Hierarchical Order in Supramolecular Assemblies of Hydrogen-Bonded Oligo(*p*-phenylene vinylene)s

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Abstract: Mono- and bifunctional oligo(*p*-phenylene vinylene)s (OPVs) functionalized with ureido-*s*-triazine units have been synthesized and fully characterized. In chloroform monofunctional OPV derivatives dimerize with a dimerization constant of $K_{dim} = (2.1 \pm 0.3) \times 10^4$ L/mol, while bifunctional OPV derivatives are present as random coil polymers in this solvent. In more apolar solvents such as dodecane, the hydrogen-bonded dimers of the monofunctional OPV derivative aggregate in chiral stacks, as can be concluded from UV/vis, fluorescence and CD spectroscopy. Temperature-dependent measurements show a first-order transition at 53 ± 3 °C from the aggregated state to the molecularly dissolved phase. The bifunctional derivative also aggregates in dodecane; however, based on CD measurements, these aggregates are less organized. This behavior is presumably the outcome of a competition between favorable $\pi-\pi$ interactions and restricted conformational freedom, due to the hexyl spacer, which results in a frustrated supramolecular polymeric stack. The length of these polymers as well as the chiral order in the assemblies can be controlled by the addition of monofunctional OPV derivatives.

Introduction

Control of mesoscopic order in π-conjugated systems is a subject of great importance because it enables the tuning of macroscopic properties of electrooptical devices such as solar cells,[1] light emitting diodes (LEDs),[2] and field effect transistors (FETs).[3] Furthermore if shape, dimension, and size can be controlled in the systems, these materials can presumably be used in nanoscale devices that are small and fast and can store information with high density.[4] It is now widely accepted that well-defined π-conjugated oligomers will play a crucial role in this field, because their precise chemical structure and conjugation length gives rise to defined functional properties and facilitate enhanced control over their supramolecular structure.[5] Research efforts in this direction have mainly been focused on methodologies for the synthesis and characterization of π-conjugated oligomers with lengths up to 10 nm.[6] In the future, considerable effort will be aimed at the control of spatial orientation and packing of these oligomers by means of molecular and supramolecular architectural design.

Mesoscopic order can be achieved by applying the principles of supramolecular chemistry[7] and is similar to the one observed in nature, whereby well-defined structures are built up through self-assembly of molecules. In this construction process simple chemical systems are self-organizing into nanometer-sized structures through mutual recognition properties. Organization of π-conjugated oligomers has already been achieved by using suitable solvent/nonsolvent mixture,[8] thermotropic and lyotropic liquid crystallinity,[9,10] and by using block copolymers.[11] Only a few examples have been reported on the use of hydrogen bonding motifs to organize π-conjugated systems. Mono- and bisthiophene bisurea compounds have been self-assembled into fibers in which the thiophene rings are arranged as a result of the hydrogen bonds between the urea groups and efficient charge transport was observed within these fibers.[12] Superstructures have also been obtained by hydrogen-bonding complexation of perylene bisimide derivatives with a ditopic melamine unit. In methylcyclohexane, cylindrical strands were formed resulting

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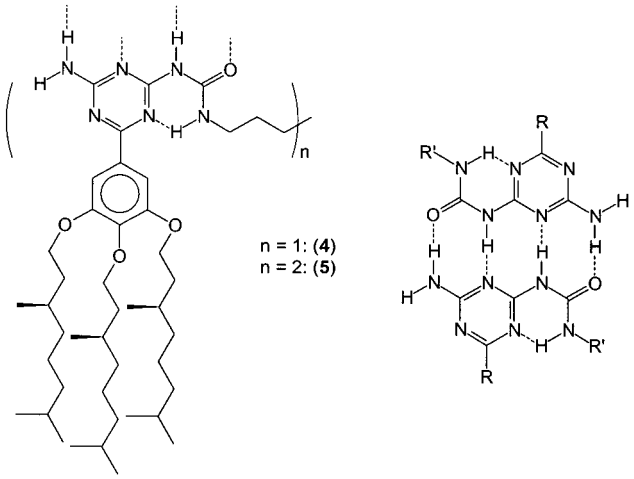
Chart 1



from hydrogen bond interactions between the melamines and solvent effects.[13]

Recently, we have found that monomers possessing two bifunctional quadruple hydrogen-bonded self-complementary ureido-pyrimidone units can form supramolecular polymers that display almost all properties of traditional polymers.[14] The chain length of these polymers could be easily adjusted with the addition of monomers possessing only one ureido-pyrimidone unit, which acts as a chain stopper. By substituting these units with oligo(*p*-phenylene vinylene)s (OPVs) we could form hydrogen-bonded π-conjugated dimers.[15] When appropriately substituted ureidotriazine hydrogen bond units are used instead of ureido-pyrimidones, it is possible to obtain liquid crystalline materials that form well-defined helical columnar structures when dissolved in dodecane (Chart 1).[16] In this construction process, the building blocks first dimerize via the hydrogen-bonded ureidotriazine units and subsequently form helical (polymeric) columnar architectures as was proven by circular dichroism (CD) spectroscopy, small-angle X-ray scattering (SAXS), and small-angle neutron scattering (SANS) measurements.[16] Perpherical chiral side groups or chiral end cappers achieved unprecedented control over supramolecular chirality.[16] In this paper we report on the synthesis and supramolecular organization of chiral π-conjugated oligo(*p*-phenylene vinylene) (OPV) molecules containing the same ureidotriazine hydrogen-bonding units, e.g. **MOPV** and **BOPV** (Scheme 1). Monofunctional **MOPV** molecules are capable of hierarchically growing by subsequent hydrogen bond and $\pi-\pi$ interactions into chiral supramolecular assemblies and showed thermochromic reversibility in apolar media. The bifunctional **BOPV** derivative probably forms a supramolecular random coil polymer in chloroform and frustrated stacks in dodecane, while the chain length of these supramolecular polymers can be adjusted by the addition of **MOPV**.

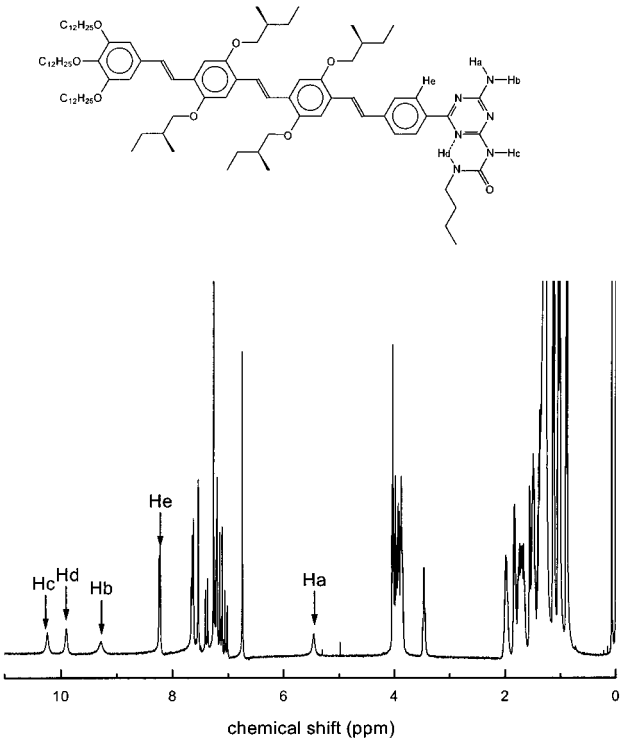


Figure 1. ^{1}H NMR spectrum of **MOPV** in $CDCl_3$ at room temperature.

