabrication. Attention was diverted to conjugated organic molecules which showed electroluminescence properties[3]. A single crystal of anthracene was first discovered in 1963 to exhibit electroluminescence[4]. The most important milestone was due to Tang and Van Slyke's discovery of the double-layer green thin-film organic electroluminescent device[5]. This kind of multi-layer set-up is now common in organic LED devices. Typical fabrication of such a device (Figure 1) constitutes three layers: (1) a transparent ITO electrode which serves as the anode; (2) an electro-active material, i.e. a fluorophore, that is either dissolved in a polymeric binder and coated from solvent or vacuum evaporated directly onto the anode; (3) a low work function metal cathode such as calcium, magnesium or aluminum.

In order to increase the efficiency of device, a layer of the electron transporting material can be introduced between the emitting layer and the metallic cathode to enhance the transfer of an electron from the cathode to the fluorophore. In a similar manner, insertion of a hole transporting material between the anode and the emitting layer can facilitate the transfer of an electron from the lumiphore to the anode. In general, electron transporting materials are those which can easily accept an electron whereas hole transporting materials are those which can be easily oxidized electrochemically. Typical examples are summarized in Figure 2 (ref. 3).

In 1989, interest in organic LED was intensified when a group of researchers at Cambridge University reported electroluminescence from diodes containing poly(phenylene-vinylene) (PPV) and its homologues[6]. Since then polymeric materials, having added advantages of ease of fabrication and large area of application, has become an important area of research in optoelectronic materials. After the initial discovery, a number of polymeric LED materials have been reported using different conjugated polymers emitting in various ranges of the visible spectrum[3]. Representative examples of these polymers are shown Figure 3.

This review briefly summarizes, from a synthetic point of view, the current interest of electroluminescent polymeric materials. Particular emphasis will be focused on the use of organometallic catalysts or reagents in the synthesis of these polymers.
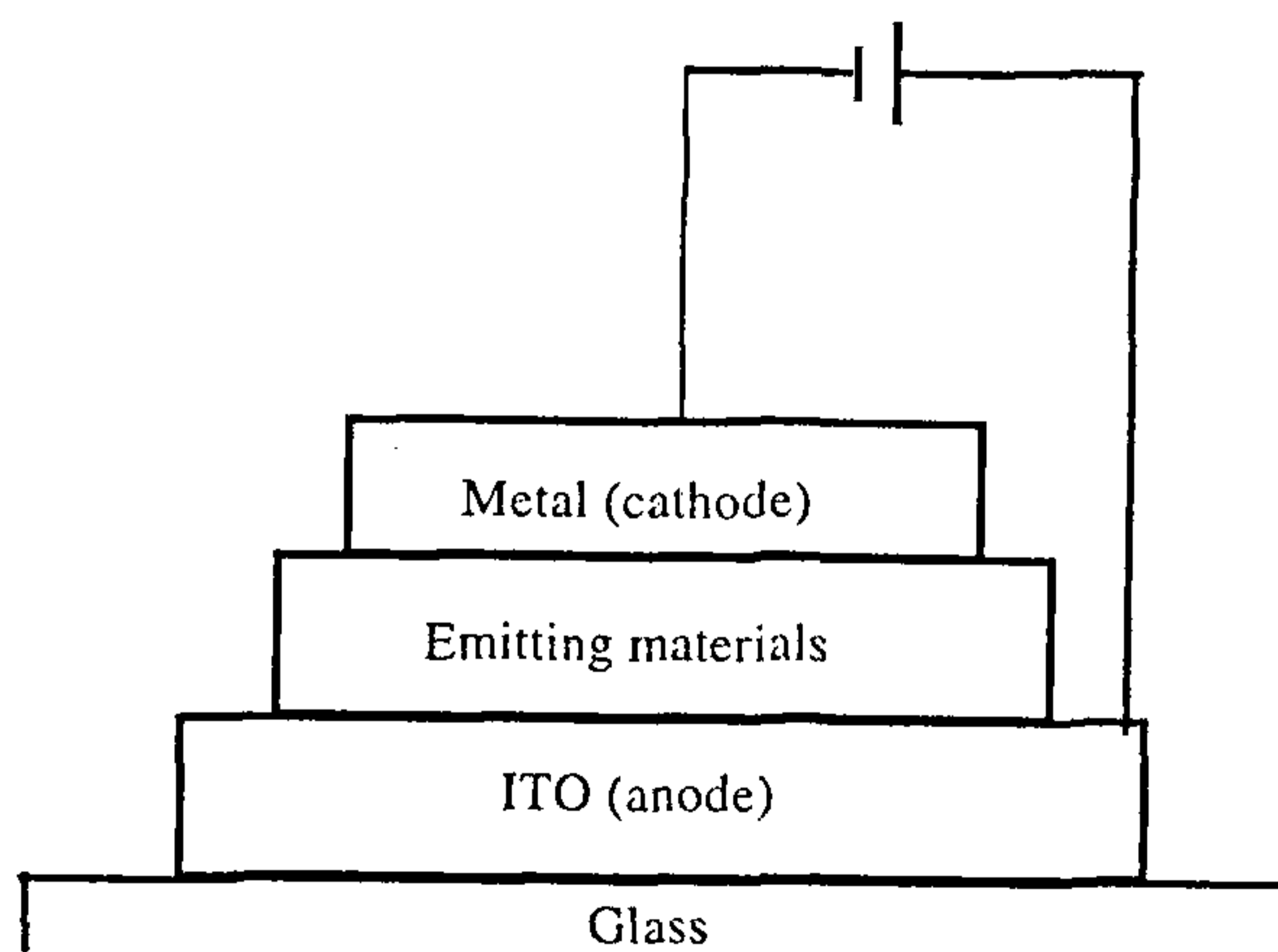

Figure 1. Electroluminescent device.

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Criteria for polymeric electroluminescent materials

With the advent of both basic and applied research in the area of polymeric electroluminescent materials, design and synthesis of new materials became a major challenge. Emission frequency, efficiency, durability, processibility, and purity, *inter alia*, are important factors for consideration.

All organic electroluminescent materials, whether they are polymers or oligomers, are conjugated molecules. Accordingly, their emission frequencies depend on the effective conjugation length. Table 1 outlines the energies and colours of emission at different wavelengths. The

emission energies may affect the turn on voltage and the life time of the electroluminescent devices. It is noteworthy that the energy of shorter wavelength emission may surpass certain bond energies of organic molecules. Selected bond energies are tabulated in Figure 4 for comparison.

The quantum yield of photoluminescence of a molecule apparently plays a crucial role on the electroluminescence. Although doping can sometimes improve the quantum efficiency of a device, it is generally believed that the higher photoemission quantum yield will give a better electroluminescent efficiency. Aggregation or excimer formation in the thin film may result in large Stoke's shift in the emission spectra than those measured in solution. Structural variation by introducing bulky substituent to prohibit the stacking could solve this problem.

