# FULL PAPER

# Photoinduced Electron Transfer in a Mesogenic Donor – Acceptor – Donor System

**Emiel Peeters, Paul A. van Hal, Stefan C. J. Meskers, René A. J. Janssen,\* and E. W. Meijer[a]**

**Abstract:** A novel donor – acceptor – donor molecule consisting of two oligo(*p*-phenylene vinylene) (OPV4) units attached to a central perylene bisimide (PERY) core is described. This OPV4 – PERY – OPV4 is the first mesogenic molecule that incorporates both *p*- and *n*-type semiconducting properties and possesses a liquid-crystalline mesophase, in which donor and acceptor functionalities self-assemble into an ordered material. Upon photoexcitation of the donor, a subpicosecond electron-transfer reaction occurs in OPV4 – PERY – OPV4, both in solution and in (ordered) thin solid films. The lifetime of the charge-separated state is significantly longer in (ordered) thin films than in solution as a result of a reduction of geminate recombination by migration and spatial separation of charges in the film.

**Keywords:** conducting materials · donor – acceptor systems · electron transfer · laser spectroscopy · liquid crystals

## Introduction

Multiple opto-electronic applications are envisaged for π-conjugated oligomer and polymer semiconductors.[1] The performance of such devices critically depends on the degree of mesoscopic ordering of the π-conjugated moieties in the solid state. Interactions between the π-conjugated moieties are known to affect macroscopic properties such as luminescence quantum efficiency[2] and charge-carrier mobility.[3] Ultimately, precise control over the spatial orientation is required to further enhance the performance of organic semiconductor devices. For this reason, considerable interest in mesogenic molecules exists, in which complementary and antagonistic interactions of rigid and flexible parts are utilized to create liquid-crystalline materials that exhibit high-charge-carrier mobilities as a result of a high degree of order.[4] A variety of appropriately derivatized triphenylenes,[5] hexabenzocoronenes,[6] and phthalocyanines[7] have been firmly established as hole transport (*p*-type) discotic liquid-crystalline materials with high mobilities, while electron-carrier (*n*-type) discotic mesogens are emerging in recent years.[8]

The simultaneous supramolecular arrangement of both *p*-type and *n*-type π-conjugated systems is especially important for future organic photovoltaic cells. Promising power-conversion efficiencies have been reported for spontaneously formed interpenetrating networks of electron- and hole-accepting organic semiconductors.[9] In these bulk-heterojunctions, the large interfacial area between donor and acceptor ensures efficient charge generation, and the poor charge transport associated with the disordered nature of the interpenetrating D – A network is thought to limit the performance. We anticipate that the mobility of electrons and holes will be favorably influenced when it is possible to create an interpenetrating liquid-crystalline phase of both donor and acceptor on a nanoscopic scale.[10] A covalent linkage between donor and acceptor provides a first approach to achieve dimensional control over phase separation in D – A networks. In fact amorphous films of π-conjugated oligomers or polymers covalently attached to fullerenes have recently been used successfully in photovoltaic devices.[11]

In this paper, we report the synthesis and characterization of a molecule in which two electron-rich oligo(*p*-phenylene vinylene) (OPV4) units, covalently linked to an electron-deficient perylene bisimide (PERY) core, are combined with six flexible dodecyloxy chains to create a liquid-crystalline material (OPV4 – PERY – OPV4, Scheme 1). Although both oligo(*p*-phenylene vinylene)s[12] and perylene bisimides[13] have previously been modified to create liquid-crystalline materials, OPV4 – PERY – OPV4 is the first mesogenic molecule that possesses both *p*- and *n*-type semiconducting properties. We demonstrate the dual functionality of this novel material by showing that upon photoexcitation, the PERY core acts as an electron acceptor, and the OPV4 as an electron donor.

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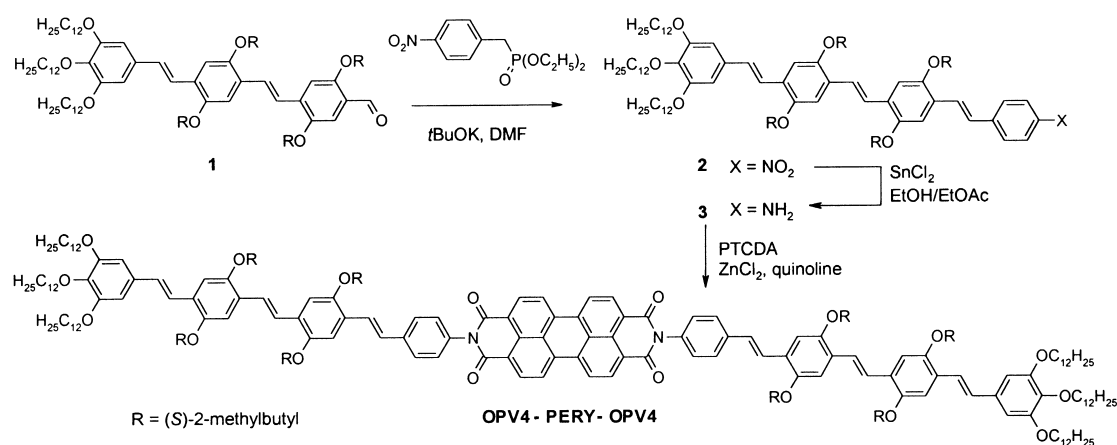
Scheme 1. Synthesis of a molecule with two oligo(*p*-phenylene vinylene) (OPV4) units, covalently linked to a perylene bisimide (PERY) core, and six flexible dodecyloxy chains (OPV4 – PERY – OPV4).

