

Synthesis and Properties of Thiophene–Cyclopentadienone Cooligomers

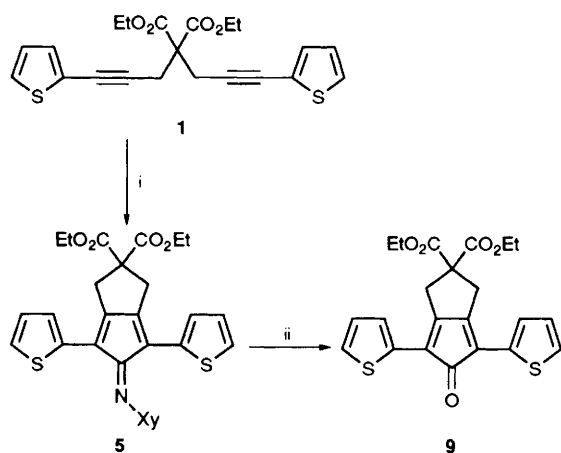
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Thiophene–cyclopentadienone cooligomers, which have long absorption maxima in the VIS–near IR region and low band-gaps (*ca.* 1.3 eV), are synthesized.

Polythiophenes have been the focus of research on conducting polymers and molecular electronics during the last ten years.¹ Current interest has been directed towards the synthesis of thiophene-based polymers containing other unique π -conjugated ring systems in the main chain because of the possibilities for developing novel electronic structures, such as low band-gaps ($E_g < 1.5$ eV) in the neutral state.^{2,3} We have already shown, in the synthesis of a thiophene–silole copolymer, that the combination of an electron-rich thiophene ring and an electron-deficient silole ring causes considerable perturbation in the π -electron system.⁴ We now pay attention to the unique electronic properties of the cyclopentadienone ring⁵ and use it instead of the silole ring as



Scheme 1 Reagents and conditions: i, 2,6-xylyl isocyanide, Ni(cod)₂, THF; ii, CSA, THF/H₂O. Xy = 2,6-xylyl.

the electron-deficient component. Reported herein is the first synthesis⁶ of thiophene–cyclopentadienone cooligomers as a model for their copolymers.

We have already reported the two step synthesis of cyclopentadienone rings based on the nickel(0)-promoted intramolecular cyclization of diynes with isocyanides.⁷ We have now applied this procedure to thiophene containing diynes, as represented by the synthesis of three-ring systems shown in Scheme 1.

The intramolecular cyclization of diynes **1–4** with 2,6-xylyl isocyanide (2 equiv. per diyne unit) was carried out in the presence of bis(1,5-cyclooctadiene)nickel(0), Ni(cod)₂ (1 equiv. per diyne unit) to form the corresponding iminocyclopentadienes **5–8** in 25–84% yields. **5–8** were subsequently hydrolysed by use of D-10-camphorsulfonic acid (CSA, 1 equiv. per iminocyclopentadiene ring) in aqueous THF to afford the corresponding cyclopentadienones **9–12** in 45–72% yields.

The three-ring system of thiophene–cyclopentadienone cooligomer, **9**, is obtained as blue needles, and the five-ring system, **11**, is a blue–green solid. Both **9** and **11** are soluble in common organic solvents such as THF, CH₂Cl₂, and CHCl₃. Compound **9** is air stable. Whilst **11** is also air stable in the solid state, it gradually decomposes in solution even under a nitrogen atmosphere.

The UV–VIS–near IR absorption data, summarized in Table 1, indicate that the T–C and T–I combinations cause considerable red shifts compared with the thiophene homologomers (T = thiophene, C = cyclopentadienone, I = iminocyclopentadiene) and that the exchange of an iminocyclopentadiene ring for a cyclopentadienone ring leads to large bathochromic shifts. For example, the exchange in **5** (λ_{\max} 507 nm) giving **9** (λ_{\max} 587 nm) leads to *ca.* 80 nm red