The polymer is often cast as a thin film onto the ITO anode in the LED device. Consequently, the solubility of the polymer in a solvent is crucial for processing spin coating. Introduction of a long chain aliphatic substituent may enhance solubility of polymers in organic solvents. Alternatively, the presence of the sulfonate group may enable the polymer to dissolve in water.

Above all, the most important factor that influences the efficiency of an electroluminescent device is the purity of
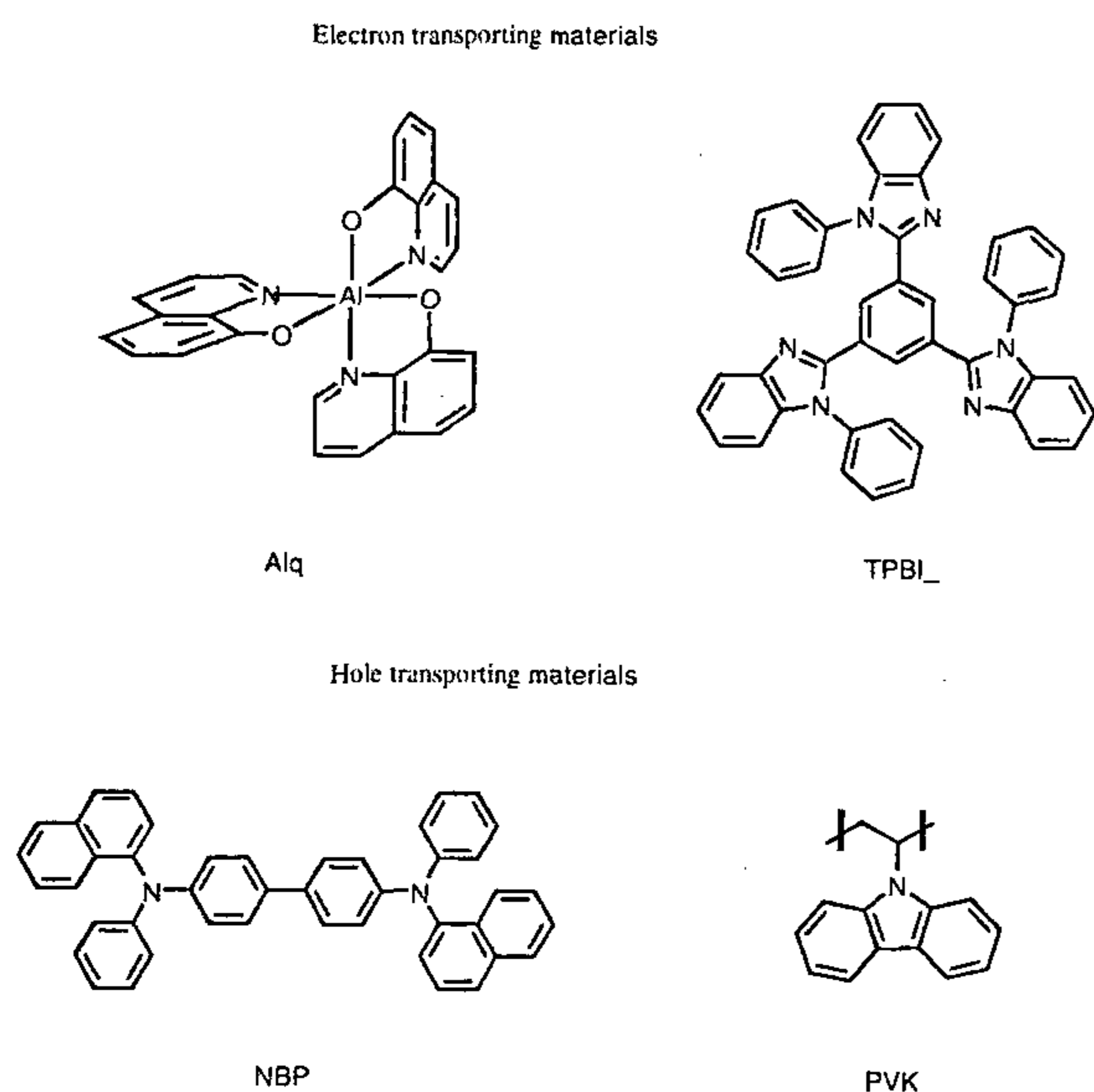
Electron transporting materials

Alq   TPBI_

Hole transporting materials

NBP   PVK

Figure 2. Typical electron and hole transporting materials.

Table 1. Emission frequency, colour and energy

I (nm)	Colour	Energy (eV)	(kcal)
400	Violet	3.1	71
450	Blue	2.7	63
500	Blue-green	2.5	57
550	Yellow-green	2.3	52
600	Orange	2.1	48
650	Red	1.9	44

λ_{em} = 564 nm
A. B. Holmes (1990)

λ_{em} = 620 nm
A. B. Holmes (1992)

λ_{em} = 710 nm
A. B. Holmes (1993)

λ_{em} = 388 nm
W. R. Salaneck(1996)