## Results and Discussion

**Synthesis**: The synthetic route towards the liquid-crystalline OPV4 – PERY – OPV4 is depicted in Scheme 1. Reaction of aldehyde **1**[14] with diethyl(4-nitrobenzyl) phosphonate in a Wittig – Horner reaction afforded nitro compound **2** in a yield of 57 % after column chromatography. Subsequent reduction of the nitro group by using stannous dichloride in a mixture of ethanol and ethyl acetate yielded the amine-terminated oligomer **3**. OPV4 – PERY – OPV4 was obtained after a condensation reaction of **3** with 3,4,9,10-perylenetetracar-boxy-dianhydride (PTCDA) at 200 °C in freshly distilled quinoline. The condensation reaction was catalyzed by addition of a small amount of zinc dichloride. After workup, size exclusion chromatography (SEC) analysis of the crude product showed the presence of higher molecular weight contaminations. Pure OPV4 – PERY – OPV4 was obtained after extensive preparative size exclusion chromatography in a yield of 45 % and was fully characterized by FTIR, $^1$H NMR and $^{13}$C NMR spectroscopy, and mass spectrometry.

**Liquid-crystalline properties**: The thermal behavior of OPV4 – PERY – OPV4 has been investigated with polarization microscopy and DSC (differential scanning calorimetry). Amorphous thin films have been obtained by drop casting OPV4 – PERY – OPV4 from solution in chloroform onto glass substrates. Upon heating, a transition from the glassy state to a liquid-crystalline (LC) mesophase is observed at 215 °C (Figure 1). The transition to the isotropic (I) liquid state occurs at 310 °C.[15] Upon cooling, the material re-enters the liquid-crystalline state at 305 °C, and at 200 °C the material crystallizes. Repetitive heating and cooling show that the K → LC and LC → I transitions are reversible. DSC analysis does not show any reproducible transitions in the temperature regime from 20 to 325 °C. The observation of the liquid-crystalline mesophase shows that the donor and acceptor functionalities in OPV4 – PERY – OPV4 can self-assemble into an ordered material.

**Electro-optical properties**: Cyclic voltammetry of OPV4 – PERY – OPV4 dissolved in dichloromethane revealed a



Figure 1. Texture of the liquid-crystalline mesophase of OPV4 – PERY – OPV4 between 215 and 310 °C, as observed with polarization microscopy.

reversible two-electron oxidation wave of the OPV4 moieties at 0.78 V versus SCE and two reversible one-electron reduction waves of the PERY core at −0.55 V and −0.74 V, respectively. The UV/Vis absorption spectrum of OPV4 – PERY – OPV4 in toluene is depicted in Figure 2 and shows
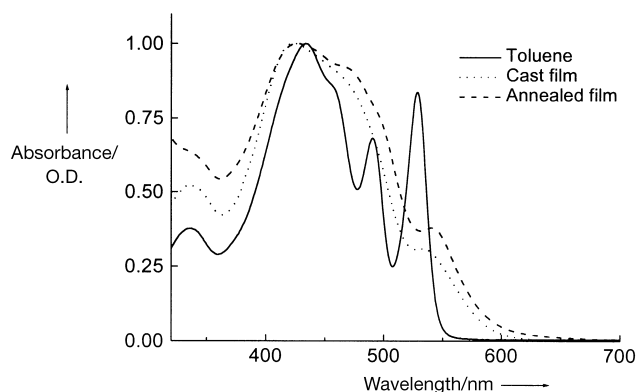


Figure 2. UV/Vis spectra of OPV4 – PERY – OPV4 in toluene and as thin solid films before and after thermal annealing.

