Antibatic photovoltaic response in zinc-porphyrin-like oligothiophenes

We present the synthesis of oligohexylthiophenes starting from 3, 4’-dihexyl-[2, 2’]-bithiophene (1) 3, 4’, 4”, 4’’-tetrahexyl-[2, 2’, 5’, 2”; 5”, 2’’]-quaterthiophene (2), 3, 4’, 4”, 4’’-octahexyl-[2, 2’, 5’, 2”; 5”, 2’’; 5”’, 2’’’]-octithiophene (3) and 3, 4’, 4”, 4’’-octahexyl-[2, 2’. 5’, 2”; 5”, 2’”; 5”’, 2’’”; 5””; 2’’’; 5”’’, 2’’’’; 5”’’’, 2’’’’’]-hexadecathiophene (4) by regioselective bromination using N-bromosuccinimide and regioselective lithiation using lithiumdiisopropylamide in ethylbenzene/THF/heptane followed by reaction with trimethyl-stannylchloride and subsequent palladium catalysed Stille coupling. We further synthesised 5,15-bis(3, 4’, 4”, 4’’, 4’’, 4’’’, 4’’’, 4’’’’-octahexyl-[2, 2’. 5’, 2”; 5”, 2’”; 5”’, 2’’”; 5””; 2’’’; 5”’’, 2’’’’; 5”’’’, 2’’’’’]-hexadecathiophene (4) by regioselective bromination using N-bromosuccinimide and regioselective lithiation using lithiumdiisopropylamide in ethylbenzene/THF/heptane followed by reaction with trimethyl-stannylchloride and subsequent palladium catalysed Stille coupling. All the products were characterised by size exclusion chromatography (SEC), NMR, MALDI-TOF and elemental analysis and purified by preparative SEC before subjecting them to photophysical studies. UV-vis and emission spectroscopy were used to determine quantum yields and energy transfer. The photon balance was established and used to rationalise the photovoltaic behaviour of 4 and 5. While 4 gave rise to photovoltaic devices giving a moderate photovoltaic response that was symbatic with the absorption spectrum, 5 showed a photovoltaic response that was antibatic with a part of the absorption spectrum of the zinc-porphyrin constituent. We ascribe this behaviour to efficient internal conversion of the energy absorbed by (and the energy transferred to) the zinc-porphyrin constituent. (c) 2004 Elsevier B.V. All rights reserved.

Direct emissive pattern formation in PPV-type polymer with built-in photoresist properties and the application to light emitting devices

General information
Publication status: Published
Organisations: Solar Energy Programme, Risø National Laboratory for Sustainable Energy
Contributors: Krebs, F. C., Spanggaard, H.
Pages: 53-59
Publication date: 2005
Peer-reviewed: Yes

Publication information
Journal: Synthetic Metals
Volume: 148
ISSN (Print): 0379-6779
Ratings:
Scopus rating (2005): SJR 0.923 SNIP 0.786
Web of Science (2005): Indexed yes
Original language: English
DOIs:
Significant improvement of polymer solar cell stability

General information
Publication status: Published
Organisations: Solar Energy Programme, Risø National Laboratory for Sustainable Energy
Contributors: Krebs, F. C., Spanggaard, H.
Pages: 5235-5237
Publication date: 2005
Peer-reviewed: Yes

Publication information
Journal: Chemistry of Materials
Volume: 17
Issue number: 21
ISSN (Print): 0897-4756
Ratings:
Scopus rating (2005): SJR 2.739 SNIP 1.942
Web of Science (2005): Indexed yes
Original language: English
DOIs:
10.1021/cm051320q

Synthesis, light harvesting, and energy transfer properties of a zinc porphyrin linked poly (phenyleneethynylene)

General information
Publication status: Published
Organisations: Risø National Laboratory for Sustainable Energy, Solar Energy Programme
Contributors: Nielsen, K., Spanggaard, H., Krebs, F. C.
Pages: 1180-1189
Publication date: 2005
Peer-reviewed: Yes

Publication information
Journal: Macromolecules
Volume: 38
ISSN (Print): 0024-9297
Ratings:
Scopus rating (2005): SJR 2.623 SNIP 1.645
Web of Science (2005): Indexed yes
Original language: English
DOIs:
10.1021/ma048489u

Synthesis of conjugated polymers containing terpyridine-ruthenium complexes: Photovoltaic applications

General information
Publication status: Published
Organisations: Risø National Laboratory for Sustainable Energy, Solar Energy Programme
Contributors: Duprez, V., Biancardo, M., Spanggaard, H., Krebs, F. C.
Pages: 10436 -10448
Publication date: 2005
A brief history of the development of organic and polymeric photovoltaics