λ_{em} = 446 nm
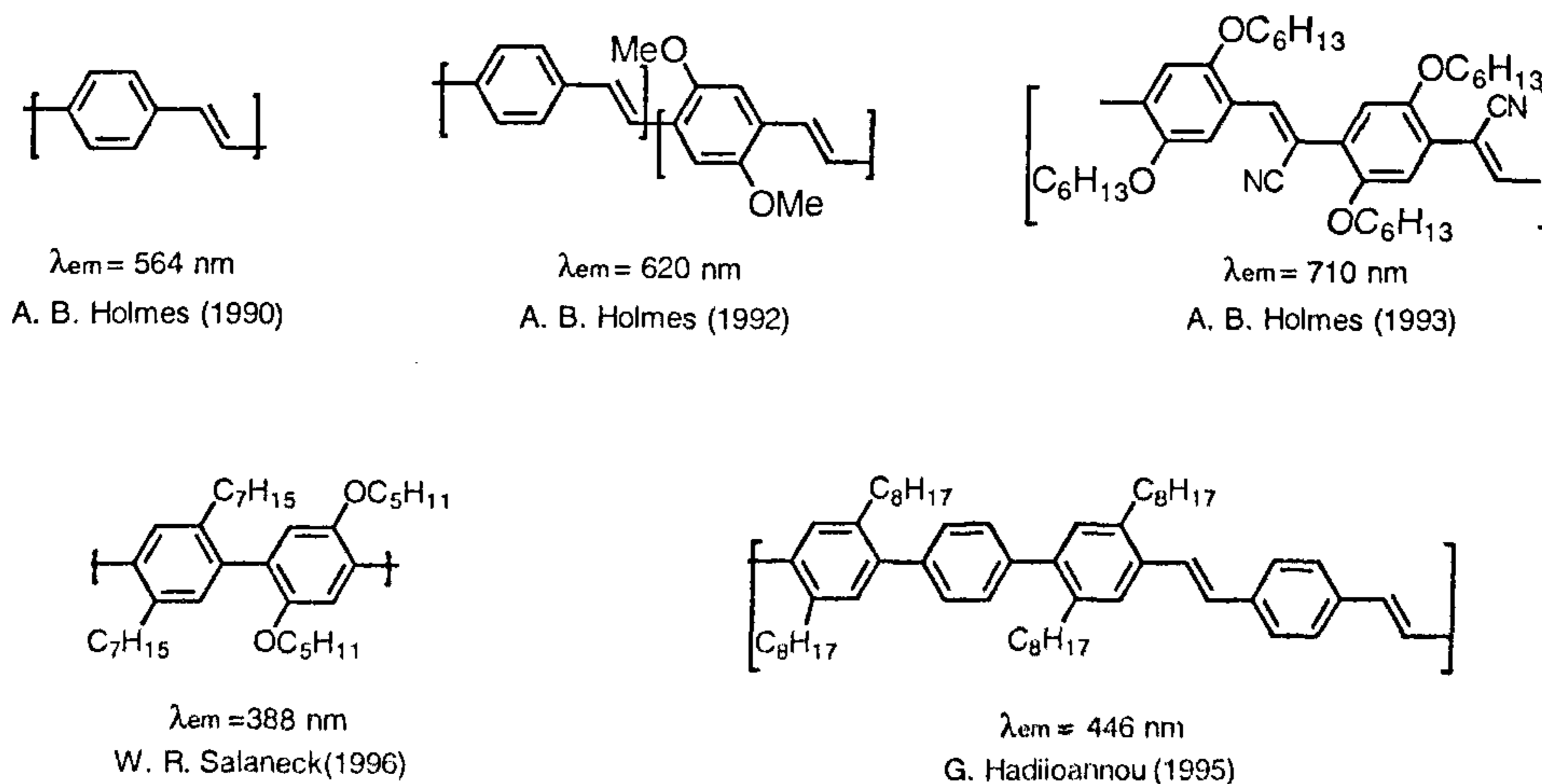G. Hadiioannou (1995)

Figure 3. Selected conjugated polymeric electroluminescent materials.

the materials. Well-defined small molecules can easily be obtained in high purity. However, polymers are difficult to purify. The presence of side products or a trace amount of metallic catalyst may change the behaviour and hence the reproducibility of the device.

Syntheses of conjugated polymers

Synthetic methods have been developed for easy production of polymers of high purity with a control over the molecular weight. Synthesis of PPV or polyacetylenic materials is mostly dependent on the synthesis of aryl-vinylene or arylacetylenic subunits and the final coupling of these monomeric units under suitable conditions to afford the corresponding polymers. The strategies used in the syntheses of these conjugated systems include the carbon–carbon double bond formation and the carbon–carbon single bond formation involving C_{sp^2}.

Carbon–carbon double bond formation

Carbon–carbon double bond in conjugated polymers such as PPV can easily be synthesized by conventional

Csp3-H	91–104	Csp2-H	103	Csp-H	125
Csp3-Csp3	85–88	Csp3-Csp2	85–88	Csp3-Csp	117
Csp2-Csp2	100	Csp2-Csp	128	Csp-Csp	150
Csp2Csp2 Csp3-Csp3	72			Csp3-Si	90
Csp3-O	80–92	Csp2-O	91–103		
Csp3-N	79	Csp2-N	91		

Figure 4. Selected bond energies (kcal/mol).
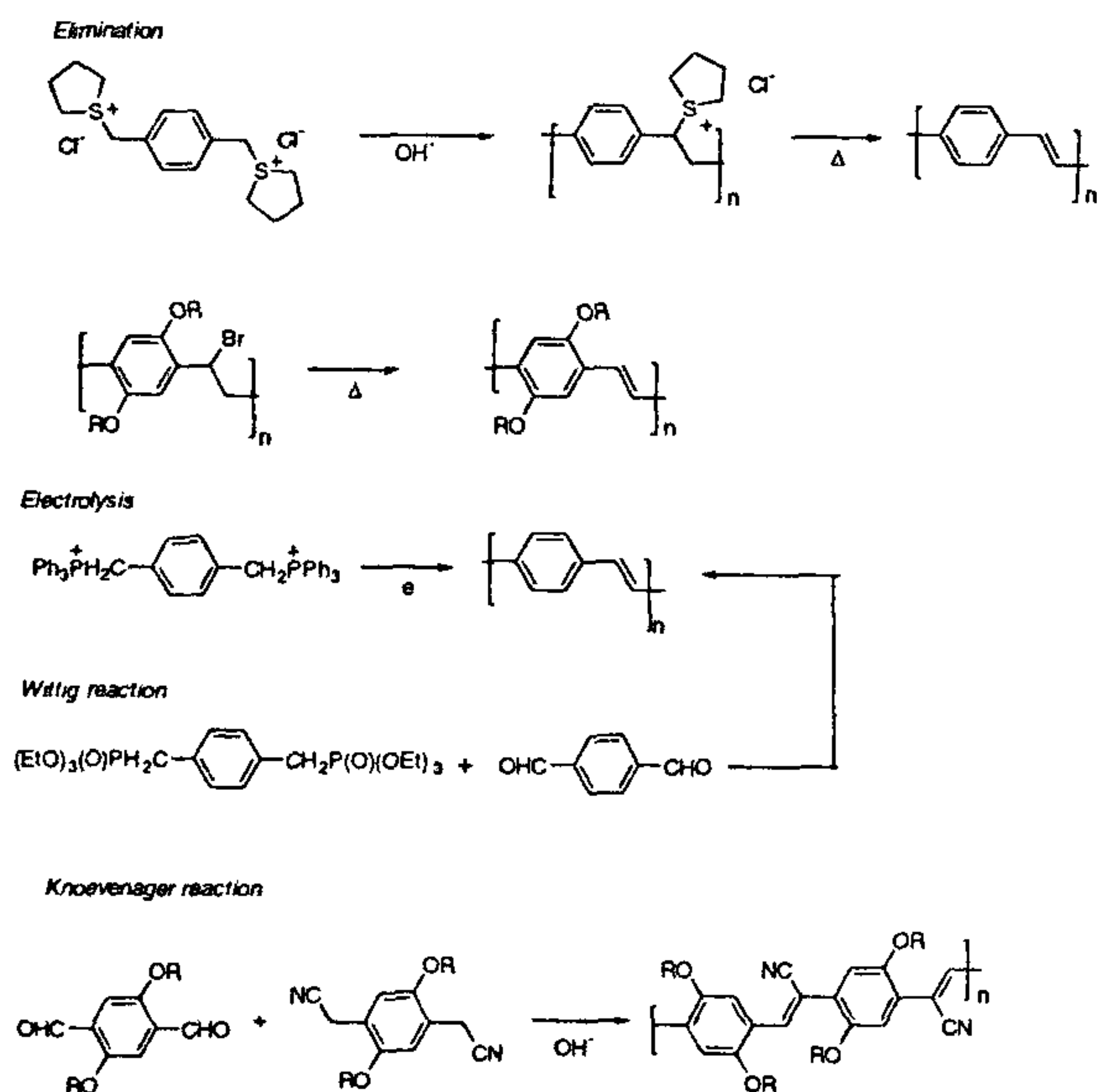
Scheme 1. Representative syntheses of PPV.

elimination or condensation reactions. Scheme 1 summarizes typical examples using the nonorganometallic route for the preparation of PPV polymers. They are: (i) elimination protocol via the halo[7] or sulfonium precursor[8], (ii) electrochemical polymerization[9], (iii) Wittig reaction[10], or (iv) Knoevenagel condensation[11] (Scheme 1).

