

from the fact that, not employing carbohydrate building blocks at all, minimal use of protecting groups is needed.

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Supramolecular Hydrogen-Bonded Oligo(*p*-phenylene vinylene) Polymers**

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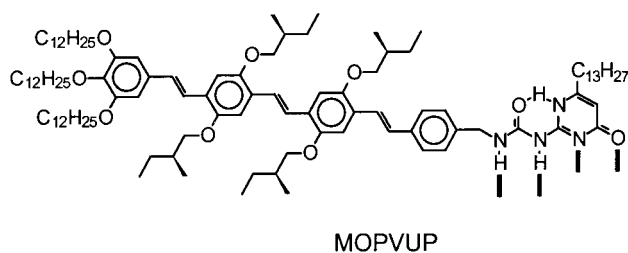
In plastic electronics, π -conjugated oligomers and polymers are applied as advanced materials in a manifold of electro-optical devices such as light-emitting diodes (LEDs),^[1] field-effect transistors (FETs),^[2] and important for the present study, solar cells.^[3] Oligomers possess, due to their well-defined chemical structure, specific electronic and optical properties.^[4] However, the material properties of oligomers are generally secondary to those of their polymeric analogues, since entanglements of macromolecular chains, which are responsible for the typical polymer properties, are lacking. An attractive approach would be to combine the well-defined character of π -conjugated oligomers with the processability of polymers.

Recently, we reported on supramolecular polymers based on the dimerization of strong quadruple hydrogen-bonding self-complementary 2-ureido-4[1*H*]pyrimidinone units ($K_{\text{dim}} = 6 \times 10^7 \text{ M}^{-1}$ in chloroform),^[5] which exhibit real macroscopic polymeric properties such as an increase of viscosity.^[6] Improvement of material properties of low molecular weight telechelic polymers was therefore realized.^[7] These recent developments pave the way to combine the finest properties of conjugated oligomers and polymers by incorporating well-defined π -conjugated moieties in these hydrogen-bonded polymeric assemblies. Furthermore, it provides easy access to multifunctional copolymers by simply mixing the different components containing the quadruple hydrogen-bonded units. A few examples of the combination of π -conjugated oligomers with hydrogen-bonding motifs have been reported. Self-assembled fibers of mono- and bithiophene urea compounds have been described which show efficient charge transport.^[8] More recently, mono- and bifunctional oligo(*p*-vinylene phenylene)s, (OPV)s, functionalized with ureido-s-triazine have been reported that form stacks in dodecane.^[9] In a previous paper we disclosed monofunctionalized ureido-pyrimidinone with OPVs (MOPVUP) and hydrogen-bonded π -conjugated dimers were obtained.^[10]

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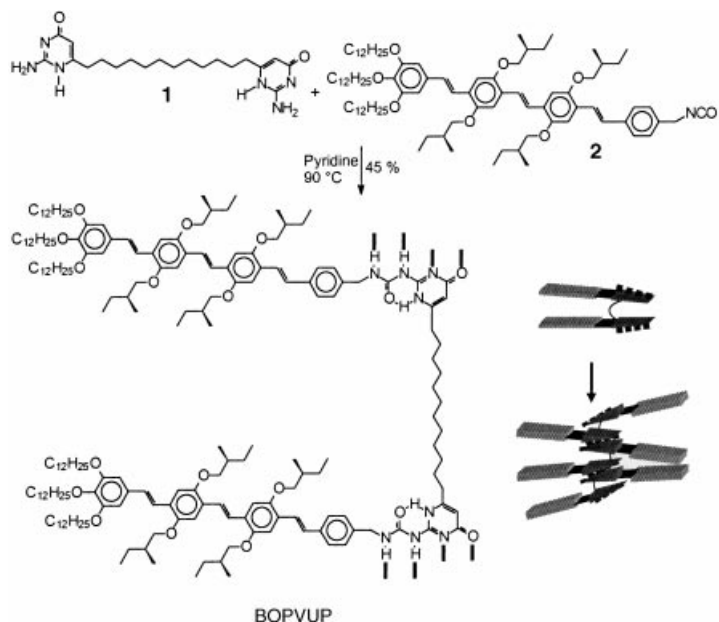
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Here we report on the synthesis and electronic properties of bifunctional ureido-pyrimidinone BOPVUP, which contains well-defined π -conjugated oligomers (see Scheme 1). The applicability of these processable π -conjugated supramolecular polymers in a photovoltaic device shows for the first time that supramolecular concepts can be used in electronic devices.