Results and Discussion

Synthesis and Characterization. **MOPV** and **BOPV** with homochiral side chains were synthesized from aldehyde derivative **1**[17] which was converted via a Wittig−Horner coupling reaction to nitrile derivative **2** by using diethyl(4-cyanobenzyl)-phosphonate (Scheme 1). After reaction with Dicyandiamide, key intermediate **3** was obtained which was subsequently reacted with butylisocyanate and hexamethylenediisocyanate in dry refluxing pyridine, yielding **MOPV** and **BOPV**, respectively. The chiral hydrogen-bonded π-conjugated OPV-oligomers were fully characterized by ^{1}H NMR, ^{13}C NMR, and IR spectroscopy, MALDI-TOF mass spectrometry, and elemental analysis. IR measurements in chloroform revealed the different NH stretch-vibrations corresponding to monomeric and dimerized **MOPV**s.[16] ^{1}H NMR spectra of **MOPV** in chloroform showed the appearance of the NH signals at δ 5.46 (H_a), 9.28 (H_b), 9.9 (H_d), and 10.24 (H_c), typical for dimerized hydrogen-bonded ureidotriazine species (Figure 1). Analysis of the downfield shift of the H_e-proton as a function of the **MOPV** concentration yielded an association constant of $K_{dim} = (2.1 \pm 0.3) \times 10^4$ L/mol. This binding constant is similar to that of nonfunctionalized ureido-*s*-triazine units,[16] indicating no $\pi-\pi$ stacking between dimers of **MOPV**. The absence of $\pi-\pi$ stacking is supported by the fact that during the dilution experiments the H-resonances of the OPV unit did not shift. **BOPV** displayed the same ^{1}H NMR NH resonances as found for **MOPV**. However, now broadening of the specific hydrogen-bonded signals was observed and also the OPV-protons displayed a significant broadening which is presumably due to intermolecular interactions and/or restricted rotational freedom of the OPV units within a supramolecular polymer chain. Due to this broadening no association constants could be determined but most likely the two units are self-assembled in supramolecular random coil polymers with the same dimerization constant.[14]

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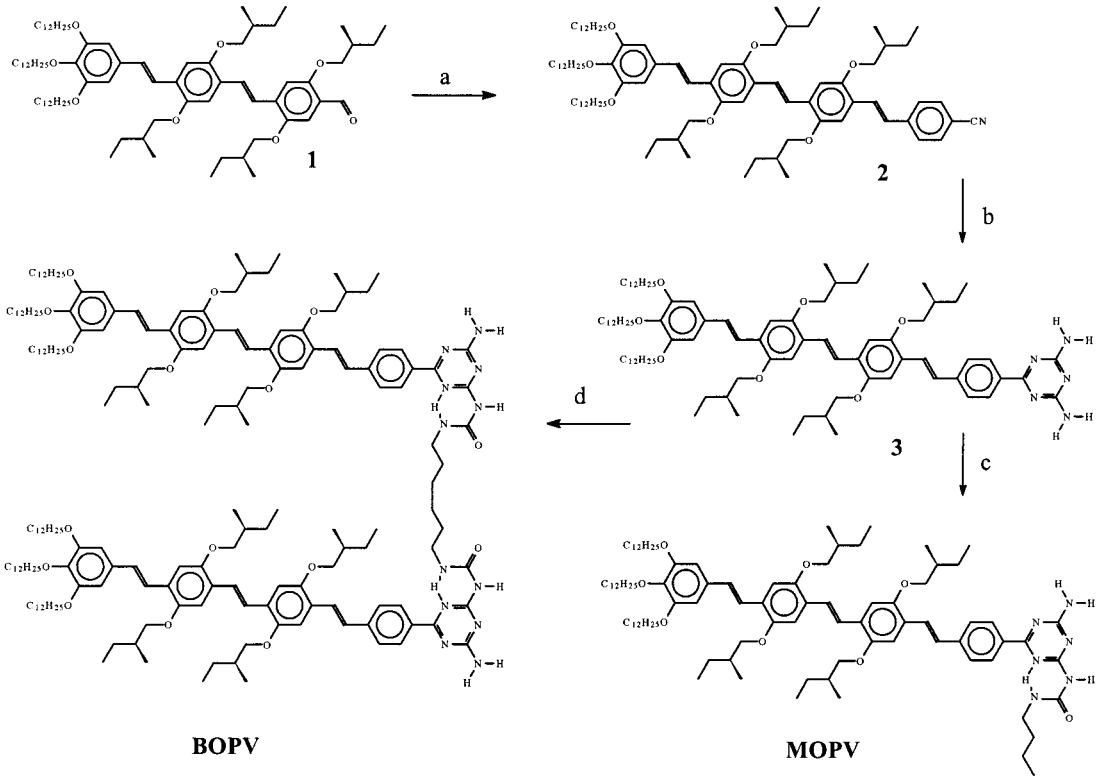
Scheme 1



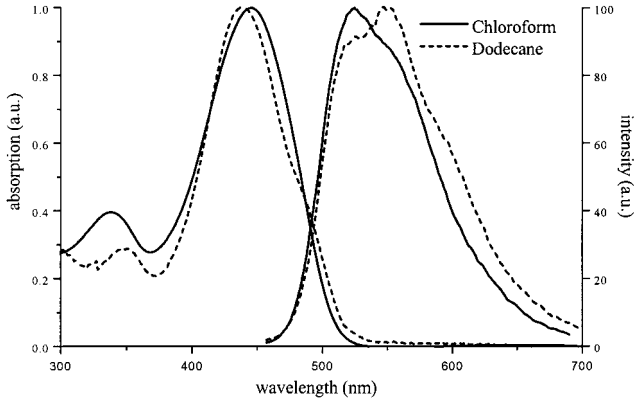


Figure 2. Normalized UV−vis and fluorescence spectra of **MOPV** in dodecane and chloroform at room temperature.

