Poly(zinc(II)-5,15-porphyrinylene) from silver(I)-promoted oxidation of zinc(II)-5,15-diarylporphyrins

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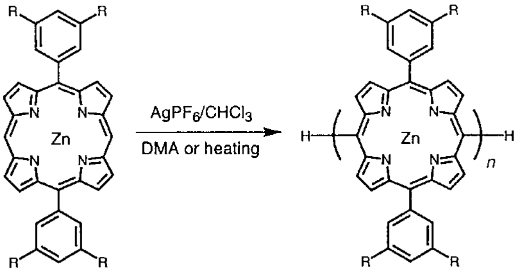
Received (in Cambridge, UK) 30th November 1999, Accepted 23rd December 1999

Zinc(II)-5,15-diarylporphyrins have been effectively polymerized to give poly(Zn(II)-porphyrinylene) in high yields in the reaction with 1.5 equiv. $AgPF_6$ in $CHCl_3$ either in the presence of 0.5% *N*,*N*-dimethylacetamide or upon heating.

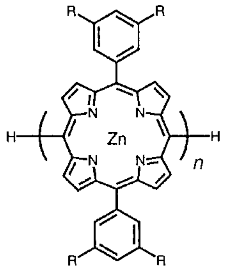
Linearly π-conjugated polymers and oligomers have attracted considerable attention in light of their potential applications in the fields of electronics, optical devices, sensors and solar energy conversion.[1] Among these, poly(arene)s represented by poly(*para*-phenylene)s (PPP), poly(pyrrole)s, and poly(thiophene)s have attracted considerable attention owing to their increasing conductivities upon doping.[2] Porphyrins are an appealing building block for the modular construction of such linear π-conjugated systems, since they offer a variety of desirable features such as rigidity, high stability, intense electronic absorption, a small band gap, strong fluorescence emission, and the possibility to tailor optical and redox properties by appropriate metallation.[3] However, to the best of our knowledge, directly linked poly(porphyrinylene) has not been reported so far. Recently we found that a *meso*–*meso* coupling reaction of 5,15-diaryl zinc(II)-porphyrins can be effected by treatment with an Ag(I) salt[4a] or by anodic electrochemical oxidation.[4b] Interestingly the *meso*–*meso* coupling regioselectivity is quite high, allowing the formation of straight and directly linked porphyrin arrays up to the octamer by the latter method.

Now we report that the Ag(I)-promoted *meso*–*meso* coupling reaction can be extended to the preparation of long poly(porphyrinylene)s simply by the addition of *N*,*N*-dimethylacetamide (DMA) or slight heating [reaction (1)]. Formally, the formation of one *meso*–*meso* bond is accompanied by the loss of two hydrogens and thus seems to need two equivalents of oxidant. This is nicely illustrated by the reaction of **1a** with 1.5 equiv. $AgPF_6$ in $CHCl_3$ at 20 °C for 4 h which gave, besides the recovery of unreacted **1a** (40–50%), **2a** (25–30%), **3a** (5–7%), and **4a** (1–2%) together with small amounts of higher oligomers (Fig. 1a).[4] In marked contrast, reaction under similar conditions but with the presence of a small amount of DMA (0.5% to $CHCl_3$) gave rise to enhanced oligomerization in only 0.5 h (Fig. 1b). The reaction mixture was examined by MALDI-TOF MS and a combined GPC–HPLC and UV-vis absorption method (Fig. 2). The former registered detectable peaks from 688 to 16500 Da (corresponding to 1- to 22-mers) with a repeat unit of *ca.* 750 Da, indicating the formation of diverse oligomeric porphyrin arrays up to the 22-mer.[5] The spectra in Fig. 2b that were taken for the GPC–HPLC fractions as their free bases[6] display progressive red-shifts and broadening of the split Soret bands and Q-bands and are consistent with the highly regioselective *meso*–*meso* coupling even for larger porphyrin arrays. On the basis of the relationship of the molecular weights of discrete oligo(porphyrinylene)s *versus* the retention time of



(1)