Target supramolecular polymer BOPVUP was obtained in 45% yield by reaction of isocyanate **1**^[10] with diisocytosine derivative **2**^[11] in dry pyridine at 90 °C (Scheme 1) and has



Scheme 1. Schematic representation of the synthetic protocol used to prepare the supramolecular polymer BOPVUP.

unequivocally been characterized by ^1H , ^{13}C NMR, FT-IR, matrix-assisted laser desorption/ionization time-of-flight (MALDI-TOF) MS, and elemental analysis. In this compound, two OPV-ureido-pyrimidinone units are linked through a dodecyl spacer at the 6-position of the isocytosine rings. BOPVUP forms supramolecular polymers in solution by strong association of the hydrogen bonding units. MALDI-TOF MS analysis indicates no contamination with a mono-adduct ($M_r = 3062.62$) m/z 3063.29 (Figure 1 b). The ^1H NMR spectrum in CDCl_3 shows a strong downfield chemical shift of the N–H protons to $\delta = 13.1$, 12.1 and 10.9 (Figure 1 a), in agreement with the keto-tautomer. A dilution experiment shows no change in chemical shift, while no cyclic structures are observed. The association constant, is similar to that of other ureido-pyrimidinones, namely 10^8 M^{-1} . This value deter-

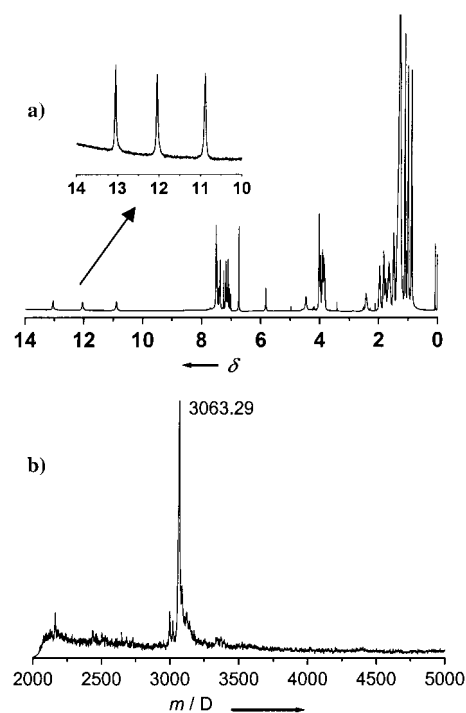


Figure 1. a) ^1H NMR spectra of BOPVUP recorded in CDCl_3 ; b) MALDI-TOF MS spectra of BOPVUP.

mines the virtual degree of polymerization, which is calculated to be about 10000 at a concentration of 1 M .^[5]

UV/Vis and fluorescence spectra were recorded in chloroform and dodecane solutions ($\sim 10^{-4} \text{ M}$) at room temperature (Figure 2). For both solutions, the electronic absorption

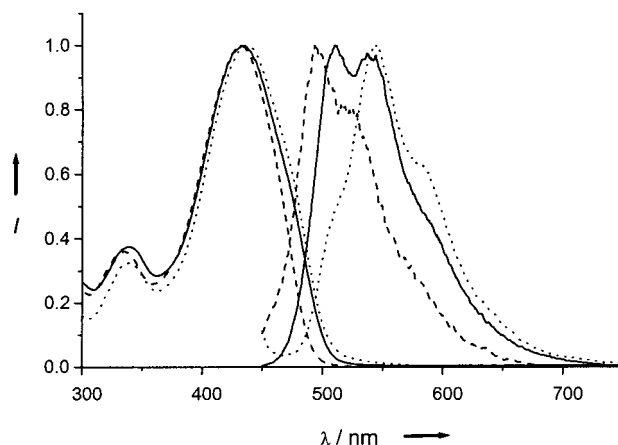


Figure 2. Electronic absorption and emission spectra of BOPVUP; in dodecane (solid line); in chloroform (dashed line) and in a film (dotted line).