specific absorptions of the OPV4 ($\lambda_{max} = 434$ nm) and PERY ($\lambda_{max} = 491$ nm and $\lambda_{max} = 529$ nm) moieties. From the close correspondence of the electrochemical and optical data of OPV4 – PERY – OPV4 with those of isolated model com-pounds (OPV4 and PERY), we conclude that the chromo-

phores do not have a strong charge-transfer interaction in the ground state in solution. In solid thin films of OPV4–PERY–OPV4, a small blue shift of the absorption maximum of OPV4 and an accompanying red shift of the first vibronic of the perylene absorption are observed (Figure 2). The UV/Vis spectra of amorphous films cast from solution in chloroform and films that were annealed by first heating to 320 °C, followed by slowly cooling to room temperature to create large ordered domains are rather similar and are consistent with a π-stacking interaction between the chromophores in the solid state. It is interesting to note that the blue shift of the OPV4 absorption in OPV4–PERY–OPV4 is similar to the blue shift associated with the π stacking of OPV$n$ molecules.[16] Likewise perylene bisimides are known to exhibit a red shift upon aggregation.[17] Hence, the UV/Vis absorption spectrum observed for OPV4–PERY–OPV4 in the solid state suggests that π stacking preferentially occurs between alike units. The fluorescence of OPV4–PERY–OPV4 in toluene and in thin solid films (both before and after annealing) is strongly quenched when compared with that of OPV4 and PERY model compounds, irrespective of the chromophore that is excited (OPV4 at 403 nm or PERY at 529 nm). The fluorescence quenching indicates that a fast nonradiative deactivation of the excited state occurs for both chromophores in OPV4–PERY–OPV4.

**Photoinduced electron transfer**: Photoinduced absorption (PIA) spectroscopy has been used to investigate the origin of the fast nonradiative decay in OPV4–PERY–OPV4 in more detail. Near-steady-state PIA spectra of a thin film of OPV4–PERY–OPV4 cast from chloroform and recorded at 80 K by exciting at 458 nm (primarily excitation of OPV4) or at 528 nm (selective excitation of PERY) reveal the formation of a charge-separated state (Figure 3). The PIA spectrum of a thermally annealed film was virtually identical, but somewhat more intense. The specific low-energy absorption of the OPV4$^{\cdot+}$·radical cations at 0.72 eV[18] and the absorption bands of the perylene bisimide radical anion at 1.27, 1.52, and 1.75 eV[19] give direct spectral evidence of an electron-transfer reaction that originates from either the photoexcited donor or acceptor. The intensity of the PIA bands increases with the square root of pump intensity ($-\Delta T \propto I^{\alpha}$; $\alpha = 0.51–0.61$), indicative of a bimolecular recombination of nongeminate positive and negative charges. The intensity of the PIA bands decreases continuously with increasing modulation frequency, consistent with a distribution of lifetimes extending into the millisecond domain.

Subpicosecond transient pump-probe spectroscopy (150 fs pulses) was performed at room temperature on OPV4–PERY–OPV4 in solution in THF and on thin films on quartz to assess the formation of charges on short timescales. Upon preferential photoexcitation of the OPV4 moiety at 450 nm, a negative differential transmission is observed at 1450 nm (0.86 eV) (Figure 4). At this wavelength, the low-energy absorption of the OPV4$^{\cdot+}$ radical cations is probed and, hence, these transient signals give direct information on the temporal evolution of the charges formed in OPV4–PERY–OPV4. Both in solution and in a cast thin film, charges are formed in less than 1 ps after photoexcitation ($k_{ET} \geq 10^{12}$ s$^{-1}$).
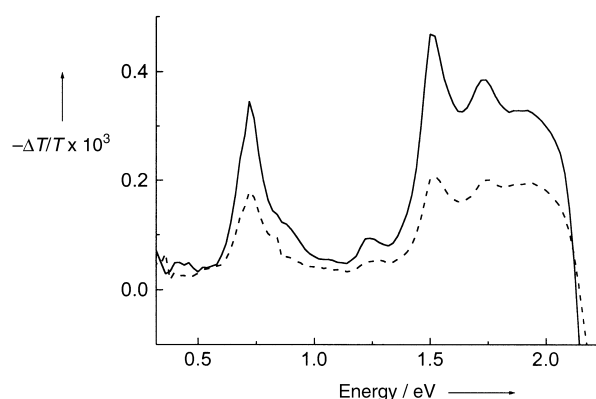


Figure 3. Photoinduced absorption spectra of a cast thin solid film of OPV4–PERY–OPV4 recorded at 80 K with excitation at 458 nm (solid line) and 528 nm (dashed line).

The lifetime of the charge-separated state is short; monoexponential decays fitted to the transient absorption signals give 11 ps ($k_R = 9.1 \times 10^{10}$ s$^{-1}$) and 46 ps ($k_R = 2.2 \times 10^{10}$ s$^{-1}$) for the lifetime in solution in THF and cast film, respectively. The short lifetime is likely to result from the close proximity of donor and acceptor in OPV4–PERY–OPV4, which increases charge recombination. The fourfold increase of lifetime in the cast film is rationalized by the migration of photogeneric charges to neighboring molecules. For the annealed, more ordered film, the lifetime of the charge-separated state is best fitted to a biexponential decay with time constants of 14 ps ($k_R = 4.1 \times 10^{10}$ s$^{-1}$) and 170 ps ($k_R = 5.9 \times 10^{9}$ s$^{-1}$). The longer lifetime in the ordered film might reflect the higher mobility of the charges that escape the fast geminate recombination. The seeming discrepancy of the lifetimes of the charge-separated state in the film in the near-steady-state (ms) and fast (ps) PIA experiments is due to the fact that the latter predominantly probes geminate electron-hole pairs, while at longer times charges are probed that have escaped from geminate recombination.[20]