1a; R = Bu^t
1b; R = OC_8H_{17}



2a; *n* = 2; **3a**, *n* = 3; **4a**, *n* = 4

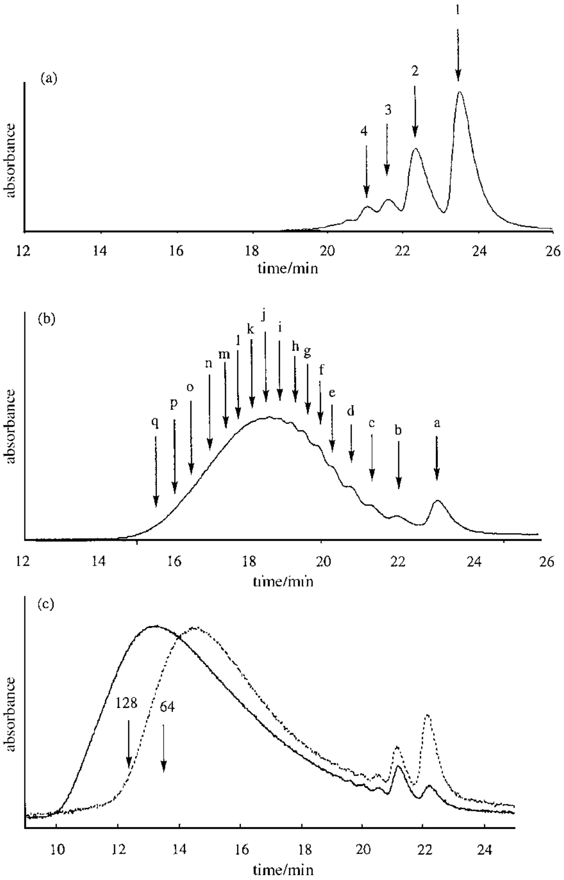


Fig. 1 GPC–HPLC charts of the reaction of **1a** and **1b** with 1.5 equiv. $AgPF_6$ in $CHCl_3$ detected at 413 nm: (a) **1a**, room temperature, 4 h, no DMA, arrows 1–4 indicate bands corresponding to **1a**, **2a**, **3a**, and **4a**, respectively; (b) **1a**, room temperature, 4 h, 0.5% DMA; (c) **1b**, 45 °C, 0.5% DMA, 11 h (dotted line); **1b**, 45°C, 0.5% DMA, 82 h (solid line), the retention times of the discrete 64-mer and 128-mer are indicated by arrows. The absorption spectra of fractions indicated by arrows a–q are shown in Fig. 2b.

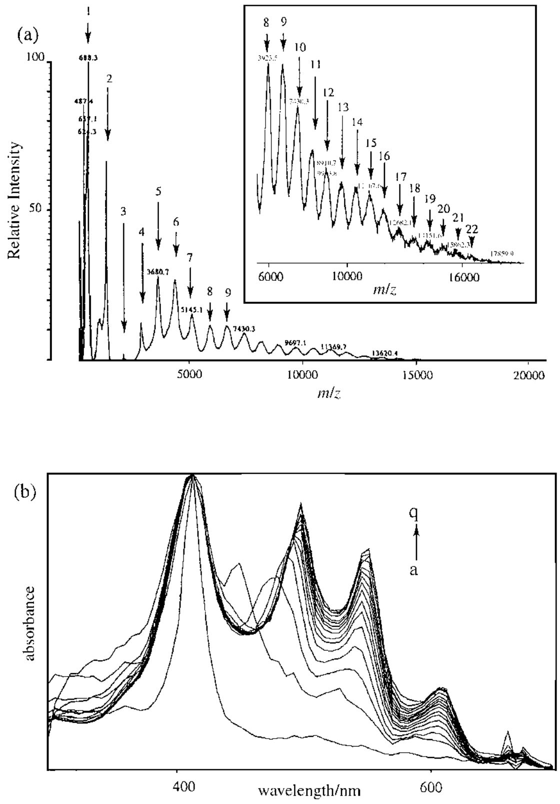


Fig. 2 Product mixture in the reaction of **1a** with 1.5 equiv. $AgPF_6$ in $CHCl_3$ containing 0.5% DMA: (a) MALDI-TOF MS spectrum; (b) absorption spectra of GPC–HPLC fractions after addition of TFA.