maximum is located at $\lambda_{\text{max}} = 432 \text{ nm}$ corresponding to the $\pi-\pi^*$ transition of the OPV units. Fluorescence spectra show an emission maximum at $\lambda_{\text{em,max}} = 494 \text{ nm}$ in chloroform and two emission maxima at 510 and 536 nm in dodecane. Presumably, in chloroform no electronic communication between the two OPV units exists, because the absorption

and emission maxima are similar to that of the monofunctional species MOPVUP in the same solvent.^[10] The red shift in the emission maxima found in dodecane indicates that the OPV units are then aggregated. The Cotton effect (anisotropy factor: $g = 1.86 \times 10^{-4}$) found for BOPVUP in dodecane by using circular dichroism (CD) spectroscopy is relatively weak compared to that for MOPVUP ($g = 6.74 \times 10^{-4}$), indicating that the aggregates for BOPVUP are not highly organized.

Cyclic voltammetry studies of BOPVUP performed in dichloromethane show reversible electrochemical oxidation processes at $E_{1/2} = 0.71$ V versus SCE, which are comparable to those of structurally related tetra(*p*-phenylene vinylene)s.^[12] It is noteworthy that the hydrogen bonds do not participate and are not detrimental for the redox processes.

Photovoltaic devices can be constructed of OPV moieties in combination with C_{60} derivatives in which the π -conjugated oligomers act as electron donors and the fullerenes as acceptors.^[12, 13] To illustrate that this hydrogen-bonded supramolecular π -conjugated polymer can be used in electrooptical devices, the photovoltaic properties were investigated. When BOPVUP was dissolved in toluene, highly viscous solutions were obtained, typical for polymers. These solutions could be spin-coated on glass substrates giving good quality films. Atomic force microscopy (AFM) images show that these supramolecular polymeric films are smooth with height variations in the order of 10 nm, which is similar to those reported for poly(*p*-phenylene vinylene)s (PPVs).^[14] The electronic absorption spectra of these films display a maximum at $\lambda_{\max} = 438$ nm. No CD effect was obtained, which indicated that the films are amorphous resulting in a relative high fluorescence.

Photoinduced absorption (PIA) measurements on spin-coated thin films of BOPVUP ($\lambda_{\text{ex}} = 458$ nm) reveal a band at 1.8 eV that resembles that in the OPV triplet-triplet spectrum. Moreover the photoluminescence of BOPVUP was clearly visible at 2.35 eV. Upon mixing methanofullerene phenyl-[6,6]- C_{61} -butyric acid methyl ester (PCBM, inset Figure 3) as electron acceptor in the spin-coated films of

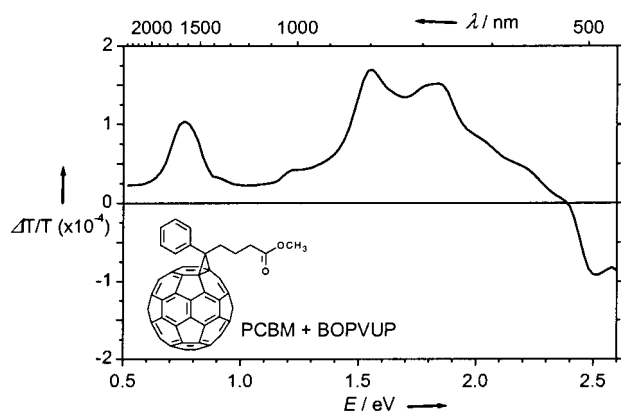


Figure 3. Photoinduced absorption spectra of a mixed BOPVUP:PCBM film (structure of PCBM is shown in the inset).