In this paper an overview of the development of organic photovoltaics is given, with emphasis on polymer-based solar cells. The observation of photoconductivity in solid anthracene in the beginning of the 19th century marked the start of this field. The first real investigations of photovoltaic (PV) devices came in the 1950s, where a number of organic dyes, particularly chlorophyll and related compounds, were studied. In the 1980s the first polymers (including poly(sulphur nitride) and polyacetylene) were investigated in PV cells. However, simple PV devices based on dyes or polymers yield limited power conversion efficiencies (PCE), typically well below 0.1%. A major breakthrough came in 1986 when Tang discovered that bringing a donor and an acceptor together in one cell could dramatically increase the PCE to 1%. This concept of heterojunction has since been widely exploited in a number of donor-acceptor cells, including dye/dye, polymer/dye, polymer/polymer and polymer/fullerene blends. Due to the high electron affinity of fullerene, polymer/fullerene blends have been subject to particular investigation during the past decade. Earlier problems in obtaining efficient charge carrier separation have been overcome and PCE of more than 3% have been reported. Different strategies have been used to gain better control over the morphology and further improve efficiency. Among these, covalent attachment of fullerenes to the polymer backbone, creating so-called double-cable polymers, is the latest. The improved PCE of plastic solar cells combined with increased (shelf and operating) lifetime, superior material properties and available manufacturing techniques may push plastic PVs to the market place within a few years. (C) 2004 Elsevier B.V. All rights reserved.
Electroluminescent devices of the homopolymer itself and of the zinc-porphyrin containing polymer were prepared and the nature of the electroluminescence was characterized. The homopolymer segments were found to optically pump the emission of the zinc-porphyrin dye moieties. The homopolymer exhibits blue-green emission and the zinc-porphyrin linked homopolymers emit near-infrared/infrared light. This was demonstrated to be due to electroluminescence pumping of the zinc-porphyrin moieties that were covalently linked to homopolymer material. When only one zinc-porphyrin dye was incorporated into the backbone of each homopolymer molecule complete suppression of homopolymer electroluminescence was observed with exclusive near-infrared emission. (C) 2004 Elsevier B.V. All rights reserved.

Production of large-area polymer solar cells by industrial silk screen printing, lifetime considerations and lamination with polyethylene terephthalate

The possibility of making large area (100 cm(2)) polymer solar cells based on the conjugated polymer poly 1,4-(2-methoxy-5-ethylhexyloxy)phenylenevinylene (MEH-PPV) was demonstrated. Devices were prepared by etching an electrode pattern on ITO covered polyethylene terephthalate (PET) substrates. A pattern of conducting silver epoxy allowing for electrical contacts to the device was silk screen printed and hardened. Subsequently a pattern of MEH-PPV was silk screen printed in registry with the ITO electrode pattern on top of the substrate. Final evaporation of an aluminum electrode or sublimation of a Buckminsterfullerene (C-60) layer followed by an aluminum electrode completed the device. The typical efficiency of the prototype devices consisting of three solar cells in series were 0.0046% (under AM1.5 conditions) with open-circuit voltages (V-oc) of 0.73 V and short-circuit currents (I-sc) of 20 muA cm(-2). The half-life based on I-sc in air for the devices were 63 h. The cells were laminated in a 125 mum PET encasement. Lamination had a negative effect on the lifetime. We demonstrate the feasibility of industrial production of large area solar cells (1 m(2)) by silk screen printing and envisage the possibility of production volumes 10000 m(2) h(-1) at a cost that is on the order of 100 times lower than that of the established monocrystalline silicon solar cells in terms of materials cost. (C) 2004 Elsevier B.V. All rights reserved.
A Mechanical Strain Sensor for Polymeric Materials and Photophysical Investigations of Large Molecules