Assemblies of MOPV. UV/vis, fluorescence, and CD spectra were recorded of **MOPV** in chloroform and dodecane at room temperature. In chloroform solution (1.4e−5 mol/L) a λ_{max} is observed at 445 nm corresponding to the $\pi-\pi^*$ transition of the OPV units while the fluorescence maximum is located at 520 nm (Figure 2). These values are typical for molecularly dissolved tetra(*p*-phenylene vinylene)s and the absence of a Cotton effect supports the proposal that these oligomers are not aggregated in chloroform.[18] In dodecane (1.4e−5 mol/L), the absorption maximum of **MOPV** is blue shifted to $\lambda_{max} = 438$ nm with a strong vibronic shoulder at 480 nm. The fluorescence is quenched by approximately 1 order of magnitude and the emission maximum is shifted to the red ($\lambda_{em} = 550$ nm). This behavior is characteristic of aggregated OPV-oligomers. CD measurements showed a strong bisignated Cotton effect at the position of the $\pi-\pi^*$ band with positive and negative sign at 420 and 465 nm, respectively. The zero-crossing of the bisignated CD spectrum occurs at 441 nm, close to the absorption maximum. The CD spectrum is consistent with an exciton model in which the OPV dimers aggregate in a chiral supramolecular stack.[18]

Temperature-dependent UV−vis, fluorescence, and CD experiments of **MOPV** in dodecane showed a transition from the aggregated phase to molecularly dissolved species when the temperature was increased (Figure 3). In the UV−vis spectra, a blue shift of the absorption maximum was observed upon increasing the temperature. At temperatures higher than 60 °C, the absorption spectra are similar to that of chloroform at room temperature. Coinciding with the changes in the UV/vis spectra, the CD intensity decreases at temperatures higher than 40 °C and is completely lost at 70 °C. Upon cooling, the CD spectrum was fully recovered, indicating full reversibility. Further proof for the existence of two different phases of **MOPV** in dodecane solutions comes from similar changes in the fluorescence spectra with temperature. An emission maximum at 550 nm with vibronic shoulder around 575 nm ($\lambda_{ex} = 425$ nm) is observed at room temperature and the fluorescence increases and shifts to the blue upon heating the sample. At 70 °C, the fluorescence spectrum of that in chloroform at room temperature is observed.

The observed thermochromic behavior as monitored with UV/vis, CD, and fluorescence could be fitted with the Boltzmann equation[19]

$$\alpha = \frac{1}{1 + e^{(T-T_m)/\Delta T}} \qquad (1)$$

in which α is the fraction of aggregated molecules, T_m is the melting temperature at which $\alpha = 0.5$, and ΔT relates to the width of the curve. When the intensity ratio of the molecularly dissolved and aggregated states (with in all cases the same

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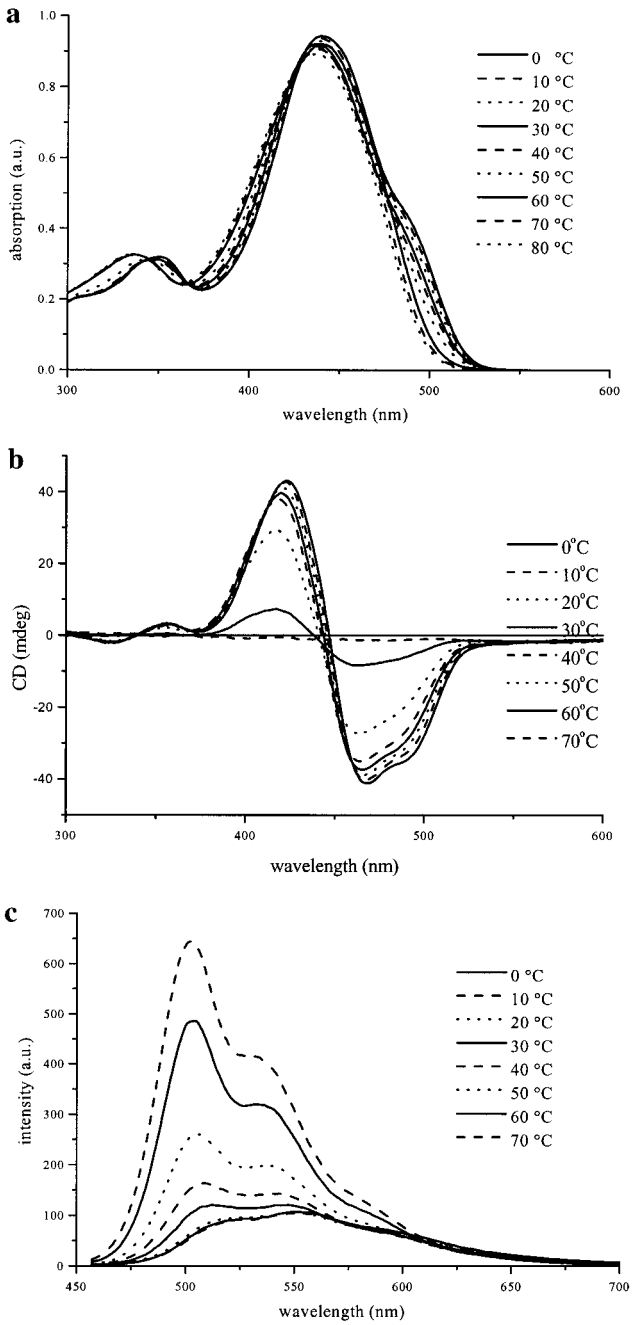

Figure 3. Temperature-dependent UV−vis (a), CD (b), and fluorescence (c) spectra of **MOPV** in dodecane.

concentration of **MOPV**) was plotted versus the temperature very good correlations were obtained (Figure 4). In all three cases, similar first-order transitions were found (T_m = 53 °C (CD), T_m = 51 °C (UV−vis), T_m = 55 °C (fluorescence)). As can be concluded from the fitted curve, the aggregation process seems to be completed within a temperature region of approximately 20 °C. The three techniques prove the existence of two phases for **MOPV** in solution, i.e., aggregates at low temperature and molecularly dissolved monomeric and dimeric species at high temperature. In addition, when analyzing carefully the UV−vis data, in the molecularly dissolved phase a linear shift of λ_{max} upon cooling was observed indicating that presumably first planarization of the OPV units takes place after which they aggregate.[19] In the aggregated phase a nonlinear red shift is observed. The red shift in the absorption upon aggregation indicates that most probably so-called J-type aggregates

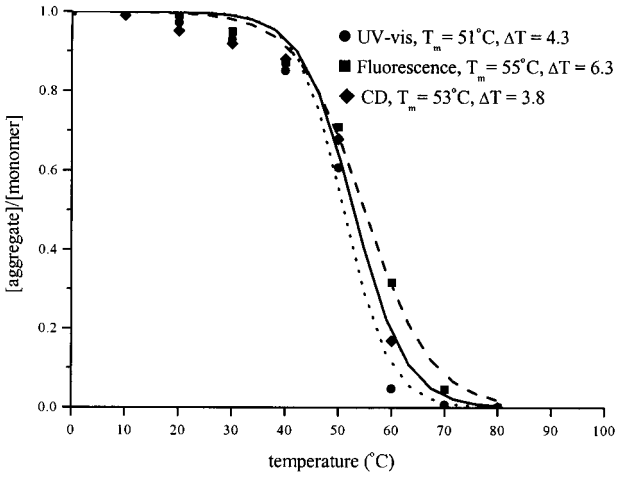

Figure 4. Normalized aggregate/monomer versus the temperature of **MOPV** in dodecane and the fitted curves.

