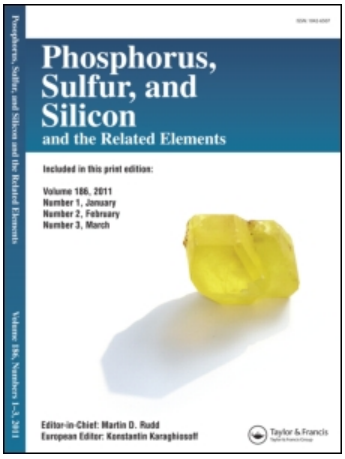


Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

The Rigidification of the x-Conjugated System: An Effcient New Strategy Towards Small Bandgap Semi-Conductors

Jean Roncali[a]; Christine Thobie-gautier[a]; Hugues Brisset[a]
[a] Ingénierie Moléculaire et Matériaux Organiques EP CNRS 66, Angers, France

To cite this Article Roncali, Jean , Thobie-gautier, Christine and Brisset, Hugues(1994) 'The Rigidification of the x-Conjugated System: An Effcient New Strategy Towards Small Bandgap Semi-Conductors', Phosphorus, Sulfur, and Silicon and the Related Elements, 95: 1, 513 — 514
To link to this Article: DOI: 10.1080/10426509408034299
URL: http://dx.doi.org/10.1080/10426509408034299

Phosphorus, Sulfur, and Silicon, 1994, Vol. 95-96, pp. 513-514
Reprints available directly from the publisher
Photocopying permitted by license only

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

JEAN RONCALI, CHRISTINE THOBIE-GAUTIER AND HUGUES BRISSET
Ingénierie Moléculaire et Matériaux Organiques EP CNRS 66, Université d'Angers, 2 Bd Lavoisier 49045 Angers.France

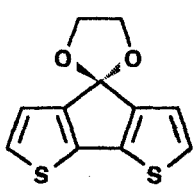
Abstract A new synthetic approach for the reduction of the bandgap of molecular and polymeric conjugated systems is presented.

INTRODUCTION

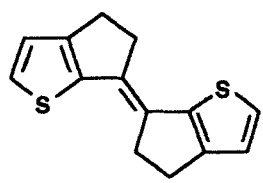
The design of small bandgap (Eg) conjugated systems has become one of the main challenge in the field of organic conductors since besides potential applications in electronic and photonic devices, small or even vanishing bandgaps open exciting perspectives towards intrinsic conductivity. Most of recent work devoted to this problem has been focused on poly(thiophene) (PT) and until now, the reduction of Eg 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 Eg.

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 Eg from 2.20 to 1.20 eV for poly(bithiophene)[1] and from 2.00 to 1.40 eV for poly(dithienylethylene).[2]

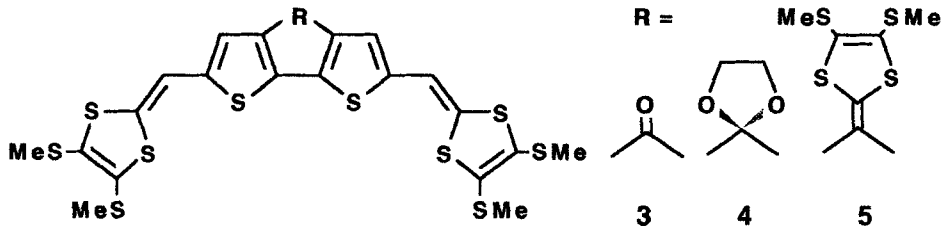


1

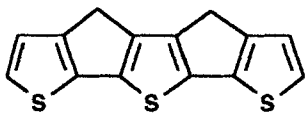


2

The extension of this strategy to the oligothiophene-tetrathiafulvalene hybrid conjugated system[3] 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 (Eg = 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.



6

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.

REFERENCES

1. H. Brisset, C. Thobie-Gautier, M. Jubault, A. Gorgues and J. Roncali, J. Chem. Soc. Chem. Commun., 1265, (1994)

2. J. Roncali, C. Thobie-Gautier, E. Elandaloussi and P. Frère, J. Chem. Soc. Chem. Commun. (in the press)

3. J. Roncali, M. Giffard, P Frère, M Jubault and A. Gorgues, J. Chem. Soc. Chem. Commun. 689, (1993).

4. H. Brisset, C. Thobie-Gautier, M. Jubault, A. Gorgues and J. Roncali, J. Chem. Soc. Chem. Commun. (in the press)