GPC–HPLC, we estimated M_w = 12 000 Da with a polydispersity of 1.46; the major oligomers eluting at *ca.* 19 min correspond to 8,9-mers and the detectable largest oligomers eluting at *ca.* 14.5 min correspond to *ca.* 50-mers. The polymerization depends on the amount of DMA, and is most effective upon addition of 0.5–3% DMA. The acceleration effect is only modest with less than 0.5% DMA and decreases with increasing amounts of DMA over 3%, and is completely suppressed upon addition of 20% DMA. Similar enhanced polymerization was also observed in the presence of DMF, HMPA, and DMSO with the enhancement order of DMA > DMF ≈ HMPA > DMSO. On the other hand, nitrogen bases such as pyridine, lutidine, triethylamine, and *N*,*N*-dimethylaniline were found to completely suppress the *meso–meso* coupling. It is also notable that even heating at 45 °C led to polymerization (M_w = 13 000 Da with a polydispersity of 1.37) after 24 h. In this thermally accelerated polymerization, however, the conversion of the monomer **1a** reached a maximum of *ca.* 70% after only 1–2 h but the increase of chain length proceeded rather slowly.

In the reaction of **1a**, there is a possibility that further polymerization may be interrupted owing to the poor solubility of the formed long porphyrin arrays. In order to circumvent this problem, we employed the much more soluble substrate **1b** as the starting monomer. **1b** turned out to be less reactive than **1a** probably due to its bulky dioctyloxy substituents; only 5% of **1b** was consumed even after 24 h in the reaction with 1.5 equiv. $AgPF_6$ in $CHCl_3$ at 20 °C [reaction (1)]. However, the addition of 0.5% DMA indeed accelerated the coupling to give poly(porphyrinylene) with M_w = 45 000 Da and a polydispersity of 1.7 after 24 h. As for **1a**, heating at 45 °C also led to the polymerization of **1b** (M_w = 21 500 Da with a polydispersity of 1.59), although a substantial induction period (10 h) was necessary to start the polymerization. When the reaction of **1b** with 1.5 equiv. $AgPF_6$ was conducted in the presence of 0.5% DMA at 45 °C, the polymerization proceeded extensively, giving poly(porphyrinylene)s with M_w = 75 000 Da and a polydispersity of 1.60 after 11 h, and M_w = 250 000 Da and a polydispersity of 2.78 after 82 h (Fig. 1c). Note that these large poly(porphyrinylene)s exhibit absorption and emission spectra similar to those of oligo(porphyrinylene) 64- and 128-mers of discrete size, which were separately prepared from **1b**.[7] Another merit of these polymers lies in their easy transformation to Ni(II) and Cu(II) complexes.[8]

The mechanism of this polymerization is not fully understood but can be considered to be initiated by one-electron oxidation of zinc(II)-porphyrin with silver(I) and the chain elongation process may be similar to those proposed for oxidative formation of PPP,[2a] involving a poly(5,15-dihydroporphyrinylene) intermediate which will be oxidized to poly(5,15-porphyrinylene)s. The superior acceleration effects of DMA over DMF suggest that it may play a reducing role to convert the cation radical intermediate to a biradical intermediate which may be more active for elongation of the chain.

In summary, sterically uncongested metalloporphyrins, **1a** and **1b**, can be polymerized in a regioselective manner to poly(zinc(II)-5,15-porphyrinylene)s in the reaction with silver(I) salt either in the presence of 0.5–3% of DMA or upon heating. Not fully optimized yet, it is evident that zinc(II)-5,15-diarylporphyrin can be polymerized under much milder conditions compared to the polymerization conditions of smaller aromatic and heteroaromatic molecules. Exploring synthetic conditions that allow the preparation of poly(porphyrinylene) with less polydispersity would be an interesting next target and is actively in progress in our laboratory.

This work was supported by Grants-in-Aid for Scientific Research from the Ministry of Education, Science, Sports and Culture of Japan and by CREST (Core Research for Evolutional Science and Technology) of Japan Science and Technology Corporation (JST). N. Y. is grateful for a JSPS Research Fellowship for Young Scientists.

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5 MALDI-TOF MS was measured for the reaction mixture of **1a**. The peak at 688 corresponds to a parent peak of the demetallated free base form of **1a** and the envelopes in the higher molecular weight region contain many species with variable numbers of incorporated Zn(II) ions.

6 Owing to the poor solubilities of zinc(II)-porphyrin arrays formed from **1a**, GPC–HPLC analysis was performed on the reaction mixtures of free base porphyrin arrays by addition of a small amount of TFA. The observed absorption spectra were quite similar to those of discrete long free base porphyrin arrays. The reaction mixtures of **1b** were directly analyzed as Zn(II) complexes.

7 N. Aratani, A. Osuka, Y. H. Kim, D. H. Jeong and D. Kim, submitted for publication.

8 Polymers with M_w = 6–7 × 10^4 are quite soluble in common organic solvents and are quantitatively converted to completely metallated polymers.

Communication a909444j