Attempts to prepare photovoltaic devices of OPV4–PERY–OPV4 were not successful; most devices (glass/ITO/OPV4–PERY–OPV4/Al) exhibited poor diode behavior as
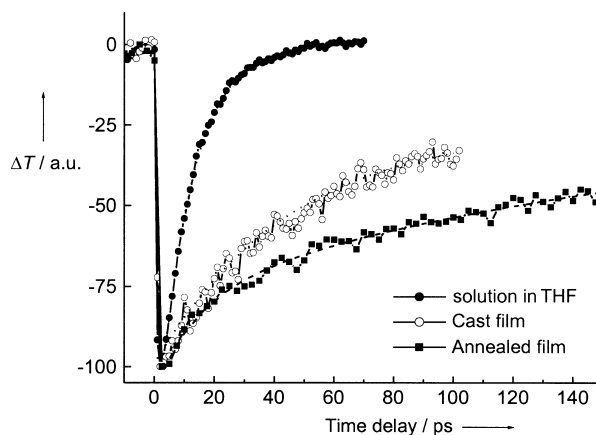


Figure 4. Differential transmission dynamics of OPV4–PERY–OPV4 (solution in THF, cast film, and annealed film) recorded at 1450 nm (low-energy absorption of OPV4$^{\cdot+}$ radical cations) after excitation at 450 nm. Dotted lines are fits to monoexponential or biexponential decay.

a result of the presence of shunts irrespective of whether cast or annealed films were used. Applying thick layers could prevent shunts, but these devices exhibited little or no photovoltaic effect. The poor performance of the photovoltaic cells is not clearly understood at present, but seems related to unbalanced charge transport of holes or electrons or an adverse macroscopic orientation of the crystalline phase at the electrodes.

## Conclusion

We have prepared a novel material, OPV4–PERY–OPV4, comprising both *p*- and *n*-type organic semiconductors, that exhibits a liquid-crystalline mesophase between 215 and 310°C and forms positive and negative charge carriers upon photoexcitation. The lifetime of the charge-separated state is significantly longer in (ordered) thin films than in solution as a result of a reduction of geminate recombination by migration and spatial separation of charges. The incorporation of OPV4–PERY–OPV4 in working photovoltaic devices was not successful, and, hence, future research will be directed to design liquid-crystalline *p–n* junctions, in which the orientation of the functional segments is optimized for charge transport.

## Experimental Section

**General methods**: $^1$H NMR and $^{13}$C NMR spectra were recorded at room temperature on a Varian Gemini 300 or a Varian Mercury 400 MHz spectrometer. Chemical shifts are given in ppm ($\delta$) relative to tetramethylsilane. Infrared spectra were run on a Perkin-Elmer Spectrum One UATR FTIR spectrophotometer. Matrix-assisted laser desorption ionization time-of-flight (MALDI-TOF) mass spectrometry was conducted on a Perseptive Biosystems Voyager DE-Pro MALDI-TOF mass spectrometer. GC-MS measurements were performed on a Shimadzu GC/MS-QP5000. Elemental analysis was carried out on a Perkin-Elmer 2400 series II CHN analyzer. Thermal optical properties were studied using a Jenaval polarization microscope equipped with crossed polarizers and a Linkam THMS 600 hot stage. Differential scanning calorimetry was performed on a Perkin Elmer DSC Pyris 1 at a heating rate of 40°C min$^{-1}$. Cyclic voltammograms were measured in 0.1M tetrabutylammonium hexafluorophosphate (TBAPF$_6$) as a supporting electrolyte in dichloromethane by using a Potentioscan Wenking POS73 potentiostat. The working electrode was a Pt disk (0.2 cm$^2$), the counter electrode was a Pt plate (0.5 cm$^2$), and a saturated calomel electrode (SCE) was used as a reference electrode, calibrated against Fc/Fc$^+$. UV/Vis absorption spectra were recorded on a Perkin Elmer Lambda 900 spectrophotometer. Fluorescence spectra were recorded on an Edinburgh Instruments FS920 double-monochromator spectrometer and a Peltier-cooled red-sensitive photomultiplier.

**Materials**: (*E,E*)-4-{4-(3,4,5-Tridodecyloxystyryl)-2,5-bis[(*S*)-2-methylbutoxy]styryl}-2,5-bis[(*S*)-2-methylbutoxy]benzaldehyde was synthesized according to a literature procedure.[14] All solvents were of AR quality, and chemicals were used as received. Bio-Beads S-XI Beads were obtained from Bio-Rad Laboratories.

