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Synthesis and ring opening metathetic polymerisation of porphyrazine benzonorbornadiene derivatives

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Abstract

Benzonorbornadiene substituted porphyrazines are homo- and copolymerised (ROMP) with norbornene using $Cl_2(Cy_3P)_2Ru{=}CHPh$ to provide dark-green and blue polymers. These novel materials have been characterised using GPC, UV–vis and EPR spectroscopy. © 1999 Elsevier Science Ltd. All rights reserved.

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The unique electronic, optical, and photophysical properties of porphyrinic macrocycles make them attractive candidates for the design of novel polymer systems. Polymer blends or copolymers both containing phthalocyanines, for example, were found to have higher intrinsic conductivities, usually better catalytic and electrocatalytic activities as well as better electrochemical properties than the parent macrocycles.[1] In addition, polymers containing porphyrin moieties in their side chain are of interest as photocatalysts[2] and oxygen carriers which mimic living systems.[3] Among other methods,[4] radical polymerisation has found widespread application in the synthesis of polymers and copolymers of covalently bound porphyrinic ligands.[5] More recently, iterative Diels–Alder reactions have proved effective for the preparation of fused macrocyclic ladder polymers.[6]

We have described the synthesis and novel physical properties of porphyrazinethiolates,[7] aminoporphyrazines,[8] porphyrazinols[9] and complexes thereof. We have also reported a new family of tetraazamacrocycles in which one of the pyrrole rings is cleaved (seco-porphyrazines),[10] and the synthesis of *trans*-heterofunctionalised porphyrazine derivatives.[11] As a first step towards the assembly of multiporphyrazine arrays, we have linked two porphyrazinedithiolates by the mutual chelation of a nickel ion producing the first trinuclear metal-linked porphyrazine dimer.[12] The considerable need for synthetic routes leading to structurally well-defined polymers containing macrocyclic ligands, prompted us to study the ring opening metathetic polymerisation (ROMP) of porphyrazine benzonorbornadiene

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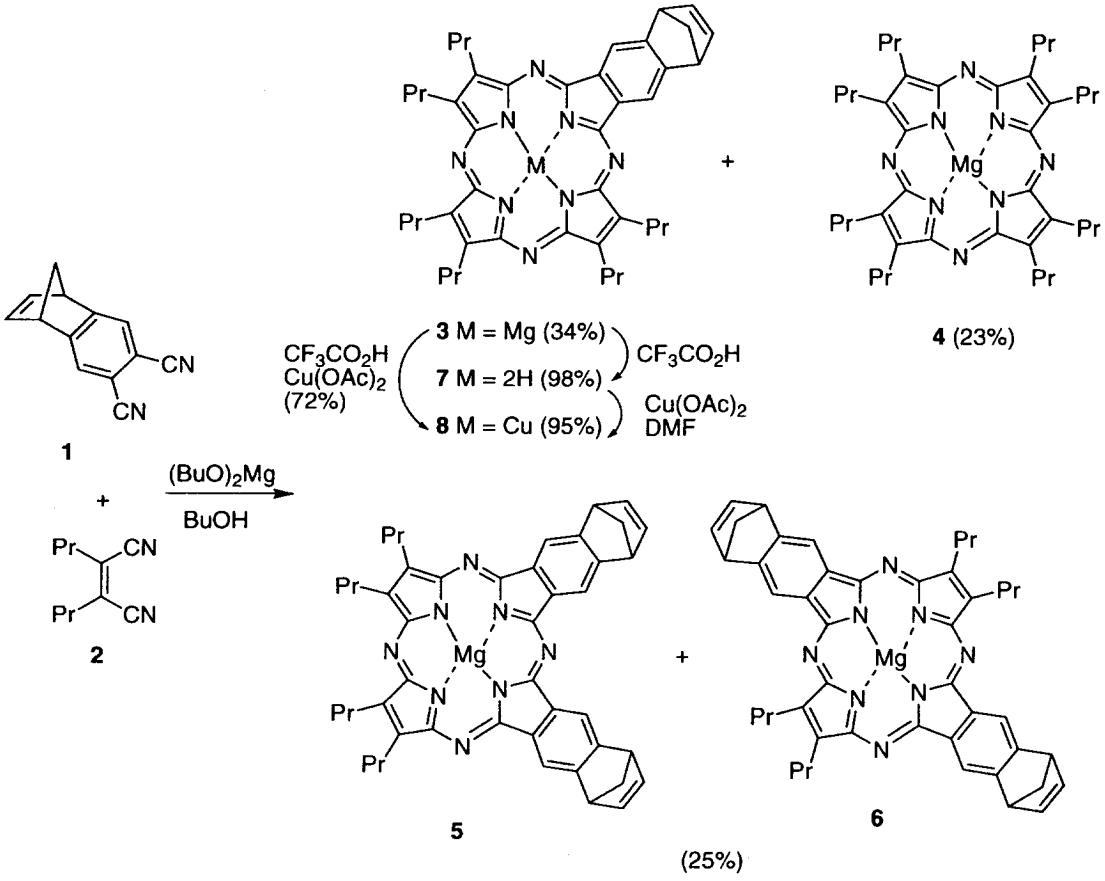
derivatives. To the best of our knowledge, this is the first time in which this strategy has been used in connection with porphyrinic macrocycles. Herein we report our initial efforts towards the preparation and study of linear ring-opening metathesis polymers derived from the novel norporphyrazines **3**, **7** and **8** using $Cl_2(Cy_3P)_2Ru{=}CHPh$.[13]