are formed.[20] We assume, based on the optical data, that MOPV grows hierarchically, first forming dimers that subsequently develop into in chiral stacks (Figure 5). In other words, due to dimer formation by hydrogen bonding, the molecules exhibit properties similar to those based on traditional π-conjugated oligomers.[8]

Assemblies of BOPV. UV/vis, fluorescence, and CD spectra were also recorded for **BOPV** in chloroform and dodecane (Figure 6, CD data not shown). In chloroform solution (7.1e−6 mol/L), an absorption maximum at λ_{max} = 445 nm is found which is at the same position as obtained for **MOPV**. The emission spectrum of **BOPV** in chloroform (λ_{ex} = 445 nm) has a maximum at $\lambda_{em,max}$ = 528 nm and, similar to the monomeric species, no Cotton effect was observed in the CD spectra, all in agreement with a random coil supramolecular polymer system. The absorption maximum of **BOPV** in dodecane is red shifted (λ_{max} = 453 nm) which differs from the behavior of **MOPV**. The fluorescence spectrum in dodecane is, however (λ_{ex} = 453 nm, $\lambda_{em,max}$ = 545 and 576 nm), similar to that of the monomeric species in this solvent. Surprisingly, in contrast to the strong bisignated CD spectrum of **MOPV**, only a weak Cotton effect was observed for the concentrated solution (6.78e−5 mol/L) of **BOPV**. The weak Cotton effect found for **BOPV** indicates aggregation in dodecane; however, we propose that these aggregates are not as well organized and are of a different type from that formed by **MOPV**, i.e. frustrated stacks (Figure 7).

These results are opposite to the results we found with monofunctional triazine molecules without a π-conjugated OPV part (**4**, Chart 1) that shows no Cotton effect in dodecane while in the case of the bifunctional derivative (**5**, Chart 1) a Cotton effect was observed and it was concluded that the presence of a covalent linker between the triazine units was important in maintaining the positional ordering in the formation of supramolecular chiral structures. Dimers of **4** are also stacked, but the columns lack the hexamethylene chain that induces positional order between disks of **5**. Within the columns formed by **4**, the dimerized molecules have no specific interactions other than nondirected $\pi-\pi$ interactions and are therefore rotating freely. In the case of **MOPV** this rotational freedom is restricted due to favorable $\pi-\pi$ stacking of the OPV units and helical stacks are formed with a small angle between the dimers. This behavior is similar to that of all known π-conjugated oligomers.[8] In the case of **BOPV** a competition exists between favorable

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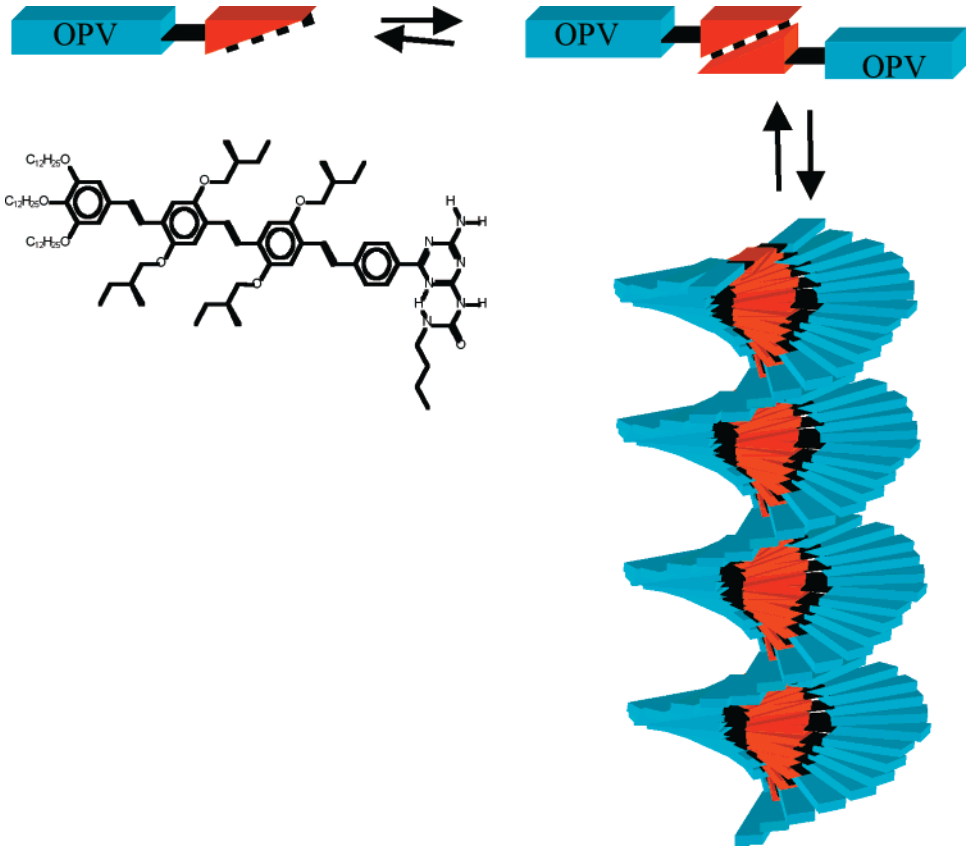

Figure 5. Schematic representation of the hierarchical organization of **MOPV** in dodecane.

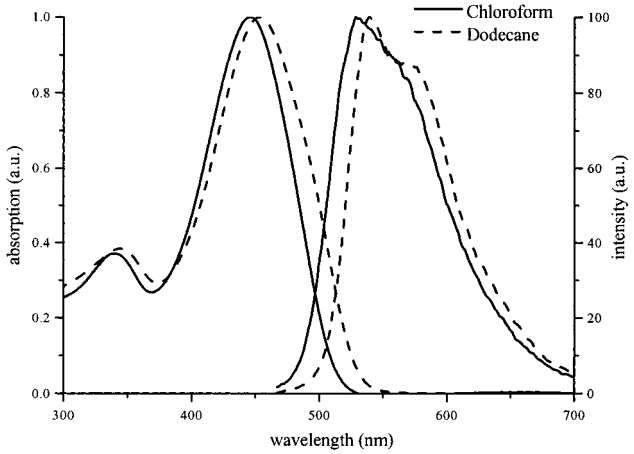

Figure 6. Normalized UV−vis and fluorescence spectra of **BOPV** in dodecane and chloroform at room temperature.

$\pi-\pi$ stacking of the OPV units and the restricted conformation due to the hexamethylene spacer resulting in so-called frustrated stacks.