Carbon–carbon single bond formation

The burgeoning synthetic methodologies have provided powerful arsenal to design and make new conjugated organic materials. It is particularly noteworthy that the use of organometallic catalysts or reagents can pave the way for the carbon–carbon bond formation involving a C_{sp^2} or C_{sp} at the reaction centre. Thus, cross coupling reactions (e.g. Kumada-Corriu reaction[12], and Suzuki reaction[13]) are extremely powerful for the synthesis of C_{sp^2}-C_{sp^2} single bond. Sonogashira reaction[14], on the other hand, serves as a useful entry for the preparation of alkynylarenes. Heck reaction[15] furnishes a coupling between an aryl halide and an alkene. Scheme 2 summarizes representative examples to elucidate usefulness of organometallic chemistry in conjugated polymer syntheses.
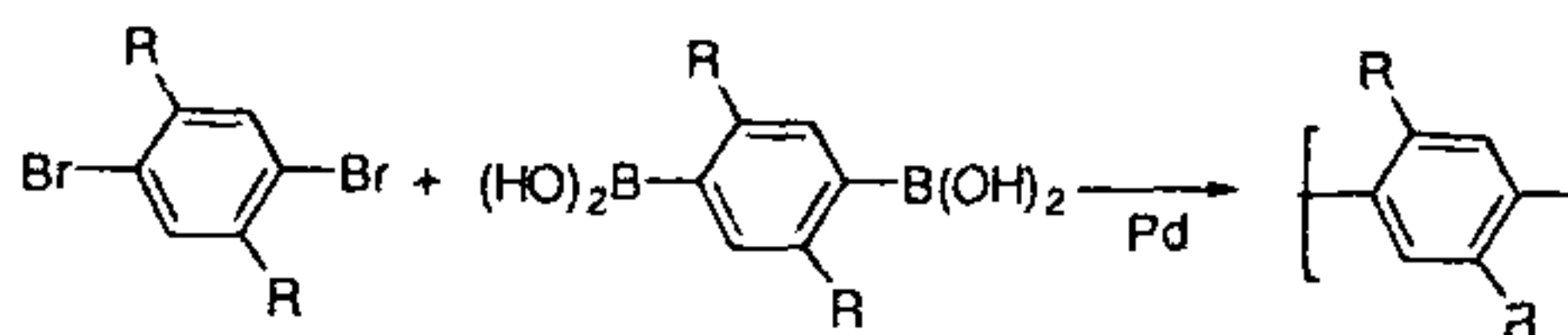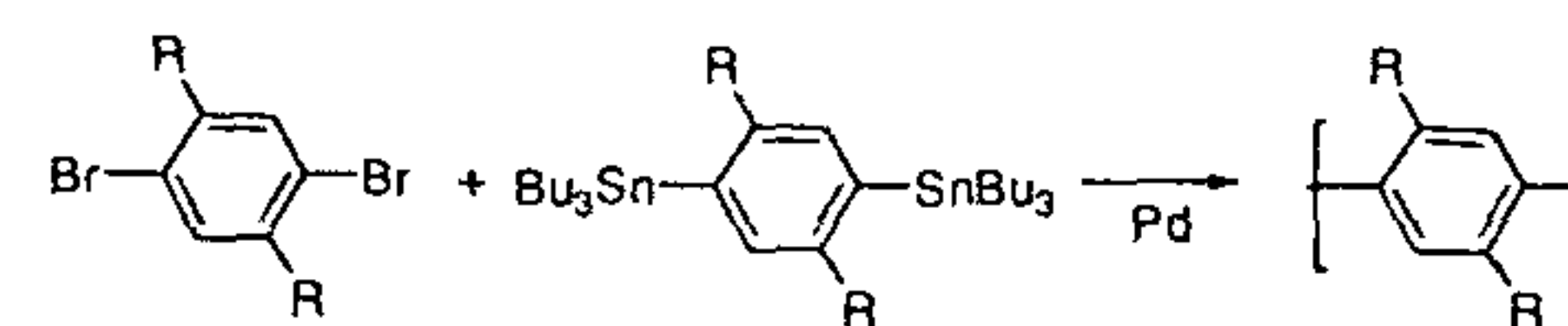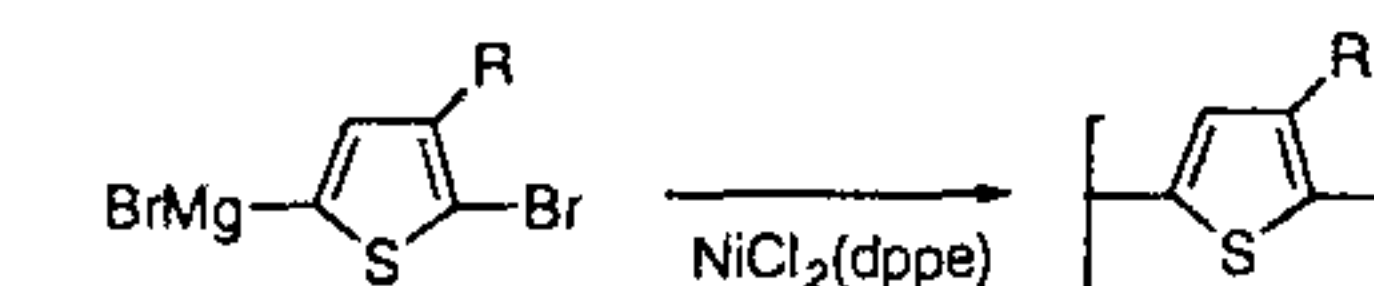
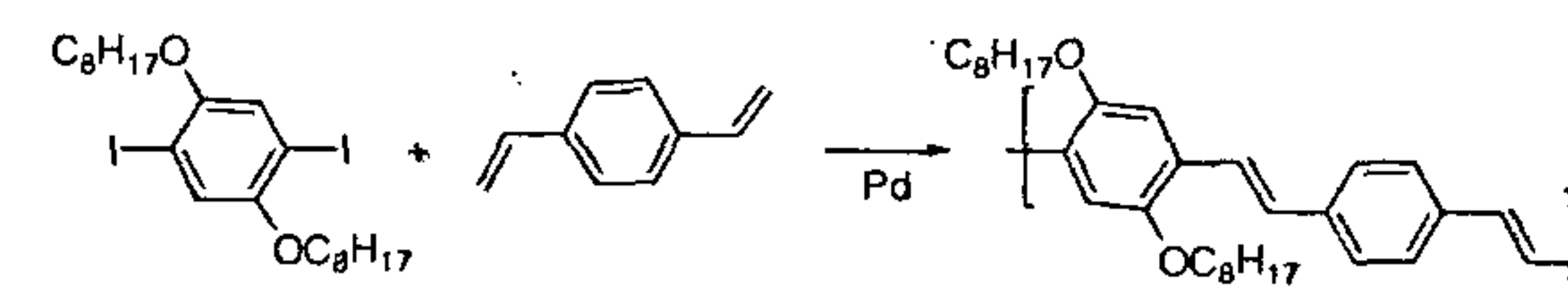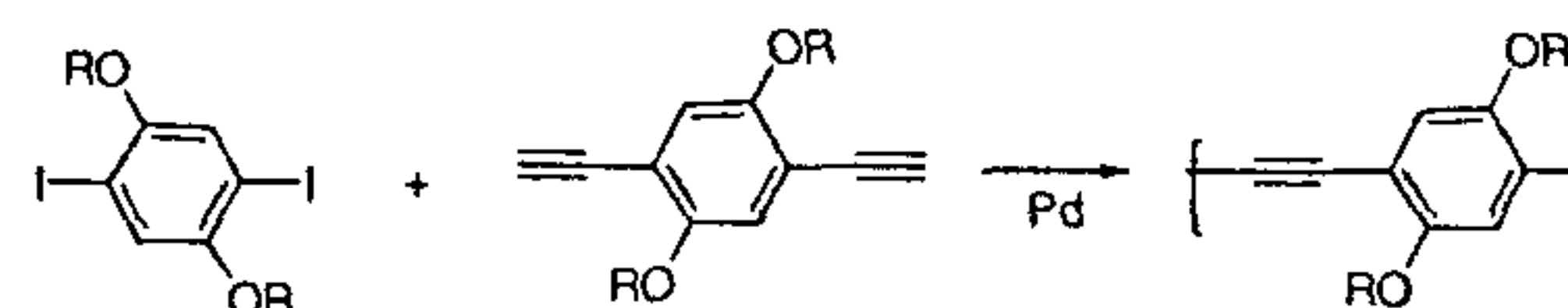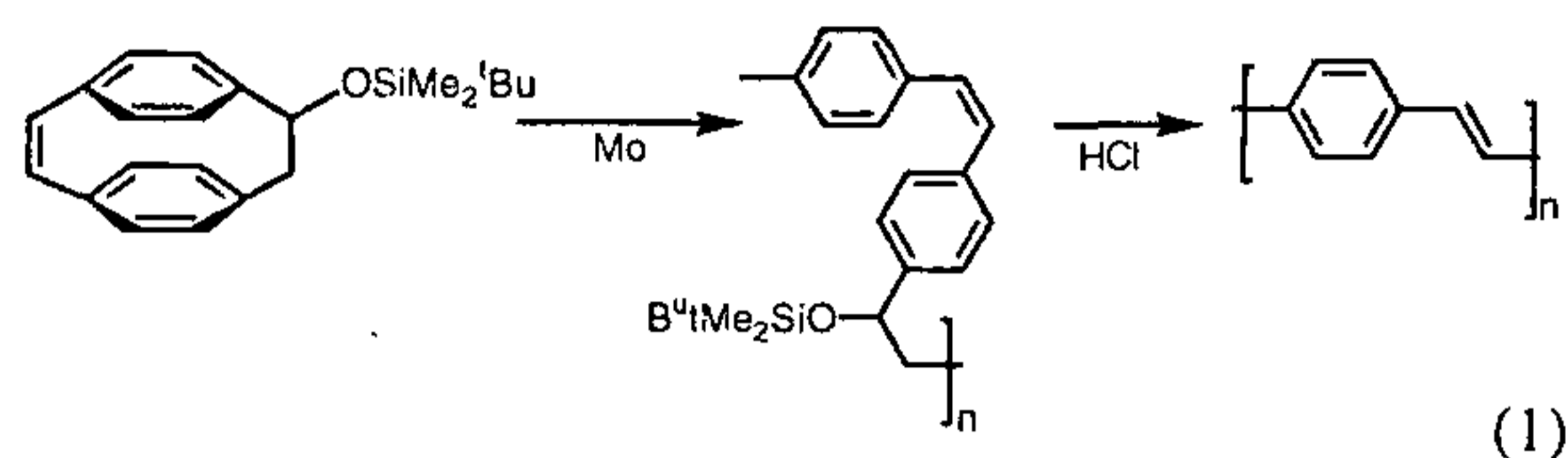Scheme 2. Use of organometallic catalysts for the synthesis conjugated polymers.

