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THE RIGIDIFICATION OF THE π -CONJUGATED SYSTEM: AN EFFICIENT NEW STRATEGY TOWARDS SMALL BANDGAP SEMI-CONDUCTORS

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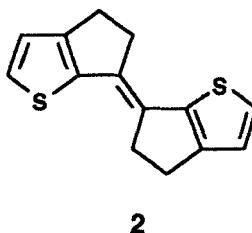
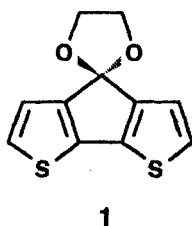
Abstract A new synthetic approach for the reduction of the bandgap of molecular and polymeric conjugated systems is presented.

INTRODUCTION

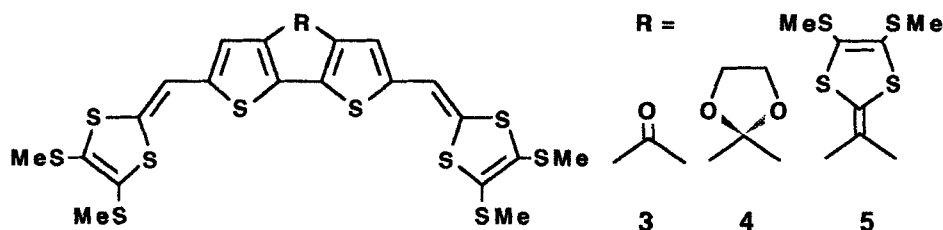
The design of small bandgap (E_g) conjugated systems has become one of the main challenge in the field of organic conductors since besides potential applications in electronic and photonic devices, small or even vanishing bandgaps open exciting perspectives towards intrinsic conductivity. Most of recent work devoted to this problem has been focused on poly(thiophene) (PT) and until now, the reduction of E_g has been achieved by increasing the quinonoid character of the conjugated backbone. We propose here an alternative strategy based on the rigidification of the conjugated system. This new approach allows both a reduction of bond-length alternation, and the suppression of the rotational disorder which severely limits the decrease of E_g .

SMALL BANDGAP RIGID CONJUGATED SYSTEMS

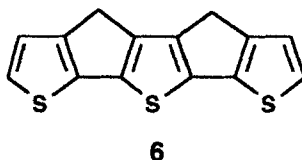
A first illustration of the efficiency of this strategy is provided by the synthesis of new conducting polymers derived from rigidified bithiophene (**1**) and dithienylethylene (**2**). Compared to their non-rigid respective analogues these polymers show a decrease of E_g from 2.20 to 1.20 eV for poly(bithiophene)¹ and from 2.00 to 1.40 eV for poly(dithienylethylene).²



The extension of this strategy to the oligothiophene-tetrathiafulvalene hybrid conjugated system³ achieved in (3-5) led in each case to a dramatic reduction of the HOMO-LUMO gap while the optical spectrum of thin solid films confirms the small bandgap ($E_g = 1.20$ eV) of these new molecular semi-conductors.⁴



As a further step towards fully rigid PT, a rigidified analogue of terthienyl (6) has been synthesized as a simplified model compound.



Whereas both the CV and the optical spectrum of the resulting polymer indicate a bandgap of 1.20 eV compared to 2.30 eV for poly(terthienyl), the considerable decrease of the HOMO-LUMO gap from 3.00 to 1.20 eV observed between terthienyl and 6 strongly suggests that very small and perhaps vanishing bandgaps can be reached by rigidification of longer systems.

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