

A New Synthetic Method for Oligo(phenylenevinylenes) Terminated with Porphyrins

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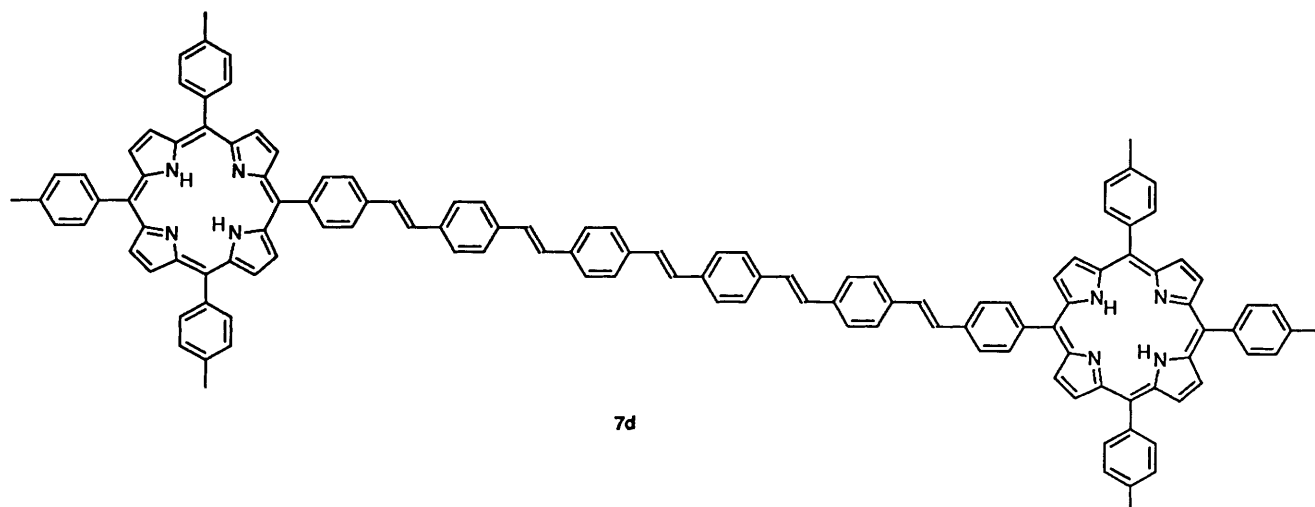
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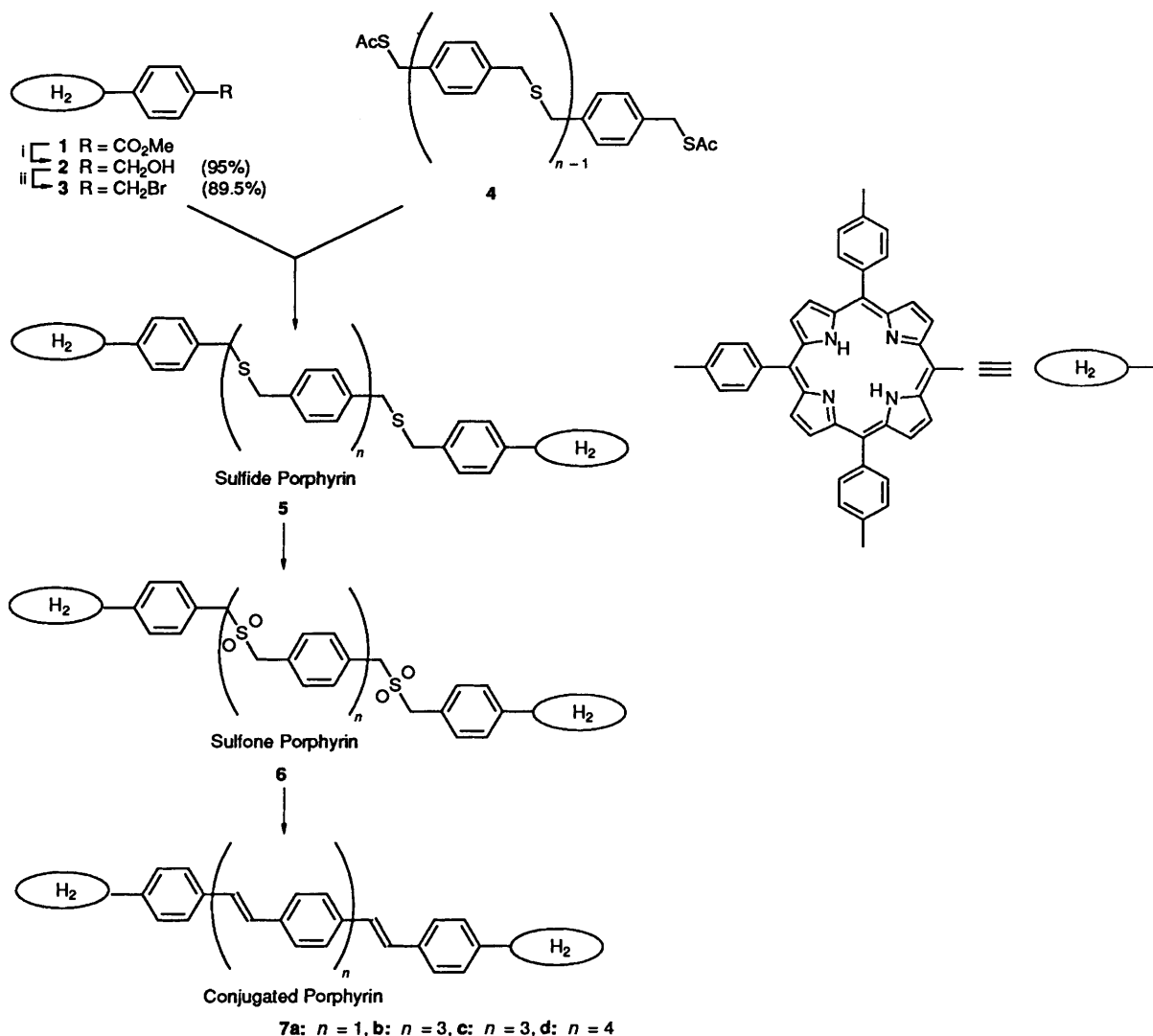
A facile, high-yield synthesis of oligo(phenylenevinylenes) terminated with porphyrins *via* the Ramberg–Backlund reaction is reported.