BOPVUP (BOPVUP:PCBM = 1:2.8 by wt) complete quenching of the OPV fluorescence was observed. PIA measurements revealed the characteristic low energy (LE)

and high energy (HE) absorption bands of the OPV⁺⁺ radical cation at 0.78 and 1.52 eV^[15] and the absorption of the methanofullerene radical anion at 1.24 eV. No photoluminescence for the fullerene moiety was discernable under these conditions, which indicated efficient electron transfer. Varying the modulation frequency from 30 to 3800 Hz revealed that the average lifetime of the charge-separated state is in the order of milliseconds.

Photovoltaic cells were prepared by spin coating a mixture of BOPVUP and PCBM in a ratio of 1:2.8 (by wt) from chlorobenzene onto a transparent ITO front electrode (140 nm) covered with a conducting layer of polyethylenedioxythiophene polystyrenesulfonate (PEDOT:PSS, 90 nm) and depositing an aluminium back electrode (100 nm) in vacuum. The dark current and photocurrent of the device under white-light illumination (88 mW cm⁻², 400–800 nm) reveal promising characteristics (Figure 4). The *I*/*V* curves of

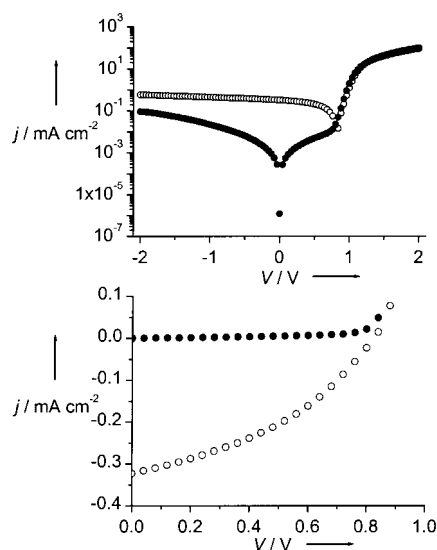


Figure 4. *I*/*V* curves of an ITO/PEDOT:PSS/BOPVUP:PCBM/Al device in the dark (●) and under white-light illumination (○).

the ITO/PEDOT:PSS/BOPVUP:PCBM/Al device show an excellent diode behavior with a rectification ratio (RR) of 1×10^3 at ± 2 V. The high RR shows that the device has no shunts. A short circuit current of $I_{\text{SC}} = 0.32$ mA cm⁻² and an open circuit voltage of $V_{\text{OC}} = 0.82$ V were measured. The fill factor, defined as $(I_{\text{max}} V_{\text{max}})/(I_{\text{SC}} V_{\text{OC}})$, where V_{max} and I_{max} are the voltage and current at maximum power, is 0.39. The values of I_{SC} and V_{OC} are favorable compared to those previously reported for solar cells based on π -conjugated oligomers or polymer and fullerene,^[12, 13, 15] although there has been substantial progress recently by introducing an interfacial layer at the Al electrode.

In conclusion, we have achieved the synthesis of a functional supramolecular hydrogen-bonded π -conjugated polymer that exhibits real macroscopic polymeric properties. A photoinduced charge-separated state was generated within spin-coated blends of the supramolecular polymer with PCBM, and promising photovoltaic devices were obtained. These results create multiple possibilities for using supra-

molecular architectures in electronic devices in which the well-defined character of π -conjugated oligomers is combined with the material properties of polymers