**Diethyl(4-nitrobenzyl) phosphonate**: Triethyl phosphite (2.77 g, 16.7 mmol) and 4-nitrobenzyl bromide (3.00 g, 13.9 mmol) were heated to 160°C and stirred for 2 h, while ethyl bromide was distilled from the reaction mixture. Subsequently, the mixture was cooled to 70°C, and the excess of triethyl phosphite was distilled under reduced pressure. The residue was dissolved in ethyl acetate and filtered over silica gel. The solvent was removed in vacuo to yield 3.32 g (88%) of diethyl(4-nitrobenzyl) phosphonate.

IR (UATR): $\tilde{v}$ = 2984, 2909, 1600, 1517, 1344, 1244, 1048, 1017, 958, 859, 770, 693 cm$^{-1}$; $^1$H NMR (CDCl$_3$): $\delta$ = 8.20 (d, 2H), 7.51 (dd, 2H), 4.20–4.00 (m,

4H), 3.27 (d, 2H), 1.27 (t, 6H); $^{13}$C NMR (CDCl$_3$): $\delta$ = 146.78, 139.60, 130.46, 123.47, 62.21, 33.70, 16.08; GC-MS ($M_W$ = 273.08): *m/z* (%): 272.95 [*M*$^+$].

**(*E,E,E*)-4-[4-{4-(3,4,5-Tridecyloxystyryl)-2,5-bis[(*S*)-2-methylbutoxy]styryl}-2,5-bis[(*S*)-2-methylbutoxy]styryl]nitrobenzene (2)**: Diethyl(4-nitrobenzyl) phosphonate (0.32 g, 1.16 mmol) was dissolved in anhydrous DMF (5 mL) under an argon atmosphere, and *t*BuOK (0.16 g, 1.40 mmol) was added to the solution at room temperature. After the mixture was stirred for 15 min, a solution of **1** (1.28 g, 1.06 mmol) in DMF (30 mL) was added dropwise to the reaction mixture. After addition was completed, the solution was stirred for 4 h and subsequently poured onto a mixture of crushed ice (100 g) and HCl (45 mL, 6 N). The mixture was extracted three times with CH$_2$Cl$_2$, and the collected organic fractions were washed with HCl (3 N) and dried over MgSO$_4$, and the solvent was removed in vacuo. The product was purified by column chromatography (silica gel, hexane/CH$_2$Cl$_2$ 1:1) to afford 0.80 g (57%) of **2** as a dark red solid.

$^1$H NMR (CDCl$_3$): $\delta$ = 8.22 (d, 2H), 7.67 (d, 1H), 7.62 (d, 2H), 7.61 (d, 1H), 7.55 (d, 1H), 7.44 (d, 1H), 7.24 (s, 1H), 7.23 (s, 1H), 7.21 (d, 1H), 7.15 (s, 1H), 7.13 (s, 1H), 7.09 (d, 1H), 6.79 (s, 2H), 4.15–3.80 (m, 14H), 2.10–1.96 (m, 4H), 1.96–1.26 (m, 68H), 1.26–0.80 (m, 33H); $^{13}$C NMR (CDCl$_3$): $\delta$ = 153.38, 151.91, 151.27, 151.25, 151.00, 146.50, 144.82, 138.29, 133.38, 129.28, 128.89, 128.41, 127.28, 127.24, 126.74, 126.16, 125.29, 124.29, 123.61, 122.59, 111.31, 110.48, 109.98, 109.50, 105.24, 74.71, 74.58, 74.43, 74.17, 73.83, 69.34, 35.61, 35.59, 35.53, 35.38, 32.41, 32.39, 32.05, 30.82, 30.24, 30.22, 30.19, 30.17, 30.14, 30.10, 29.91, 29.88, 29.85, 29.50, 27.34, 26.86, 26.84, 26.63, 26.61, 25.71, 23.17, 23.12, 17.31, 17.27, 12.23, 14.58, 12.03, 11.97, 11.86.

**(*E,E,E*)-4-[4-{4-(3,4,5-Tridecyloxystyryl)-2,5-bis[(*S*)-2-methylbutoxy]styryl}-2,5-bis[(*S*)-2-methylbutoxy]styryl]aniline (3)**: Under an argon atmosphere, SnCl$_2 \cdot$ 2 H$_2$O (0.67 g, 4.70 mmol) was added to a suspension of **2** (0.78 g, 0.58 mmol) in a mixture of ethanol (4 mL) and ethyl acetate (4 mL). The reaction mixture was heated to 75°C, stirred for 5 h, cooled to room temperature, and subsequently poured onto crushed ice. The aqueous phase was extracted three times with diethyl ether. The collected organic fractions were dried over MgSO$_4$, and the solvent was removed in vacuo. The product was purified by column chromatography (silica gel, gradient hexane/ethyl acetate 4:1 → hexane/ethyl acetate 2:1) to afford 0.57 g (75%) of **3** as an orange solid.