Molecules in which porphyrin units are linked by various bridging groups have been the subject of numerous studies in recent years.¹ These molecules are able to mimic the fundamental functions of the photosynthetic reaction centres, such as the antenna function, the stabilization of charge separation and sequential electron transfer. In addition to their importance for the understanding of biological systems, they are increasingly attracting attention as precursors for molecular electronics and materials for supermolecular chemistry. In this paper we wish to report a novel synthesis of dimeric porphyrins which are linked by extended π -systems with phenylenevinylene repeating units such as **7d**. Poly(*p*-phenylenevinylene) is also the subject of continuing research in connection with the design of battery electrodes and of electrically conducting materials.² Therefore compound **7d** is very interesting for the transport and storage of information on a molecular basis. Recently a molecule consisting of two porphyrins connected through a stilbene group has been prepared in about 30% yield by MuMury coupling.³ This system is a highly efficient electron acceptor, for the stilbene bridge is coplanar with the two porphyrin frameworks in the charged state.³ K. Müllen has prepared a number of oligo(phenylenevinylenes) by the Wittig reaction to study the mechanism for the charge storage, the yields being in the range of 30–40%.⁴ These yields are too low to allow construction of more complex molecular systems due to low yields in the carbon–carbon bond forming steps. More efficient methods are required to construct the more complicated systems involving linkage of more than one porphyrin unit. Our method is based on the Ramberg–Backlund reaction as shown in Scheme 1.⁵ This method is far superior to other ones for the following reasons. First, phenylenevinylene repeating units **4** are readily prepared by the simple reaction of the appropriate benzyl bromides and thiol esters as shown in