To tune the virtual chain length of our supramolecular polymers, **MOPV** was used as a chain stopper in supramolecular polymer chains formed by **BOPV**.[14,16] To promote the exchange of the molecules, we first heated the solutions up to 70 °C for 5 min and then after the solutions were cooled to 20 °C the CD spectra were recorded. A nonlinear behavior of the Cotton effect as a function of the **MOPV** mol fraction was observed indicating exchange of the compounds and a statistical distribution of **MOPV** and **BOPV** in the stacks (Figure 8). It therefore eliminates the coexistence of individual stacks of **MOPV** and **BOPV**, which should yield a linear behavior of the Cotton effects versus the concentration of **MOPV**. The Cotton effect is already dropped by a factor 5 at a 0.7 mol fraction of **MOPV**. This behavior shows that indeed the chain length of the supramolecular polymers formed by **BOPV** can be tuned. Detailed SANS and SAXS measurements are required to determine the changes in stack length of **MOPV** and **BOPV** and the mixtures thereof.

Conclusion

Mono- and bifunctional OPVs functionalized with ureido-*s*-triazine units have been successfully synthesized with the aim to bridge the gap between π-conjugated oligomers and polymers. Monofunctional OPV derivatives dimerize in chloroform solution with a dimerization constant of $K_{dim} = (2.1 \pm 0.3) \times 10^4$ L/mol. In dodecane this compound is aggregated in helical columns, as could be concluded from UV/vis, fluorescence, and CD spectroscopy. Temperature-dependent measurements showed a melting transition at 53 ± 3 °C from the aggregated state to the molecularly dissolved phase. The bifunctional derivative is also aggregated in dodecane but based on the CD measurements these aggregates are less organized. We propose the formation of frustrated stacks. The length of these polymers could be controlled by the addition of monofunctional OPV derivatives. This behavior illustrates that it is possible to incorporate **MOPV** as a chain stopper into the supramolecular coil polymers formed by **BOPV** and that the length of these polymers can be tuned. With this type of system we can combine the ordering of well-defined oligomers with the processing advantages of polymers. Research to adjust the spacer length to obtain a perfect fit between chirality due to $\pi-\pi$ stacking and the spacer and detailed SAXS and SANS analyses are in progress.

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 (δ) relative to

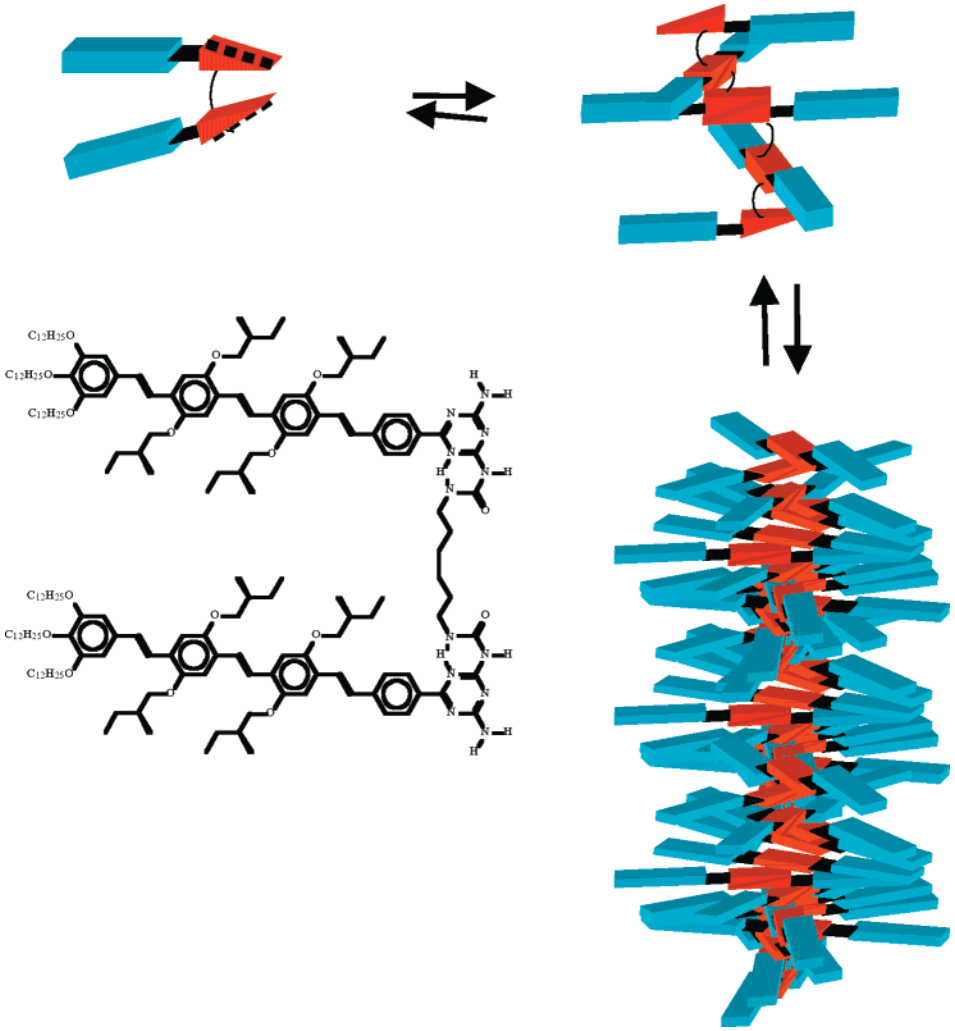

Figure 7. Schematic representation of the hierarchical organization of **BOPV** in dodecane.

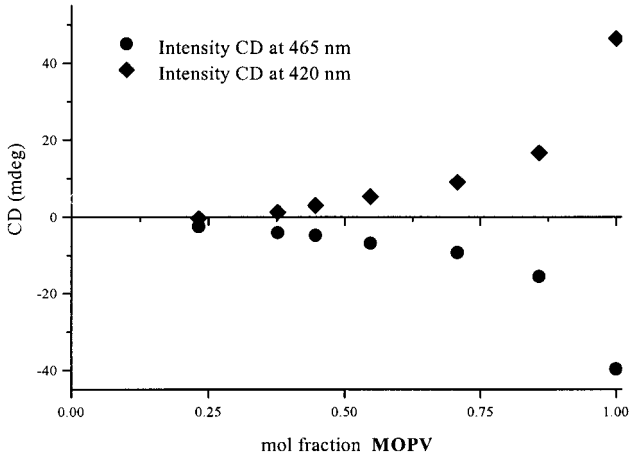

Figure 8. Change of the CD intensity of **MOPV** in dodecane in different mixtures of **MOPV** and **BOPV**.

tetramethylsilane. Abbreviations used are s = singlet, d = doublet, t = triplet, q = quartet, and br = broad. Infrared spectra were run on a Perkin-Elmer 1650 FT-IR spectrometer or on a Perkin-Elmer Spectrum One UATR FT-IR spectrophotometer. MALDI-TOF MS spectra were measured on a Perspective DE Voyager spectrometer utilizing a α-cyano-4-hydroxycinnamic acid matrix. 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. UV/vis and fluorescence spectra were performed on a Perkin-Elmer Lambda 40 spectrophotometer and a Perkin-Elmer LS-50 B instrument, respectively. CD spectra were recorded on a JASCO J-600 spectropolarimeter. For the fluorescence measurements, solutions with an optical density of less than 0.1 were used.