IR (UATR): $\tilde{v}$ = 3354, 3057, 2957, 2919, 2851, 1609, 1578, 1505, 1466, 1422, 1387, 1340, 1254, 1203, 1119, 1048, 962, 850, 808, 737 cm$^{-1}$; $^1$H NMR (CDCl$_3$): $\delta$ = 7.53 (s, 2H), 7.41 (d, 1H), 7.34 (d, 2H), 7.31 (d, 1H), 7.21 (s, 1H), 7.19 (s, 1H), 7.11 (s, 1H), 7.10 (s, 1H), 7.07 (d, 1H), 7.04 (d, 1H), 6.75 (s, 2H), 6.64 (d, 2H), 4.08–3.78 (m, 14H), 3.68 (br s, 2H), 2.05–1.92 (m, 4H), 1.92–1.18 (m, 68H), 1.18–0.80 (m, 33H); $^{13}$C NMR (CDCl$_3$): $\delta$ = 153.39, 151.33, 151.19, 151.14, 146.23, 138.25, 133.43, 128.93, 128.78, 128.59, 127.83, 127.75, 127.63, 126.88, 126.76, 122.86, 122.70, 122.27, 119.94, 115.31, 110.62, 109.93, 109.74, 105.18, 74.58, 74.29, 74.21, 73.66, 69.20, 35.31, 35.24, 35.14, 32.08, 30.51, 29.91, 29.89, 29.86, 29.82, 29.59, 29.55, 29.52, 26.51, 26.29, 22.84, 17.00, 16.92, 14.25, 11.67, 11.63, 11.53; MALDI-TOF MS ($M_W$ = 1296.04) *m/z* (%): 1296.24 [*M*$^+$].

**N,N′-Bis[(*E,E,E*)-4-[4-{4-(3,4,5-tridecyloxystyryl)-2,5-bis[(*S*)-2-methylbutoxy]styryl}-2,5-bis[(*S*)-2-methylbutoxy]styryl]phenyl]perylene bisimide (OPV4–PERY–OPV4)**: Under an argon atmosphere 3,4,9,10-perylenetetracarboxylic dianhydride (43 mg, 0.11 mmol) and ZnCl$_2$ (20 mg) were added to a solution of **3** (430 mg, 0.33 mmol) in freshly distilled quinoline (2 mL). The suspension was heated to 200°C and stirred for 16 h. The reaction mixture was cooled to room temperature, and water (1 mL) and ethanol (15 mL) were added. The suspension was filtered, and the residue was purified by repetitive precipitation from CHCl$_3$ in methanol. The product was purified by column chromatography (silica gel, ethyl acetate to elute impurities and CH$_2$Cl$_2$ to collect the product) and four times by preparative size exclusion chromatography (Bio-Beads S-X3, 3 × THF, 1 × CH$_2$Cl$_2$) to yield 147 mg (45%) of OPV4–PERY–OPV4 as a crystalline dark red solid.

IR (UATR): $\tilde{v}$ = 2957, 2922, 2853, 1705, 1669, 1595, 1578, 1504, 1465, 1422, 1345, 1255, 1201, 1116, 1043, 962, 851, 809, 793, 735 cm$^{-1}$; $^1$H NMR (CDCl$_3$): $\delta$ = 8.79 (d, *J* = 8.2 Hz, 4H), 8.71 (d, *J* = 8.2 Hz, 4H), 7.72 (d, *J* = 8.2 Hz, 4H), 7.57 (d, *J* = 16.1 Hz, 2H), 7.52 (s, 4H), 7.38 (d, *J* = 15.7 Hz, 2H), 7.36 (d, *J* = 8.1 Hz, 4H), 7.25 (d, *J* = 16.5 Hz, 2H), 7.23 (d, *J* = 16.5 Hz, 2H), 7.19 (s, *J* = 16.6 Hz, 2H), 7.15 (s, 2H), 7.10 (s, 2H), 7.03 (d, *J* = 16.1 Hz, 2H), 6.74 (s, 4H), 4.05–3.95 (m, 12H), 3.95–3.84 (m, 16H), 1.98 (m, 8H), 1.83

(m, 12 H), 1.78 – 1.62 (m, 16 H), 1.49 (m, 12 H), 1.4 – 1.2 (m, 96 H), 1.13 (m, 24 H), 1.02 (m, 24 H), 0.88 (t, $J = 6.3$ Hz, 18 H); $^{13}$C NMR (CDCl$_3$): $\delta =$ 163.35, 153.34, 151.53, 151.16, 151.05, 150.98, 138.79, 138.27, 134.70, 133.84, 133.36, 131.53, 129.06, 128.81, 128.05, 127.84, 127.43, 127.37, 126.93, 126.59, 126.46, 124.96, 123.49, 123.20, 122.64, 122.47, 111.16, 110.56, 109.74, 109.48, 105.30, 74.72, 74.63, 74.40, 74.28, 73.85, 69.38, 35.58, 35.46, 35.34, 32.34, 32.27, 30.77, 30.17, 30.15, 30.12, 30.07, 29.85, 29.80, 29.77, 26.83, 26.78, 26.56, 23.11, 17.30, 17.22, 14.54, 12.03, 12.01, 11.94, 11.85; MALDI-TOF MS ($M_W = 2948.09$): $m/z$ (%): 2948.47 [$M^+$]; elemental analysis calcd (%) for C$_{196}$H$_{278}$N$_2$O$_{18}$: C 79.79, H 9.50, N 0.95; found: C 79.14, H 9.71, N 0.93.