Miscellaneous reactions

Ring opening metathesis polymerization (ROMP) is a very useful reaction for the synthesis of polymers containing olefinic moieties. This reaction has been extended to the synthesis of PPV derivatives (eq. (1))[16].
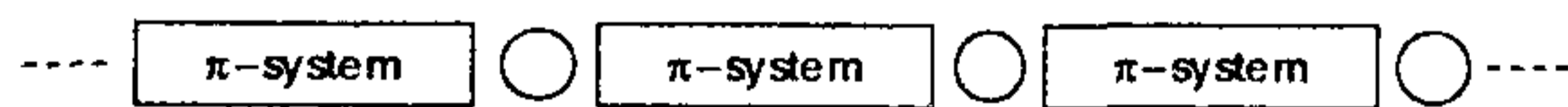
$$\tag{1}$$

Annulation of polyphenylene derivatives has led to the ladder-type almost planar poly(paraphenylenes) (eq. (2))[17].

$$\tag{2}$$
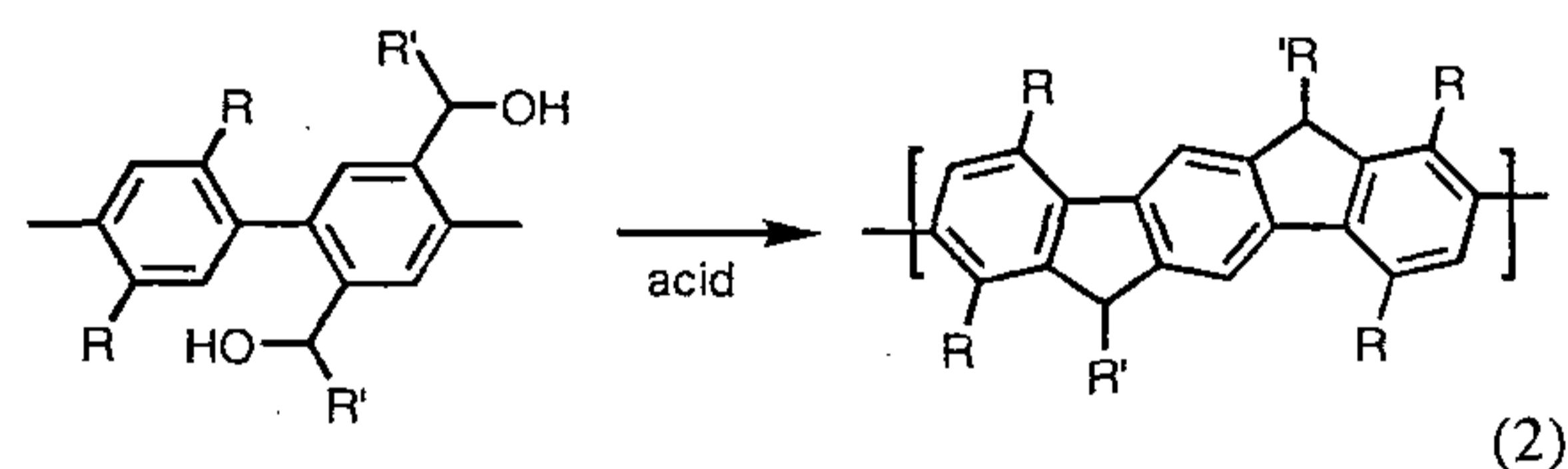
Conjugated system-spacer-copolymers

Various model systems suggest that the photophysical properties of certain conjugated polymers can be represented by those of a short fragment of the corresponding oligomeric chromophores[18]. There has been an increasing study on the use of spacers between well-defined conjugated chromophores in polymers. An obvious advantage in this strategy is that polymers can increase the processibility and, in the meantime, the emission wavelength can be predicted[19]. In particular, such short conjugated segments could furnish desired HOMO–LUMO energy gap such that efficient multicolour display applications coul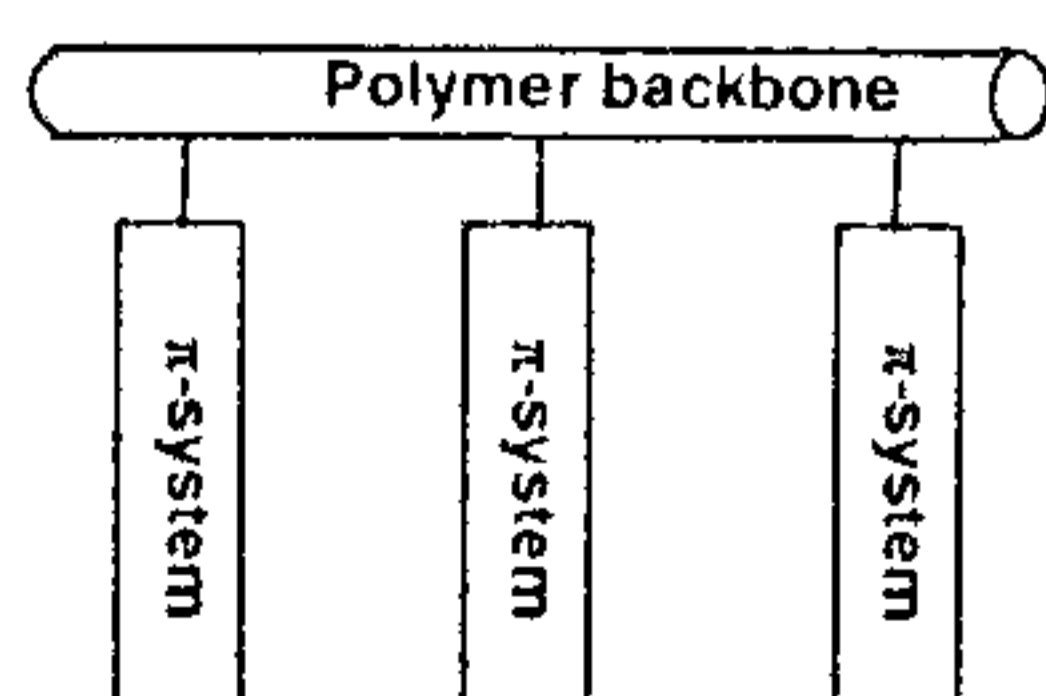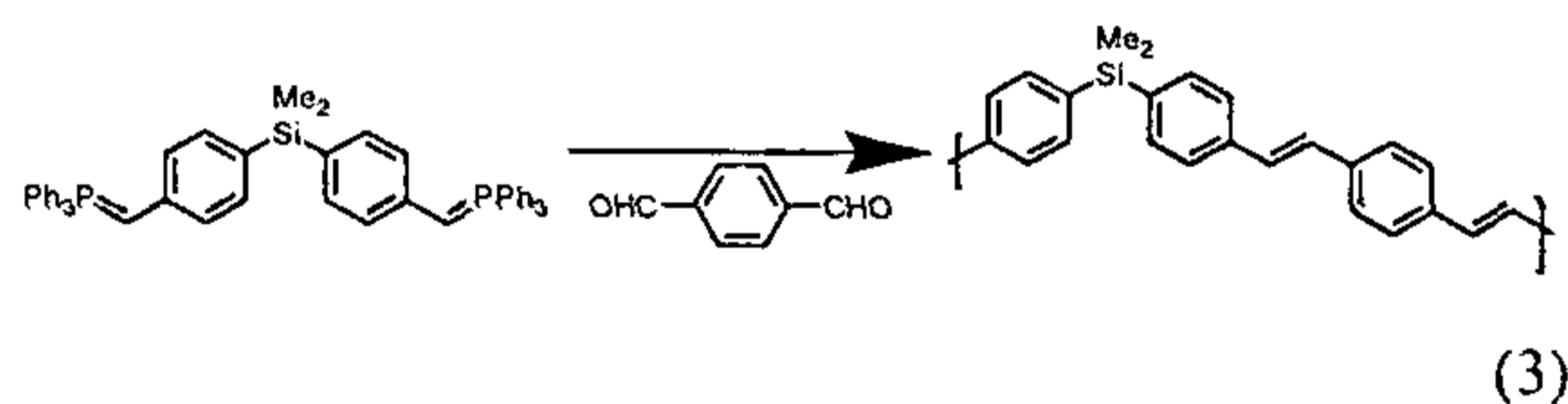d be achieved. Two approaches using insulating linkers are shown in Figure 5. The conjugated moiety can be part of a polymeric backbone as demonstrated in case a. The second method considers the chromophores as pendent to the polymeric skeleton (case b). In both cases, the photophysical properties of the polymers appear to be the same as those of the corresponding monomeric chromophores.