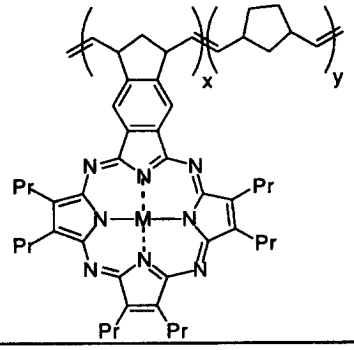
Mixed Linstead[14] macrocyclisation of dinitrile **1**[15] with a seven-fold excess of dinitrile **2**[16] using magnesium butoxide, gave the expected porphyrazine **3** (34%) after chromatography on silica along with MgOPPz **4**[16] (23%) and an inseparable mixture of porphyrazines **5** and **6** (25%) (Scheme 1). The magnesium complex **3** was demetallated with trifluoroacetic acid to produce the free base **7** (98%) which was converted into the corresponding paramagnetic copper complex **8** (95%) on reaction with one equivalent of copper(II) acetate. Alternatively, compound **8** was obtained in 72% yield directly from reaction of the magnesium complex **3** with trifluoroacetic acid in the presence of copper(II) acetate. The latter procedure proved to be the method of choice for large scale preparations of porphyrazine **8**.



Scheme 1.

The porphyrazines **3**, **7** and **8** were copolymerised with norbornene using $Cl_2(Cy_3P)_2Ru{=}CHPh$ (0.5 mol%) in degassed dichloroethane (freeze–pump–thaw method, Schlenk-tube). A coloured precipitate was formed as soon as the monomer mixture came into contact with the catalyst solution. After 5 h at room temperature, the reaction mixture was quenched by the addition of ethyl vinyl ether. Complete precipitation of the copolymer with methanol was followed by washing with methanol and acetone until the washings were clear. No unreacted porphyrazine monomer was detected in the washings or by GPC

Table 1
Ring opening metathetic polymerisation of porphyrazines under the conditions described in the text. The x and y values reflect the feed ratios (mol%) of the monomers porphyrazine and norbornene respectively



Entry	Monomer(s)	x (%)	y (%)	Yield (%)	M_w	M_n	M_w/M_n
1	**3** + norbornene	1.3	98.7	99	135000	82000	1.7
2	**3** + norbornene	0.13	99.87	99	106000	67000	1.6
3	**7** + norbornene	1.4	98.6	99	142000	83000	1.7
4	**7** + norbornene	0.14	99.86	99	116000	71000	1.6
5	**8** + norbornene	0.13	99.87	99	134000	80000	1.7
6	norbornene	0	100	99	140000	86000	1.6
7	**3** + norbornene	50	50	66	4200	4000	1.1
8	**3**	100	0	55	4500	4100	1.1
9	**7**	100	0	55	12000	8100	1.4

(vide infra). Air-dried copolymers of reasonable number–average molecular weights (M_n) and relatively narrow polydispersities (M_w/M_n) (Table 1, Entries 1–5) were obtained as blue or green materials with a rubbery texture, in essentially quantitative yields. Molecular weight distributions were determined by GPC using polystyrene as the standard in $CHCl_3$. Solutions were prepared with solvent plasticised (freshly synthesised) materials, since the air-dried copolymers were only soluble in hot pyridine.