Materials. (*E*)-4-{4-Methyl-2,5-bis[(*S*)-2-methylbutoxy]styryl}-2,5-bis[(S)-2-methylbutoxy]benzaldehyde was synthesized according a literature procedure.[17] All solvents were of AR quality and chemicals were used as received. Bio-Beads S-XI Beads were obtained from Bio-Rad Laboratories.

(*E*)-4-{4-Methyl-2,5-bis[(*S*)-2-methylbutoxy]styryl}-2,5-bis[(*S*)-2-methylbutoxy]benzaldehyde Dimethyl Acetal. Amberlite IR 120 (5.00 g), trimethyl orthoformate (40 mL), and (*E*)-4-{4-methyl-2,5-bis[(*S*)-2-methylbutoxy]styryl}-2,5-bis[(S)-2-methyl butoxy]benzaldehyde (5.00 g, 8.82 mmol) were added to 300 mL of methanol. The suspension was stirred under an argon atmosphere at 70 °C for 2 h. The reaction mixture was cooled to room temperature and 5.00 g of Na_2CO_3 was added. The suspension was filtrated and the solvent was removed in vacuo to yield 5.40 g (100%) of the desired compound, which was used without further purification. ^{1}H NMR ($CDCl_3$) δ 1.19−0.89 (m, 24H, C*H*$_3$), 1.50−1.22 (m, 4H, C*H*), 1.78−1.55 (m, 4H, C*H*), 2.04−1.88 (m, 4H, C*H*), 2.27 (s, 3H, ArC*H*$_3$), 3.45 (s, 6H, OC*H*$_3$), 4.00−3.75 (m, 8H, OC*H*$_2$), 5.69 (s, 1H, C*H*(OCH$_3$)$_2$), 6.78 (s, 1H, Ar*H*), 7.13 (s, 1H, Ar*H*), 7.15 (s, 1H, Ar*H*), 7.22 (s, 1H, Ar*H*), 7.49 (d, 1H, CH=C*H*), 7.55 (d, 1H, C*H*=CH); ^{13}C NMR ($CDCl_3$) δ 11.47, 11.60, 14.21, 16.50, 16.80, 16.89, 22.77, 26.33, 26.37, 26.47, 31.71, 35.01, 35.07, 35.23, 54.36, 73.43, 73.80, 74.43, 74.73, 99.83, 108.42, 109.24, 111.93, 116.38, 121.83, 123.54, 125.19, 126.43, 127.68, 128.43, 150.52, 150.65, 151.09, 151.78.

(*E*)-*N*-Phenyl-3,4,5-tridodecyloxybenzaldimine. A mixture of aniline (0.51 g, 5.50 mmol) and 3,4,5-tridodecyloxybenzaldehyde (3.00 g, 4.55 mmol) was stirred at 60 °C under an argon atmosphere. Every hour

the reaction vessel was evacuated to remove the water, which was formed during the reaction. After 6 h the excess of aniline was removed in vacuo. Recrystallization from a chloroform/methanol/ethanol mixture afforded 3.18 g (95%) of the desired compound as a white solid: ^{1}H NMR ($CDCl_3$) δ 0.90 (t, 9H, CH_3), 1.63−1.15 (m, 54H, CH_2), 1.94−1.75 (m, 6H, CH_2CH$_2$O), 4.18−4.00 (m, 6H, CH_2O), 7.13 (s, 2H, Ar*H*), 7.28−7.18 (m, 3H, Ar*H*), 7.40 (t, 2H, Ar*H*), 8.33 (s, 1H, C*H*═N); ^{13}C NMR ($CDCl_3$) δ 14.23, 22.81, 26.22, 29.49, 29.52, 29.72, 29.76, 29.82, 29.87, 30.47, 32.05, 69.27, 73.63, 107.16, 120.94, 125.77, 129.19, 131.39, 141.31, 152.32, 153.52, 160.31; IR (UATR) υ (cm^{-1}) 2954, 2917, 2872, 2849, 1624, 1579, 1506, 1473, 1463, 1436, 1390, 1373, 1333, 1229, 1154, 1116, 991, 971, 820, 768, 719, 696. Anal. Calcd for $C_{49}H_{83}NO_3$: C, 80.16; H, 11.39; N, 1.91. Found: C, 80.05; H, 11.29; N, 1.82.

(*E*,*E*)-4-{4-(3,4,5-Tridodecyloxystyryl)-2,5-bis[(*S*)-2-methylbutoxy]-styryl}-2,5-bis[(*S*)-2-methylbutoxy]benzaldehyde (1). (*E*)-4-{4-Methyl-2,5-bis[(*S*)-2-methylbutoxy]styryl}-2,5-bis[(*S*)-2 methylbutoxy]benzaldehyde dimethyl acetal (4.80 g, 7.83 mmol) and (*E*)-*N*-Phenyl-3,4,5-tridodecyloxybenzaldimine (5.75 g, 7.83 mmol) were dissolved in 10 mL of anhydrous DMF. K*t*BuO (3.18 g, 28.4 mmol) was added to the solution, and the reaction mixture was heated to 80 °C and stirred for 1 h under an argon atmosphere. The reaction mixture was cooled to room temperature and poured onto a mixture of 250 g of crushed ice and 85 mL of 6 N HCl. The mixture was extracted three times with 100 mL of dichloromethane. The combined organic fractions were washed with water and dried over $MgSO_4$. After evaporation of the solvent the crude product was purified by column chromatography (silica gel, pentane/CH_2Cl_2 1:1) to afford 8.53 g (90%) of aldehyde compound **1** as an orange solid: ^{1}H NMR ($CDCl_3$) δ 1.18−0.90 (m, 33H, CH_2, CH_3), 1.89−1.18 (m, 68H, C*H*, CH_2), 2.05−1.90 (m, 4H, C*H*), 4.10−3.80 (m, 14H, OCH_2), 6.77 (s, 2H, Ar*H*), 7.08 (d, 1H, C*H*═CH), 7.13 (s, 1H, Ar*H*), 7.19 (s, 1H, Ar*H*), 7.25 (s, 1H, Ar*H*), 7.34 (s, 1H, Ar*H*), 7.41 (d, 1H, C*H*═CH), 7.53 (d, 1H, C*H*═CH), 7.66 (d, 1H, C*H*═CH), 10.48 (s, 1H, ArC*H*═O); ^{13}C NMR ($CDCl_3$) δ 11.75, 11.91, 11.93, 14.55, 11.98, 17.05, 17.18, 17.21, 23.12, 26.56, 26.78, 29.79, 29.82, 29.85, 30.04, 30.08, 30.13, 30.16, 30.18, 30.77, 32.34, 32.36, 35.25,35.31 35.47, 35.53, 69.40, 73.83, 73.97, 74.19, 74.48, 74.56, 105.37, 109.77, 110.40, 110.49, 122.06, 122.50, 124.19, 126.52, 126.61, 127.98, 129.30, 133.24, 135.29, 138.44, 150.74, 151.20, 151.52, 153.37, 156.49, 188.93; IR (UATR) υ (cm^{-1}) 2957, 2922, 2853, 2676, 1593, 1501, 1465, 1422, 1386, 1333, 1242, 1201, 1116, 1041, 965, 852, 723; MALDI-TOF MS (MW = 1206.98) *m*/*z* 1206.75 [M]$^+$.