Chromophore as part of a polymeric backbone

Since the first discovery of the randomly segmented PPV-based conjugated polymer[20], which exhibits the blue-shifted light output relative to PPV, a more rational design by employing aliphatic linkage to insulate the conjugated segments has been reported. A wide range of linkers is known in the literature and Figure 6 summarizes some typical examples[19–21]. Ether, ester, alkylidene, as well as silylene linkages are among the most commonly used spacers to connect the chromophores. Most syntheses leading to these polymers rely on condensation or Wittig reaction. It is noteworthy that these reactions, in general, do not belong to an atom-economy synthesis.

There has been an increasing use of tetrahedral silylene moiety as a bridge connecting chromophores in polymers[22]. Copolymers containing oligothiophenes and silylene spacers exhibit emission ranging from blue to red depending on the number of thiophene and silylene units. These polymers have been synthesized by the displacement of silicon-halide bond with nucleophiles[21g–j] or by Wittig reaction of a dicarbonyl compound with preformed aryl-silane linkage (eq. (3))[22].

$$\tag{3}$$

A replacement of the aryl group attached to the silicon atom in eq. (3) by a vinylic moiety may release the steric

Case a

Case b

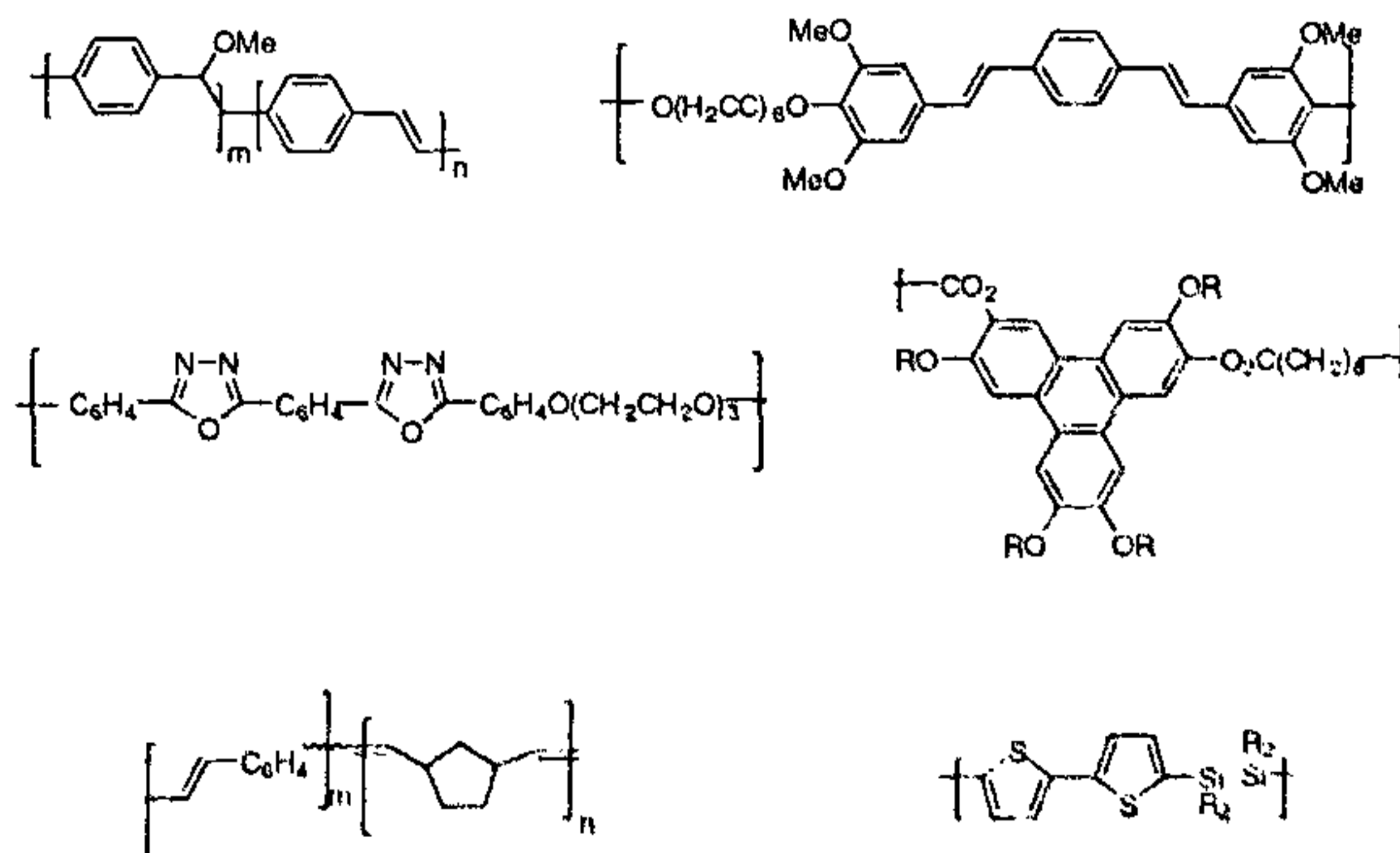**Figure 5.** Spacer-conjugated system copolymer.