A number of experiments established that the porphyrazines **3**, **7** and **8** indeed could be heteropolymerised with norbornene to form part of the polymer chain. When a mixture of norbornene, porphyrazine **3** and MgOPPz **4** (742:1:1) was subjected to the above conditions, only the unreactive octapropylporphyrazine **4** was recovered unchanged. Norbornene was successfully homopolymerised in the presence of the free base octapropylporphyrazine **4** giving a pale brown product (after the porphyrazine had been washed out), thus excluding significant amounts of physical mixtures of the polymer with the porphyrazine. Polymerisation of norbornene and porphyrazine **3** (1:1) (Table 1, Entry 7) resulted in the formation of a soluble ($CHCl_3$) blue oligomer that could be separated from the unreacted porphyrazine monomer **3** via gel filtration using Sephadex LH20 or Bio-Beads SX3. However, analysis of the product obtained revealed the presence of unreacted porphyrazine **3** (30% recovery), thus indicating preferential incorporation of the norbornene into the polymer backbone.

Homopolymerisations of porphyrazines **3** and **7** were carried out analogously but at 60°C and with 5 mol% of the catalyst. The low number–average molecular weights and polydispersities obtained (Table 1, Entries 8 and 9) suggest that the chain-growth was probably limited by steric factors (vide supra). Again,

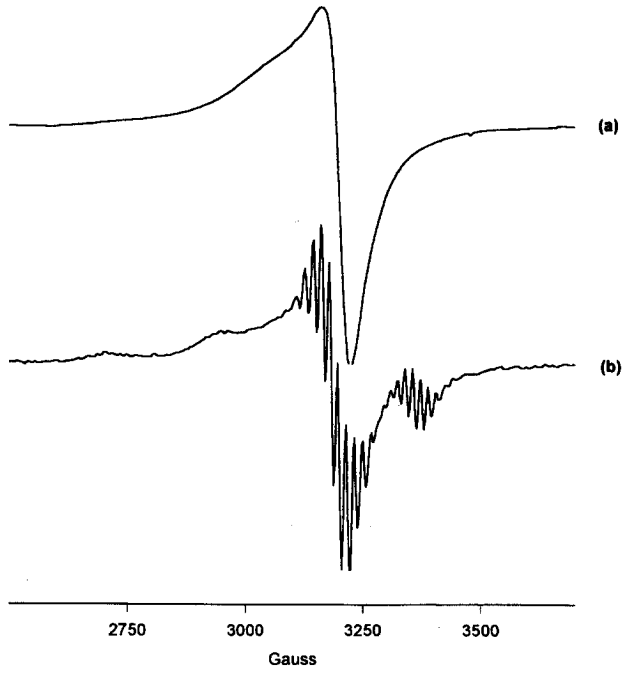


Figure 1. X-Band EPR spectra of: (a) homopolymer, and (b) copolymer

the soluble oligomers were separated from unreacted porphyrazine monomers **3** and **7** (42 and 40% recovered, respectively) via gel filtration. Interestingly, the phthalonitrile derivative **1** failed completely to undergo polymerisation under the conditions described above and was recovered unchanged.

Proton NMR spectra of the copolymers prepared using high ratios of norbornene to porphyrazine monomer (in pyridine-d_5) were essentially the same as that of the norbornene homopolymer (prepared under the same reaction conditions), while the homopolymers (in $CDCl_3$) showed only broadened resonances for the porphyrazine alkyl residues. However, the UV–vis spectra of all polymers showed the characteristic Soret and Q band absorptions resembling those of the parent macrocycles.

To examine the distribution of the Cu-porphyrazine subunits within a hetero-polymeric chain, EPR spectroscopy was employed. Although homopolymerisation of compound **8** gave poor yields of oligomerised product, that product showed the unresolved EPR signal that is the signature of a magnetically concentrated phase, as expected (Fig. 1). In contrast, the signal from the copolymer shows resolved hyperfine structure from the $^{63,65}Cu$ nuclei and resolved superhyperfine structure from the coordinating ^{14}N ligands. Such a spectrum indicates dilution of the CuPz subunit in the polymeric solid, and thus a nearly random incorporation of the CuPz 'dopant' into the growing polymer chain, rather than segregation into block copolymers. The spectrum is not as well resolved as for a highly dilute single crystal, consistent with the distribution in CuPz distances along a chain that would come from random incorporation.

This work clearly illustrates the compatibility of porphyrazine benzonorbornadiene derivatives with the ring opening metathesis polymerisation. Further studies should allow the elaboration of structurally well-defined materials with interesting novel chemical and physical properties and will be reported in due course.

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