**Photoinduced absorption spectroscopy**: Near-steady-state photoinduced absorption (PIA) spectra were recorded between 0.25 and 3 eV by exciting a thin film on quartz in an Oxford Optistat continuous flow cryostat with a mechanically modulated (typically 275 Hz) cw Ar-ion laser (Spectra Physics 2025) pump beam tuned to 458 or 528 nm (25 mW, beam diameter of 2 mm) and monitoring the resulting change in transmission ($\Delta T$) of a tungsten – halogen white-light probe beam after dispersion by a triple-grating monochromator, using Si, InGaAs, and (cooled) InSb detectors.

The femtosecond laser system used for pump-probe experiments consisted of an amplified Ti-sapphire laser (Spectra Physics Hurricane), providing 150 fs pulses at 800 nm with an energy of 750 μJ at 1 kHz. Pump (450 nm, fluence 0.5 μJ mm$^{-2}$) and probe (1450 nm) pulses were created by optical parametric amplification and twofold frequency doubling using two OPAs (Spectra Physics OPA-C). The pump beam was linearly polarized at the magic angle (54.7°) with respect to the probe beam. The temporal evolution was recorded using an InGaAs detector and standard lock-in detection at 500 Hz.

[1] R. H. Friend, R. W. Gymer, A. B. Holmes, J. H. Burroughes, R. N. Marks, C. Taliani, D. C. C. Bradley, D. A. Dos Santos, J. L. Brédas, M. Logdlund, W. R. Salaneck, *Nature* **1999**, *397*, 121.

[2] a) S. A. Jehneke, J. A. Osaheni, *Science* **1994**, *265*, 765; b) I. D. W. Samuel, G. Rumbles, C. Collison, *Phys. Rev. B*: *Condens. Matter* **1995**, *52*, 11 573.

[3] H. Sirringhaus, P. J. Brown, R. H. Friend, M. M. Nielsen, K. Bechgaard, B. M. W. Langeveld-Voss, A. J. H. Spiering, R. A. J. Janssen, E. W. Meijer, P. Herwig, D. M. de Leeuw, *Nature* **1999**, *401*, 685.

[4] J. Kopitzke, J. H. Wendorff, *Chem. Unserer Zeit* **2000**, *34*, 4.

[5] a) D. Adam, P. Schuhmacher, J. Simmerer, L. Häussling, K Siemensmeyer, K. H. Etzbach, H. Ringsdorf, D. Haarer, *Nature* **1994**, *371*, 141; b) N. Boden, R. J. Bushby, J. Clements, *J. Chem. Phys.* **1993**, *98*, 5920; c) A. Bacher, I. Bleyl, C. H. Erdelen, D. Haarer, W. Paulus, H. W. Schmidt, *Adv. Mater.* **1997**, *9*, 1031.

[6] a) A. M. van de Craats, J. M. Warman, A. Fechtenkötter, J. D. Brand, M. A. Harbison, K. Müllen, *Adv. Mater.* **1999**, *11*, 1469; b) A. M. van de Craats, J. M. Warman, K. Müllen, Y. Geerts, J. D. Brand, *Adv. Mater.* **1998**, *10*, 36; c) U. Rohr, C. Kohl, K. Müllen, A. van de Craats, J. M. Warman, *J. Mater. Chem.* **2001**, *11*, 1789; d) A. M. van de Craats, J. M. Warman, *Adv. Mater.* **2001**, *13*, 130.

[7] P. G. Schouten, J. M. Warman, M. P. de Haas, C. F. van Nostrum, G. H. Gelinck, R. J. M. Nolte, M. J. Copyn, J. W. Zwikker, M. K. Engel, M. Hanack, Y. H. Chang, W. T. Ford, *J. Am. Chem. Soc.* **1994**, *116*, 6880.

[8] a) N. Boden, R. C. Borner, R. J. Bushby, J. Clements, *J. Am. Chem. Soc.* **1994**, *116*, 10 807; b) S. Kumar, D. S. S. Rao, S. K. Prasad, *J. Mater. Chem.* **1999**, *9*, 2751; c) G. Kestemont, V. de Halleux, M. Lehmann, D. A. Ivanov, M. Watson, Y. H. Geerts, *Chem. Commun.* **2001**, 2074; d) K. Pieterse, P. A. van Hal, R. Kleppinger, J. A. J. M. Vekemans, R. A. J. Janssen, E. W. Meijer, *Chem. Mater.* **2001**, *13*, 2675.