Figure 6. Representative examples of segmented polymers containing chromophores as part of a polymeric backbone.
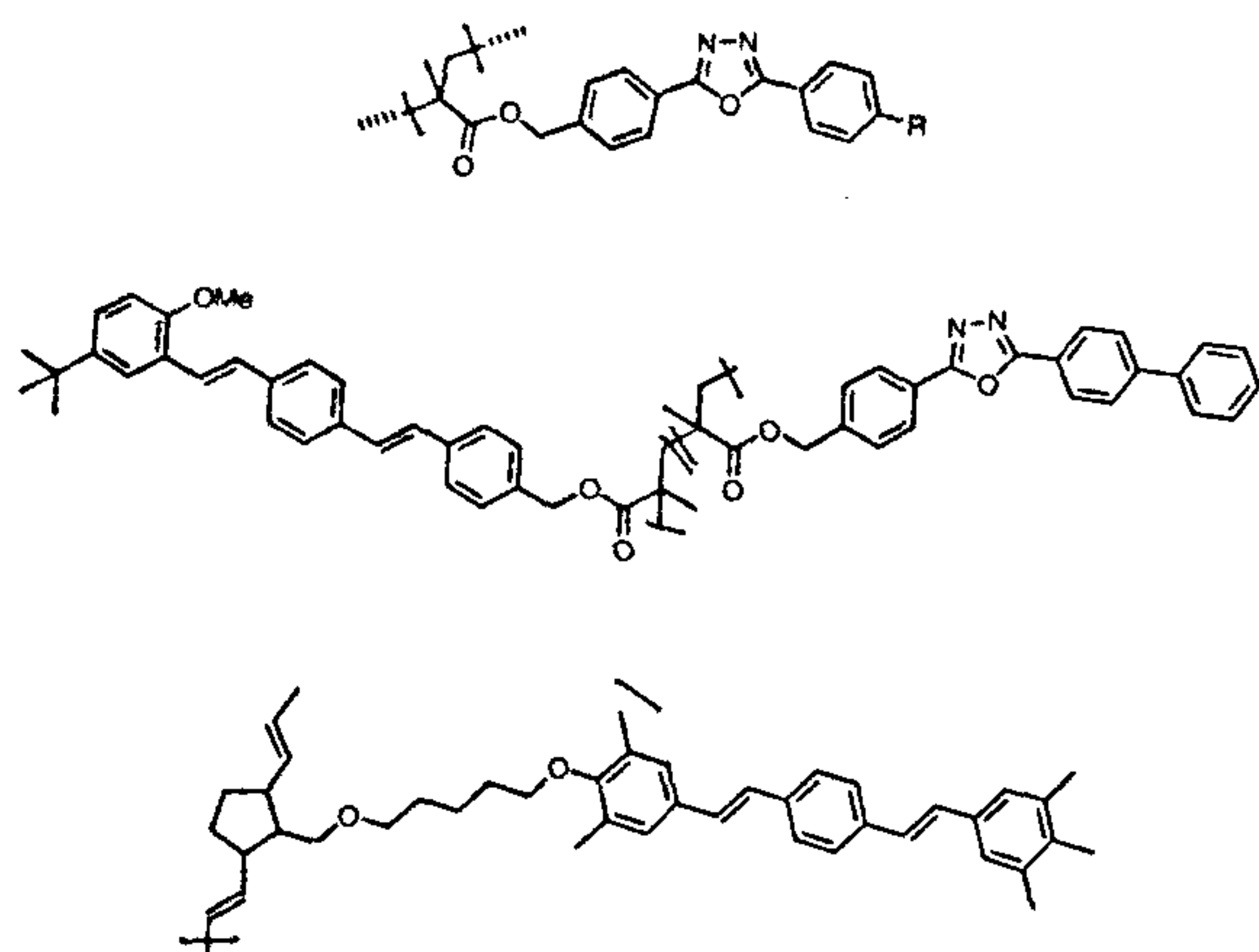
Figure 7. Representative examples of chromophores as pendent to the polymer backbone.

hindrance at silicon. Hydrosilylation is therefore the most promising procedure for the synthesis of polyvinylene-silylenes and the reaction is atom economy[23]. Indeed, reactions of arylene-spaced bisalkynylsilyl hydrides with bisalkynes under similar conditions can furnish the preparation of polymer **3** (eq. (4))[24]. The latter approach furnishes the synthesis of divinylarene-silylene-butadiyne copolymers which have shown to exhibit interesting photophysical properties. Silyl hydrides **5** are readily accessible from the silylolefination of the corresponding dithioacetals[25] and bisalkynes are obtained by Sonogashira reaction. The corresponding monomers are prepared in an analogous way for comparison.

(4)
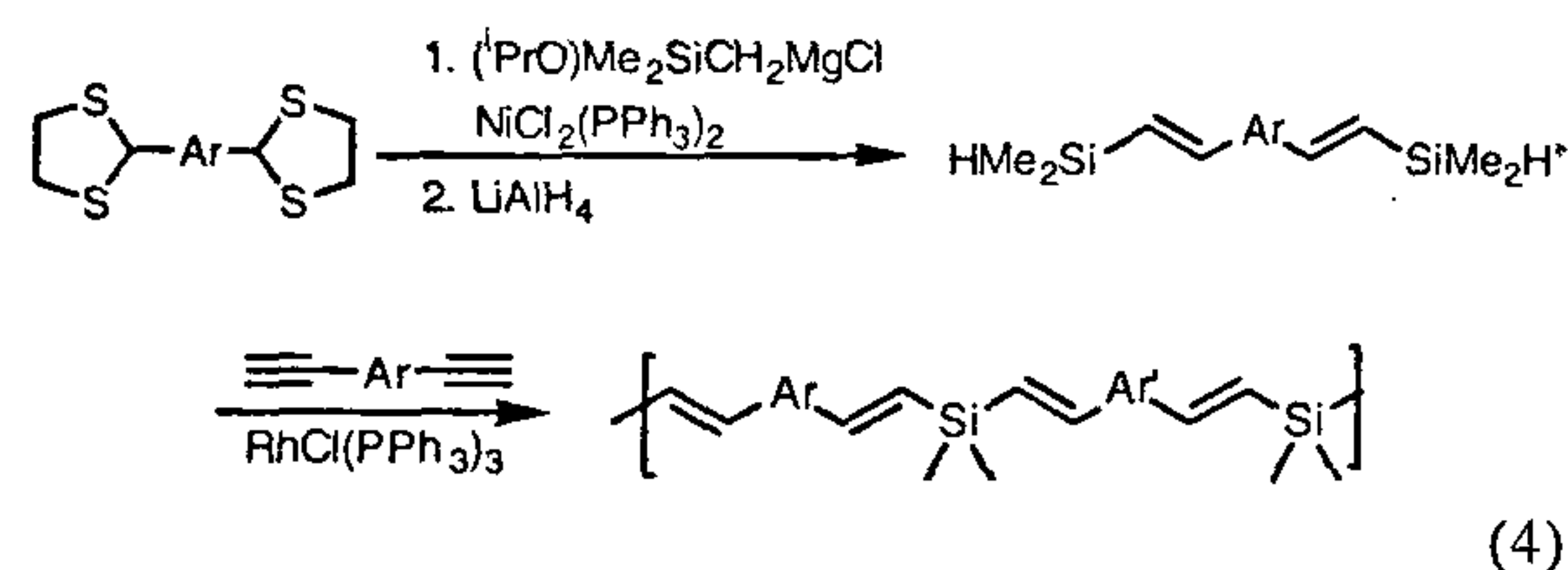
Chromophore as pendent of the polymeric backbone

Polymethacrylate and polyacrylate skeletons have been employed to hang the pendent chromophores[26]. Alternatively, ring opening metathesis polymerization of nor-bornene derivatives has been shown to be useful for the synthesis of a variety of polymers having chromophores as pendent for optoelectronic interests. Representative examples are shown in Figure 7.

Conclusions

Since the first discovery of the sandwich-like device for organic LEDs in 1987, significant advances in this area have been witnessed. Prototype devices for commercial production are expected in the near future. Chemists, in particular, synthetic organic chemists, have played a pivotal role in designing and synthesizing appropriate materials for this interdisplinary research. It is noteworthy that organometallic chemistry has provided powerful arsenal for the construction of carbon–carbon bond at the C_{sp^2} or C_{sp} centre. Compounds emitting at different wavelengths in the visible region are therefore easily accessible. This does not mean that the job has already been done. Instead, new highly *stable, long-lived* organic materials, especially those exhibiting luminescence at shorter wavelength, say, in the blue light region, remain to be a challenge for synthetic organic chemists. Whereas polymers are easier for fabrication, new design of more efficient and easily purified polymer materials will keep chemists busy in the years ahead. The chemistry thus developed could also be used for other potential optoelectronic applications. The future is bright for chemists.

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