Diethyl(4-cyanobenzyl) Phosphonate. A mixture of triethyl phosphite (2.54 g, 15.30 mmol) and 4-cyanobenzyl bromide (2.00 g, 10.20 mmol) was stirred at 160 °C for 2 h. During this time 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 product, diethyl(4-cyanobenzyl) phosphonate, was used without further purification: ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.19 (t, 6H, CH_3), 3.14 (d, 2H, CH_2), 3.98 (dt, 4H, CH_2), 7.37 (dd, 2H, Ar*H*), 7.55 (dd, 2H, Ar*H*); ^{13}C NMR (100 MHz, $CDCl_3$) δ 16.07 (d), 33.78 (d), 62.17 (d), 110.55 (d), 118.43 (d), 127.68 (d), 131.19 (d), 137.34 (d); IR (UATR) υ (cm^{-1}) 2984, 2909, 2227, 1607, 1506, 1479, 1444, 1417, 1392, 1244, 1048, 1018, 958, 857, 824, 780; GC-MS (MW = 253) *m*/*z* 253 [M]$^+$.

(*E*,*E*,*E*)-4-[4-{4-(3,4,5-Tridodecyloxystyryl)-2,5-bis[(*S*)-2-methylbutoxy]styryl}-2,5-bis[(*S*)-2-methylbutoxy]styryl]phenylnitrile (2). Diethyl(4-cyanobenzyl) phosphonate (0.79 g, 3.10 mmol) was dissolved in 5 mL of anhydrous DMF and under an argon atmosphere K*t*BuO (0.46 g, 4.14 mmol) was added to the solution. After 15 min a solution of **1** (2.50 g, 2.07 mmol) in 30 mL of DMF/THF (2:1) was added dropwise to the reaction mixture. The solution was stirred for 72 h and subsequently poured onto 100 g of crushed ice. HCl (80 mL, 3 N) was added and the aqueous phase was extracted three times with diethyl ether. The collected organic fractions were washed with 3 N HCl solution and dried over $MgSO_4$. After evaporation of the solvent the product was purified by column chromatography (silica gel, hexane/CH_2Cl_2 1:2) to afford 2.47 g (91%) of **2** as a orange solid: ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.95−1.15 (m, 9H, OCH$_2$CH$_2$(CH$_2$)$_9$CH_3, 12H, OCH$_2$CH(CH_3)CH$_2$CH$_3$, 12H, OCH$_2$CH(CH$_3$)CH$_2$CH_3), 1.3 (m, 54H, OCH$_2$CH$_2$(CH_2)$_9$CH$_3$), 1.5−1.7 (m, 8H, OCH$_2$CH(CH$_3$)CH_2CH$_3$), 1.9 (m, 4H, OCH$_2$C*H*(CH$_3$)CH$_2$CH$_3$), 2.00 (m, 6H, OCH$_2$CH_2(CH$_2$)$_9$CH$_3$), 3.95−4.06 (m, 14H, OCH_2), 6.75 (s, 2H, Ar*H*), 7.03 (d, J = 16.4 Hz, 1H, ArC*H*═CH), 7.1−7.2 (m, 6H, ArCH═C*H*, Ar*H*), 7.4 (d, J = 16.4 Hz, 1H, ArCH═C*H*Ar), 7.5−7.6 (m, 4H, ArCH═C*H*, Ar*H*), 8.31 (s, 1H, Ar*H*), 8.33 (s, 1H, Ar*H*); ^{13}C NMR (100 MHz, $CDCl_3$) δ 11.39, 11.47, 11.51, 14.10, 16.78, 16.85, 22.68, 26.14, 26.40, 29.36, 29.39, 29.44, 29.66, 29.70, 29.75, 30.35, 31.93, 35.00, 35.09, 35.16, 69.12, 73.56, 74.12, 74.22, 74.45, 77.21, 105.14, 109.70, 109.94, 110.47, 110.94, 122.53, 122.94, 125.18, 126.33, 126.89, 127.39, 128.00, 128.10, 128.62, 128.74, 133.24, 135.16, 138.21, 141.43, 151.01, 151.13, 151.18, 151.51, 153.26, 167.66, 172.02; IR (KBr) υ (cm^{-1}) 3170, 3401, 3475 (N−H stretch); MALDI-TOF MS (MW = 1391.11) *m*/*z* 1390.18 [M]$^+$.

2,4-Diamino-6-[(*E*,*E*,*E*)-4-⟨4-{4-(3,4,5-trisdodecyloxystyryl)-2,5-bis[(*S*)-2-methylbutoxy]styryl}-2,5-bis[(*S*)-2-methylbutoxy]styryl⟩]-phenyl-*s*-triazine (3). In a round-bottom flask 1.97 g (1.51 mmol) of **2** and 0.13 g (1.54 mmol) of Dicyandiamide were dissolved in 20 mL of 2-methoxyethanol. After adding 0.20 g (3.56 mmol) of KOH, the solution was stirred for 8 h. Purification was achieved with column chromatography (silica gel, EtOH/CH_2Cl_2 2:98). After precipitation in methanol pure **3** (1.55 g, 74%) was obtained. ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.95−1.15 (m, 9H, OCH$_2$CH$_2$(CH$_2$)$_9$CH_3, 12H, OCH$_2$CH(CH_3)CH$_2$CH$_3$, 12H, OCH$_2$CH(CH$_3$)CH$_2$CH_3), 1.3 (m, 54H, OCH$_2$CH$_2$(CH_2)$_9$CH$_3$), 1.5−1.7 (m, 8H, OCH$_2$CH(CH$_3$)CH_2CH$_3$), 1.9 (m, 4H, OCH$_2$C*H*(CH$_3$)CH$_2$CH$_3$), 2.00 (m, 6H, OCH$_2$CH_2(CH$_2$)$_9$CH$_3$), 3.95−4.06 (m, 14H, OCH_2), 6.75 (s, 2H, Ar*H*), 7.03 (d, J = 16.4 Hz, 1H, ArC*H*═CH), 7.1−7.2 (m, 6H, ArCH═C*H*, Ar*H*), 7.4 (d, J = 16.4 Hz, 1H, ArCH═C*H*Ar), 7.5−7.6 (m, 4H, ArCH═C*H*, Ar*H*), 8.31 (s, 1H, Ar*H*), 8.33 (s, 1H, Ar*H*); ^{13}C NMR (100 MHz, $CDCl_3$) δ 11.39, 11.47, 11.51, 14.10, 16.78, 16.85, 22.68, 26.14, 26.40, 29.36, 29.39, 29.44, 29.66, 29.70, 29.75, 30.35, 31.93, 35.00, 35.09, 35.16, 69.12, 73.56, 74.12, 74.22, 74.45, 77.21, 105.14, 109.70, 109.94, 110.47, 110.94, 122.53, 122.94, 125.18, 126.33, 126.89, 127.39, 128.00, 128.10, 128.62, 128.74, 133.24, 135.16, 138.21, 141.43, 151.01, 151.13, 151.18, 151.51, 153.26, 167.66, 172.02; IR (KBr) υ (cm^{-1}) 3170, 3401, 3475 (N−H stretch); MALDI-TOF MS (MW = 1391.11) *m*/*z* 1390.18 [M]$^+$.