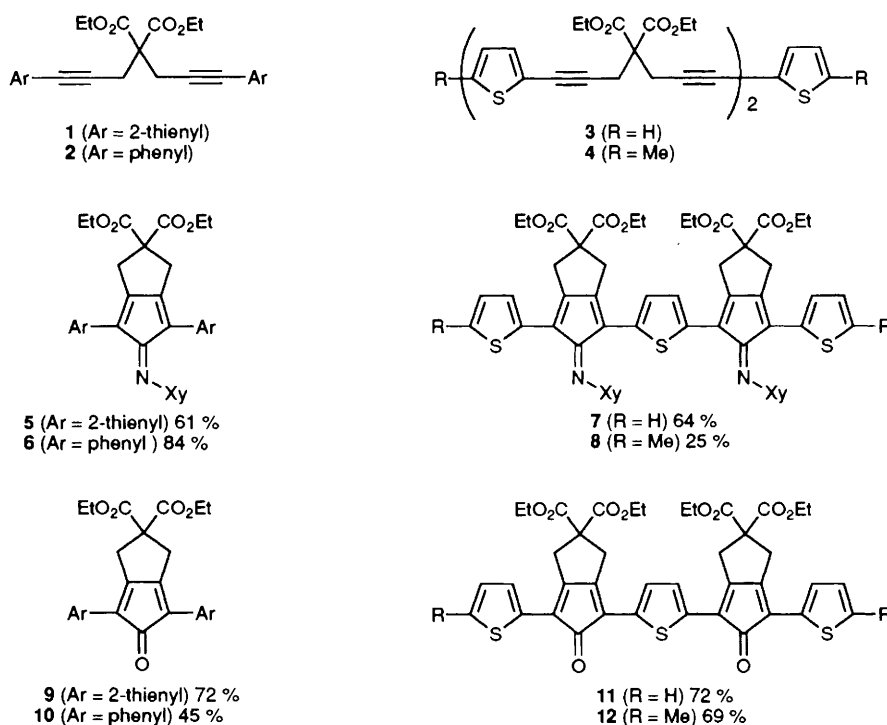


Table 1 UV-VIS-near IR absorption data for thiophene-imino-cyclopentadiene cooligomers, thiophene-cyclopentadienone cooligomers, and thiophene homooligomers.^a

Compound	UV-VIS-near IR absorption	
	λ_{\max}/nm	$\log \epsilon$
5	507	3.60
6	454	3.56
7	615	4.07
8	623	4.09
9	587	3.58
10	504	3.54
11	695	4.14
12	706	4.15
TTT ^b	353 ^c	
TTTTT ^b	418 ^c	

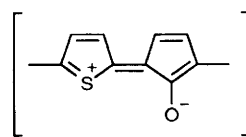
^a In chloroform, unless otherwise stated. ^b Ref. 8, T = thiophene. ^c In benzene.

shifts. The three-ring system **9** also displays *ca.* 80 nm red shifts compared to the phenyl analogue **10** (λ_{\max} 504 nm), demonstrating the uniqueness of the T-C combination. In particular, the five-ring systems, **11** (λ_{\max} 695 nm) and **12** (λ_{\max} 706 nm), exhibit about 110–120 nm red shift compared with **9**. The HOMO–LUMO separation gaps of **11** (1.3 eV) and **12** (1.2 eV), estimated from the absorption edges (λ_{edge} 960 and 1050 nm, respectively), are rather small. These large bathochromic shifts observed with T–C cooligomers may be ascribed not to the resonance effect such as **A**, but to the contribution of the relatively low LUMO of the cyclopentadienone ring (owing to the inductive effect of the carbonyl group), in light of the following two spectral properties. (1) The IR absorption peak (1718 cm^{-1}) of the carbonyl group of **13**[†] lies in a relatively higher region than that of isolated cyclopentadienone **14** (1690 cm^{-1}).^{7b} (2) Small solvent effects of UV–VIS spectra of **9** have been observed on changing from hexane (λ_{\max} 571 nm) to ethanol (λ_{\max} 577 nm).

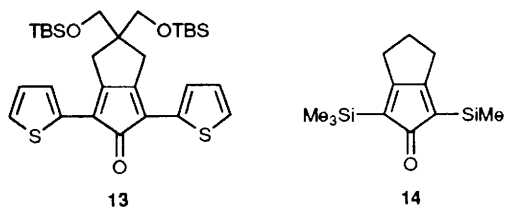
To investigate the electrochemical properties, we performed cyclic voltammetry on the five-ring systems, **11** and **12**.[‡] While **11** has irreversible two redox processes with anodic peak potentials (E_{pa}) at 0.85 and 1.00 V (*vs.* SCE), **12** shows two similar irreversible redox processes with lower E_{pa} at 0.76 and 0.85 V, respectively, due to the inductive effects of the methyl substituents.

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A



13

14

Footnotes

[†] **13** was prepared in essentially the same manner as **9** from 4,4-di(tert-butyldimethylsilyloxymethyl)-1,7-di(2-thienyl)hepta-1,4-diyne *via* two steps: nickel-promoted cyclization (78%) and hydrolysis (66%).

[‡] Cyclic voltammograms were obtained by single scan of a 10^{-4} mol dm^{-3} solution of **11** or **12** in PhCN with $\text{Bu}^n_4\text{NClO}_4$ (TBAP) (0.1 mol dm^{-3}) and a Pt electrode between 0.00 and +1.10 V at 100 mV s^{-1} .

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