[9] a) G. Yu, J. Gao, J. C. Hummelen, F. Wudl, A. J. Heeger, *Science* **1995**, *270*, 1789; b) J. J. M. Halls, C. A. Walsh, N. C. Greenham, E. A. Marseglia, R. H. Friend, S. C. Moratti, A. B. Holmes, *Nature* **1995**, *376*, 498; c) S. E. Shaheen, C. J. Brabec, F. Padinger, T. Fromherz, J. C. Hummelen, N. S. Sariciftci, *Appl. Phys. Lett.* **2001**, *78*, 841.

[10] L. Schmidt-Mende, A. Fechtenkötter, K. Müllen, E. Moons, R. H. Friend, J. D. MacKenzie, *Science*, **2001**, *293*, 1119.

[11] a) J.-F. Nierengarten, J.-F. Eckert, J.-F. Nicoud, L. Ouali, V. Krasnikov, G. Hadziioannou, *Chem. Commun.* **1999**, 617; b) J.-F. Eckert, J.-F. Nicoud, J.-F. Nierengarten, S.-G. Liu, L. Echegoyen, F. Barigelletti, N. Armaroli, L. Ouali, V. Krasnikov, G. Hadziioannou, *J. Am. Chem. Soc.* **2000**, *122*, 7467; c) E. Peeters, P. A. van Hal, J. Knol, C. J. Brabec, N. S. Sariciftci, J. C. Hummelen, R. A. J. Janssen, *J. Phys. Chem. B* **2000**, *104*, 10174; d) A. Marcos Ramos, M. T. Rispens, J. K. J. van Duren, J. C. Hummelen, R. A. J. Janssen, *J. Am. Chem. Soc.* **2001**, *123*, 6714; e) B. de Boer, U. Stalmach, P. F. van Hutten, C. Melzer, V. V. Krasnikov, G. Hadziioannou, *Polymer* **2001**, *42*, 9097.

[12] a) J.-F. Eckert, J.-F. Nicoud, D. Guillon, J.-F. Nierengarten, *Tetrahedron Lett.* **2000**, *41*, 6411; b) A. El-ghayoury, E. Peeters, A. P. H. J. Schenning, E. W. Meijer, *Chem. Commun.* **2000**, 1969; c) J.-F. Eckert, U. Maciejczuk, D. Guillon, J.-F. Nierengarten, *Chem. Commun.* **2001**, 1278; d) T. Gu, G. Accorsi, N. Armaroli, D. Guillon, J.-F. Nierengarten, *Tetrahedron Lett.* **2001**, *42*, 2309.

[13] a) R. A. Cormier, B. A. Gregg, *Chem. Mater.* **1998**, *10*, 1309; b) P. Schlichting, U. Rohr, K. Müllen, *J. Mater. Chem.* **1998**, *8*, 2651; c) D. Pressner, C. Göltner, H. W. Spiess, K. Müllen, *Acta Polym.* **1994**, *45*, 188; d) G. Göltner, D. Pressner, K. Müllen, H. W. Spiess, *Angew. Chem.* **1993**, *105*, 1722; *Angew. Chem. Int. Ed. Engl.* **1993**, *32*, 1660; e) G. R. J. Müller, C. Meiners, V. Enkelmann, Y. Geerts, K. Müllen, *J. Mater. Chem.* **1998**, *8*, 61; f) U. Rohr, P. Schlichting, A. Böhm, M. Gross, K. Meerholz, C. Bräuchle, K. Müllen, *Angew. Chem.* **1998**, *110*, 1463; *Angew. Chem. Int. Ed.* **1998**, *37*, 1434; g) C. W. Struijk, A. B. Sieval, J. E. J. Dakhorst, M. van Kijk, P. Kimkes, R. B. M. Koehorst, H. Donker, T. J. Schaafsma, S. J. Picken, A. M. van de Craats, J. M. Warman, H. Zuilhof, E. J. R. Sudhölter, *J. Am. Chem. Soc.* **2000**, *122*, 11 057.

[14] A. P. H. J. Schenning, P. Jonkheijm, E. Peeters, E. W. Meijer, *J. Am. Chem. Soc.* **2001**, *123*, 409.

[15] Thermogravimetric analysis (TGA) under nitrogen showed that there is negligible (< 1 %) weight loss up to 355 °C; only above 375 °C OPV4 – PERY – OPV4 starts to decompose (weight loss > 95 %).

[16] E. Peeters, A. Marcos, S. C. J. Meskers, R. A. J. Janssen, *J. Chem. Phys.* **2000**, *112*, 9445.

[17] H. Langhals, *Heterocycles* **1995**, *40*, 477.

[18] P. A. van Hal, E. H. A. Beckers, E. Peeters, J. J. Apperloo, R. A. J. Janssen, *Chem. Phys. Lett.* **2000**, *328*, 403.

[19] J. Salbeck, *J. Electroanal. Chem.* **1992**, *340*, 169.

[20] S. C. J. Meskers, P. A. van Hal, A. J. H. Spiering, A. F. G. van der Meer, J. C. Hummelen, R. A. J. Janssen, *Phys. Rev. B*: *Condens. Matter* **2000**, *61*, 9917.