Scheme 2. It is very important to control the length of phenylenevinylene units for the study of new organic conducting oligomers, and this can be readily accomplished by the present method. Next, the yields of connecting two porphyrins with **4** are excellent, because the carbon–sulfur bond is more readily formed than the carbon–carbon bond. The yield of the double bond formation is also good, for example, treatment of sulfone porphyrin **6d** with KOH and CCl₄ in THF (tetrahydrofuran) gave **7d** in 75% yield, in which five double bonds were formed in one step. This yield is remarkable in the field of porphyrin chemistry. Finally, terminal groups are not limited to porphyrins, but various functional moieties can be connected with oligo(phenylenevinylenes) by this method.

The preparation of **7d** is described as a typical example. The requisite starting porphyrin **3** was readily prepared from porphyrin ester **1** by reduction with LiAlH₄ followed by bromination with CBr₄ and triphenylphosphine. A solution of NaOH (27.1 mg, 0.17 mmol) in MeOH (2.58 cm³) was added to a solution of porphyrin **3** (254 mg, 0.34 mmol) and **4d** (112 mg, 0.17 mmol) in THF (50 cm³). After the mixture had been stirred overnight, it was poured into water and extracted with methylene dichloride. The crude product was purified by column chromatography (silica gel, methylene dichloride) and subsequent recrystallization from CHCl₃–MeOH gave sulfide porphyrin **5d** (280 mg, 83% yield). A solution of **5d** (250 mg, 0.13 mmol) and *m*-chloroperbenzoic acid (282 mg, 1.3 mmol) in methylene dichloride (300 cm³) was stirred at room temp. for 3 h. The reaction mixture was then poured into water and extracted with methylene dichloride. The extract was washed with aqueous sodium hydrogen carbonate and water and dried (Na₂SO₄). The crude product obtained by evaporation of the solvent was purified by the recrystallization from MeOH–CHCl₃ to give sulfone porphyrin **6d** (230 mg, 91% yield).





Scheme 1 Reagents and conditions: i, LiAlH_4 , THF, 0–5 °C; ii, CBr_4 , Ph_3P , room temp.; iii, NaOH , MeOH –THF, room temp.; iv, *m*-CPBA, CH_2Cl_2 , room temp.; v, CCl_4 , NaOH , THF, room temp.