The degree of deformation (strain) observed when a given force (stress) is applied to a polymeric material, and the relationship between deformation and force are a fundamental property when the mechanical state of a polymeric material is described. A number of methods exist to investigate this relationship on a macroscopic level (rheology measurements etc.). However, the molecular processes that parallels macroscopic deformation is not well understood. A tool that allows measurement of the molecular changes when the material is strained or stressed may produce new insight into the structure-property relationship of polymeric materials, and lay ground for new advanced polymer based materials. In addition, the current theory of rubber elasticity and molecular deformation might be experimentally probed. To investigate the molecular responds to deformation, a fluorescent sensor unit was placed in the middle of a polymer backbone, as depicted below. It was envisaged that straining the polymer chains would produce affect the fluorescent properties of the single site sensor unit. Four fluorescent strain probes with one or two carbazole units placed in the middle of an elastomeric tri-block of polystyrene-polyisoprene-polystyrene (SIS) have been prepared (see below) and their fluorescence behaviour investigated under strain. The idea with the probes 11-13 was that the carbazole-carbazole interaction could be changed with strain (see below). In the conformation shown left the carbazole units interact, and upon excitation and excimer might form. To right the carbazole moieties are isolated and excimer formation is not likely. Emission form the carbazole excimer can be distinguished from the fluorescence from the isolated carbazole. Thus the conformation change shown below should be detectable using fluorescence spectroscopy. The synthesised probes were dissolved in commercial SIS type rubbers in low levels of 0.1 weight-%. Films cast from this blend were subjected to tensile elongation while the fluorescence spectra were obtained. Below are the fluorescence spectra of probe 12 shown at varying strain levels. Thus the fluorescence of the probe changes considerably with macroscopic strain. Shown below is a plot of the relative intensity of the low wavelength peak (I_{354}/I_{370}) as function of tensile strain for the four probes. A rather large change from ca. 0.7 to 1.1 in the relative intensity at two wavelengths (I_{354}/I_{370}) was observed on elongations up to 400%. The spectroscopic change is strongest for small strain levels around 0-200% and levelled out above 300-400%. All four strain probes gave similar results on uniaxial elongation, even probe 10 with only one carbazole unit. Thus, there seems to be no significant effect of the close proximity of the two carbazole units in probes 11-13. This rules out any major contribution from excimer to monomer type shifts in the fluorescence of the probes. Since probe 10 show the same emission change as probes 11-13 it was concluded that changes in the emission vibronic bands are the major effect involved in the emission change measured.
Directional synthesis of a dye-linked conducting homopolymer

General information
Publication status: Published
Organisations: Solar Energy Programme, Risø National Laboratory for Sustainable Energy
Contributors: Krebs, F. C., Hagemann, O., Spanggaard, H.
Pages: 2463-2466
Publication date: 2003
Peer-reviewed: Yes

Publication information
Journal: Journal of Organic Chemistry
Volume: 68
ISSN (Print): 0022-3263
Ratings:
Scopus rating (2003): SJR 1.846 SNIP 1.355
Web of Science (2003): Indexed yes
Original language: English
DOIs: 10.1021/jo0268052
Source: orbit
Source-ID: 305342
Research output: Contribution to journal › Journal article – Annual report year: 2003 › Research › peer-review

Mechanical strain sensing in a SIS-type elastomer with single site strain probes based on carbazole

General information
Publication status: Published
Organisations: Risø National Laboratory for Sustainable Energy
Contributors: Spanggaard, H., Jørgensen, M., Almdal, K.
Pages: 1701-1705
Publication date: 2003
Peer-reviewed: Yes

Publication information
Journal: Macromolecules
Volume: 36
ISSN (Print): 0024-9297
Ratings:
Scopus rating (2003): SJR 2.565 SNIP 1.634
Web of Science (2003): Indexed yes
Original language: English
DOIs: 10.1021/ma0256791
Source: orbit
Source-ID: 305345
Research output: Contribution to journal › Journal article – Annual report year: 2003 › Research › peer-review

Synthesis, properties, and Langmuir-Blodgett film studies of an ionic dye terminated rigid conducting oligomer

General information
Publication status: Published
An exceptional red shift of emission maxima upon fluorine substitution

General information
Publication status: Published
Organisations: Solar Energy Programme, Risø National Laboratory for Sustainable Energy
Contributors: Krebs, F. C., Spanggaard, H.
Pages: 7185-7192
Publication date: 2002
Peer-reviewed: No
Event: Abstract from Nordic polymer days 2002, Oslo (NO), 29-31 May, .

Publication information
Journal: Journal of Organic Chemistry
Volume: 67
ISSN (Print): 0022-3263
Ratings:
Scopus rating (2002): SJR 2.313 SNIP 1.436
Web of Science (2002): Indexed yes
Original language: English
DOIs:
10.1021/jo025592d
Source: orbit
Source-ID: 304631
Research output: Contribution to journal › Journal article – Annual report year: 2002 › Research › peer-review

Nanosensors for mechanical stress in polymeric materials

General information
Publication status: Published
Organisations: Risø National Laboratory for Sustainable Energy
Contributors: Spanggaard, H.
Publication date: 2002
Peer-reviewed: No
Event: Abstract from Nordic polymer days 2002, Oslo (NO), 29-31 May, .
Source: orbit
Source-ID: 304150
Research output: Contribution to conference › Conference abstract for conference – Annual report year: 2002 › Research