Experimental Section

BOPVUP: Under an argon atmosphere, diisocytosine compound **2** (0.03 g, 0.07 mmol) was dissolved in anhydrous pyridine (5 mL) and heated to 90 °C. A solution of OPV-isocyanate **1** (0.20 g, 0.15 mmol) in anhydrous pyridine (10 mL) was added and the reaction mixture was stirred overnight at 90 °C. The solution was subsequently cooled to room temperature and the pyridine was removed by evaporation under vacuum. The residue was purified by column chromatography (silica gel, ethyl acetate then CH_2Cl_2 to remove impurities and finally $\text{CH}_2\text{Cl}_2/\text{MeOH}$ (97/3, v/v) to collect the desired product) to afford BOPVUP as an orange solid (95 mg; 45 % yield). UV/Vis (CHCl_3): λ_{max} (ϵ) = 432 nm ($258000 \text{ M}^{-1} \text{ cm}^{-1}$); ^1H NMR (400 MHz, $[\text{D}]\text{CHCl}_3$, 25 °C): δ = 13.04 (s, 2H), 12.04 (s, 2H), 10.88 (s, 2H), 7.51–7.36 (m, 14H), 7.18–7.01 (m, 14H), 6.74 (s, 4H), 5.82 (s, 2H), 4.46 (brs, 4H), 4.02–3.85 (m, 32H), 2.42 (br. t, 4H), 2.11–1.27 (m, 160H), 1.10 (s, 24H), 1.00 (s, 24H), 0.87 (brt, 18H); ^{13}C - ^1H NMR (400 MHz, $[\text{D}]\text{CHCl}_3$, 25 °C): δ = 173.4, 157.1, 154.8, 153.5, 152.8, 151.5, 151.4, 151.3, 151.2, 138.3, 137.2, 133.5, 128.8, 128.6, 127.9, 127.8, 127.7, 127.0, 128.9, 123.5, 122.8, 122.7, 11.0, 110.7, 110.1, 109.8, 106.1, 105.3, 74.7, 74.7, 74.4, 74.3, 73.8, 69.3, 43.5, 35.4, 35.3, 35.2, 32.9, 32.2, 32.1, 30.6, 30.0, 29.9, 29.7, 29.6, 29.4, 29.3, 29.2, 27.2, 26.6, 26.4, 22.9, 17.1, 17.0, 14.4, 11.8, 11.7, 11.6; IR (UATR): $\tilde{\nu}$ = 2957 cm^{-1} (m), 2922 (s), 2852 (s), 1695 (m), 1656 (m), 1583 (s), 1503 (s), 1465 (m), 1422 (s), 1386 (w), 1340 (m), 1253 (s), 1200 (s), 1115 (s), 1042 (m), 963 (s), 916 (w), 850 (m); MALDI-TOF MS (M_r = 3062.62) m/z : 3063.29; elemental analysis calcd (%) for $\text{C}_{196}\text{H}_{306}\text{N}_8\text{O}_{18}$ (M_r = 3062.62): C 75.9, H 10.1, N 3.7; found: C 75.1, H 10.0, N 3.3.

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Synthesis of the (+)-C26–C40 Domain of the Azaspiracids by a Novel Double Intramolecular Hetero-Michael Addition Strategy**

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The azaspiracid natural products (AZA **1–5**,) are causative agents of human poisonings associated with the consumption of shellfish that were first recognized in the Netherlands in 1995.^[1] Originally isolated from the mussel *Mytilus edulis* cultivated in Killary Harbor, Ireland, the azaspiracids have since been detected in a growing range of aquatic organisms and geographical locations. Physiological aspects of azaspiracid poisoning (AZP) are distinct from those of other known shellfish intoxications. These include delayed onset and prolonged duration of acute symptoms, and necrosis of the intestine, thymus, and liver. Hence, the azaspiracids represent an emerging new class of environmental toxins with serious economic and human health consequences. As a result there is an urgent need of authentic samples for continued environmental monitoring.

Structurally, the azaspiracids are complex ω -amino acids that contain within their 40-carbon backbone an unprecedented array of polycyclic, spiro-fused ring systems. Among the members of this class reported to date, minor variations in skeletal substitution occur within the C1–C25 domain, but the C26–C40 portion remains constant. The relative stereochemistries within the C6–C25 and C28–C40 domains of the azaspiracids have been assigned, but neither the stereochemical relationship between these two regions, nor the absolute stereochemistry of either has been established. These factors

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