Table 1 Preparation of **5**, **6** and **7**

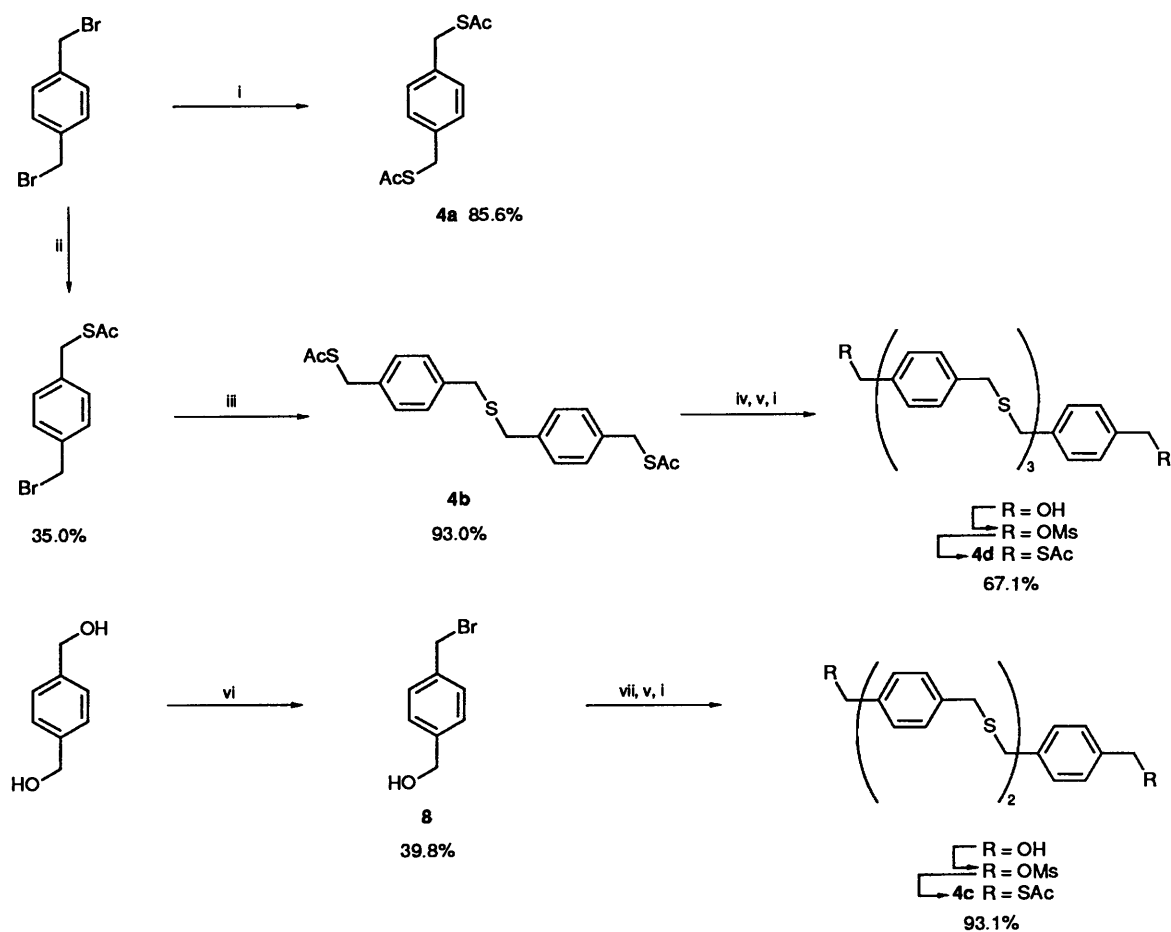
<i>n</i>	Yield (%)		
	5	6	7
1	98	89	87
2	91	90	84
3	95	90	75
4	86	91	73

To a solution of **6d** (120 mg, 0.058 mmol) in THF (100 cm^3) was added CCl_4 (0.234 cm^3 , 2.43 mmol) and a solution of KOH (110.7 mg, 0.058 mmol) in MeOH (1.87 cm^3). The resulting mixture was stirred at room temp. for 10 h and poured into water. After extraction with CHCl_3 and the usual work-up, the crude product was purified by column chromatography and recrystallized from CHCl_3 – MeOH to give compound **7d** (73 mg, 73% yield).

As the Ramberg–Becklund reaction of dibenzyl sulfone gives *trans*-stilbene stereoselectively,⁵ the double bonds in **7d** should be all *trans*. Thus porphyrin dimers linked with various lengths of phenylenevinylene unit are prepared in excellent yields by very simple procedures. The results are summarized in Table 1.* The absorption maxima of porphyrin Soret bands of **7** were

slightly red shifted and became broader than those of meso-tetraphenylporphyrin due to π -conjugation effects. However, they are little affected by the length of π -conjugation, for the porphyrin rings are not coplanar with phenylenevinylene units. This is in sharp contrast with the reduction potentials of **7**. The reduction potentials were measured by cyclic voltammetry and the results are summarized in Table 2. The redox potentials are shifted to less negative with increasing chain length of the

* All new compounds gave satisfactory elementary analyses and spectroscopic data (IR, NMR, UV–VIS, and mass spectra). Mass spectra were measured by FAB technique, where $\text{M} + 2$ peaks appeared as parent ions. Spectroscopic data for **7a** $\lambda_{\text{max}}(\text{CH}_2\text{Cl}_2)/\text{nm}$ 421, 518, 555, 593 and 648; $\delta_{\text{H}}(400 \text{ MHz}; \text{CDCl}_3)$ 8.90–8.86 (m, 16 H), 8.24 (d, 4 H), 8.10 (d, 12 H), 7.94 (d, 4 H), 7.75–7.49 (m, 20 H), 2.71 (s, 12 H), 2.68 (s, 6 H) and -2.75 (s, 4 H) (Found: M^+ , 1440. $\text{C}_{104}\text{H}_{78}\text{N}_8$ requires M , 1438). **7b** $\lambda_{\text{max}}(\text{CH}_2\text{Cl}_2)/\text{nm}$ 421, 518, 554, 594 and 649; $\delta_{\text{H}}(\text{CDCl}_3)$ 8.89–8.85 (m, 16 H), 8.22 (d, 4 H), 8.10 (d, 12 H), 7.90 (d, 2 H), 7.70–7.46 (m, 26 H), 2.70 (s, 18 H) and -2.75 (s, 4 H) (Found: M^+ , 1542. $\text{C}_{112}\text{H}_{84}\text{N}_8$ requires M , 1540). **7c** $\lambda_{\text{max}}(\text{CH}_2\text{Cl}_2)/\text{nm}$ 422, 518, 554, 594 and 648; $\delta_{\text{H}}(\text{CDCl}_3)$ 8.89–8.85 (m, 16 H), 8.20 (d, 4 H), 8.10 (d, 12 H), 7.90 (d, 4 H), 7.68–7.43 (m, 32 H), 2.70 (s, 18 H) and -2.75 (s, 4 H) (Found: M^+ , 1644. $\text{C}_{120}\text{H}_{90}\text{N}_8$ requires M , 1642). **7d** $\lambda_{\text{max}}(\text{CH}_2\text{Cl}_2)/\text{nm}$ 422, 518, 555, 592 and 648; $\delta_{\text{H}}(\text{CDCl}_3)$ 8.80–8.65 (m, 16 H), 8.20 (d, 4 H), 8.10 (d, 12 H), 7.88 (d, 4 H), 7.67–7.44 (m, 38 H), 2.70 (s, 18 H) and -2.75 (s, 4 H) (Found: M^+ , 1746. $\text{C}_{128}\text{H}_{96}\text{N}_8$ requires M , 1744).



Scheme 2 Reagents and conditions: i, AcSH (3 equiv.), DBU, THF, room temp.; ii, AcSH (1 equiv.), DBU, THF, room temp.; iii, Na₂S, acetone, room temp.; iv, **8**, NaOH, MeOH-THF room temp.; v, MeSO₂Cl, Et₃N, CH₂Cl₂, vi, CBr₄, Ph₃P, THF, room temp.; vii, **4a**, NaOH, MeOH-THF

Table 2 Redox potentials of **7** and reference compounds^a

Compound	E_1/V	E_2/V	E_3/V	E_4/V
7a	-1.25	-1.37	-1.84	
7b	-1.20	-1.36	-1.82	-2.17
7c	-1.17	-1.36	-1.81	-2.05
7d	-1.16	-1.36	-1.80	-2.04
TTP ^b	-1.39			
Phenylenevinylene ^c	-2.26	-2.72		

^a Cyclic voltammetry was performed at a Pt electrode with solution of 5×10^{-4} mol dm⁻³ solution in DMF, 0.1 mol dm⁻³ Bu₄NClO₄ as supporting electrolyte. All potentials are expressed in volts vs. Ag/AgCl (calibration with Cp₂Fe/Cp₂Fe⁺ taken to have 0.352 V). ^b meso-Tetratolylporphyrin. ^c Ar-CH=CH-C₆H₄-CH=CH-Ar, ref. 4.

oligomers. The first electron transfer may be understood as a charging of the porphyrin unit and then the phenylenevinylens should be charged. The redox potentials are much less negative than those of isolated porphyrins or phenylenevinylens. This fact suggests that the enlarged conjugation of the entire system is attained in the charged state of **7**, in which porphyrin rings are coplanar with phenylenevinylene units.

In summary, we present a new strategy for the construction of conjugated oligomers with a well defined structure such as **7d**, oligo(phenylenevinylens) terminated with two porphyrins. This method will open a new way to produce organic molecular

devices, for it may be possible to prepare oligomers showing almost the same band gap to parent polymers by controlling the conjugation length which is the most important for organic semiconductors.⁶ Such work is now in progress.

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