2-Amino-4-butylureido-6-[(*E*,*E*,*E*)-4-⟨4-{4-(3,4,5-trisdodecyloxystyryl)-2,5-bis[(*S*)-2-methylbutoxy]styryl}-2,5-bis[(*S*)-2-methylbutoxy]styryl⟩]phenyl-*s*-triazine} (MOPV). Under an argon atmosphere, 1.35 g (0.97 mmol) of **3** was dissolved in 20 mL of dry pyridine at room temperature. *n*-Butylisocyanate (24.1 mg, 0.24 mmol) was added and the reaction mixture was refluxed for 8 h. After evaporation of the solvent, the mixture was flushed with toluene to remove the pyridine. Using column chromatography (2% EtOH in CH_2Cl_2), pure **MOPV** (0.839 g, 58%) was obtained.^{1}H NMR (400 MHz, $CDCl_3$) δ 0.9 (m, 9H, OCH$_2$CH$_2$(CH$_2$)$_9$CH_3, 12H, OCH$_2$CH(CH_3)CH$_2$CH$_3$, 12H, OCH$_2$CH(CH$_3$)CH$_2$CH_3), 1.3 (m, 54H, OCH$_2$CH$_2$(CH_2)$_9$CH$_3$), 1.5−1.7 (m, 8H, OCH$_2$CH(CH$_3$)CH_2CH$_3$, 7H, NCH$_2$(CH_2)$_2$CH$_3$), 1.9 (m, 4H, OCH$_2$C*H*(CH$_3$)CH$_2$CH$_3$), 2.00 (m, 6H, OCH$_2$CH_2(CH$_2$)$_9$CH$_3$), 3.5 (q, 2H, ArNHCONHCH_2), 3.95−4.06 (m, 14H, OCH_2), 5.46 (br, 1H, ArN*H*H), 6.75 (s, 2H, Ar*H*), 7.03 (d, J = 16.4 Hz, 1H, ArCH═C*H*Ar), 7.1−7.2 (m, 6H, ArCH═C*H*, Ar*H*), 7.4 (d, J = 16.4 Hz, 1H, ArCH═C*H*), 7.5−7.6 (m, 4H, ArC*H*═CH, Ar*H*), 8.22 (s, 1H, Ar*H*), 8.24 (s, 1H, Ar*H*), 9.28 (br, 1H, ArNHCON*H*), 9.90 (br, 1H, ArN*H*CONH), 10.24 (br, 1H, ArNH*H*); ^{13}C NMR (100 MHz, $CDCl_3$) δ 11.58, 11.65, 11.71, 14.00, 14.25, 16.89, 16.95, 16.98, 20.47, 22.81, 26.25, 26.52, 29.47, 29.50, 29.56, 29.75, 29.78, 29.81, 29.82, 29.85, 30.40, 30.47, 31. 79, 32.03, 32.04, 35.11, 35.18, 35.27, 40.01, 69.05, 73.52, 73.94, 74.09, 74.34, 74.38, 77.21, 104.93, 109.26, 109.57, 110.23, 110.61, 122.12, 122.31, 122.66, 125.36, 125.79, 126.128, 126.70, 127.11, 127.18, 128.08, 128.40, 128.49, 133.07, 133.92, 137.95, 141.84, 150.73, 150.87, 150.94, 151.31, 153.03, 155.74, 163.53, 167.74, 169.77; IR (KBr) υ (cm^{-1}) 1687 (C═O stretch), 3209, 3222, 3301, 3491 (N−H stretch); IR ($CDCl_3$) υ (cm^{-1}) 3542, 3491, 3424, 3300, 3222, 3209 (hydrogen and non-hydrogen bonded N−H vibrations); MALDI-TOF MS (MW = 1490.24) *m*/*z* 1489.21 [M]$^+$, 1512.03 [M + Na]$^+$. Anal. Calcd for $C_{94}H_{148}O_8N_6$: C, 72.05; H, 10.26; N, 5.09 Found: C, 72.26; H, 9.94; N, 5.11.

1,6-Bis{2-amino-4-hexadiylureido-6-[(*E*,*E*,*E*)-4-⟨4-{4-(3,4,5-tris-dodecyloxystyryl)-2,5-bis[(*S*)-2-methylbutoxy]styryl}-2,5-bis[(*S*)-2-

methylbutoxy]styryl⟩]phenyl-*s*-triazine} ***(*BOPV)**. **3** (1.35 g, 0.971 mmol) was dissolved in 20 mL of dry pyridine under Ar atmosphere. Diisocyanatohexane (40.8 mg, 0.243 mmol) was added and the reaction mixture was refluxed for 8 h. After evaporation of the solvent, the mixture was flushed with toluene to remove the pyridine. Purification using Bio-Beads column chromatography (2 times, using THF as eluent) resulted in 0.50 g of still impure product. Half of this material was further purified with column chromatography (2% EtOH in CH_2Cl_2). Ultimately pure **BOPV** (0.175 g, 14%) was obtained. ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.9−1.1 (m, 18H, $OCH_2CH_2(CH_2)_9CH_3$, 24H, $OCH_2CH(CH_3)CH_2CH_3$, 24H, $OCH_2CH(CH_3)CH_2CH_3$), 1.3 (m, 108H, $OCH_2CH_2(CH_2)_9CH_3$), 1.5−1.7 (m, 16H, $OCH_2CH(CH_3)CH_2CH_3$, 12H $(CH_2)_6N$), 1.8−2.0 (br, 4H, $OCH_2CH_2(CH_2)_9CH_3$, 4H, $OCH_2CH(CH_3)CH_2CH_3$, 4H, $OCH_2CH_2(CH_2)_9CH_3$), 3.5 (q, 4H, ArNHCONHCH_2), 3.95−4.06 (br, 28H, OCH_2), 5.46 (br, 2H, ArN*H*H), 6.75 (s, 4H, Ar*H*), 7.1 (br, 16H, ArC*H*═CH, Ar*H*), 7.4 (br, 8H, ArCH═C*H*, Ar*H*), 8.0 (br, 4H, Ar*H*), 9.5 (br, 2H, ArNHCON*H*), 9.90 (br, 2H, ArN*H*CONH), 10.24 (br, 2H, ArNH*H*); MALDI-TOF MS (MW = 2950.41) *m*/*z* 2949.09 $[M]^+$, 2972.64 $(M + Na]^+$. Anal. Calcd for $C_{186}H_{290}O_{16}N_{12}$: C, 74.89; H, 9.97; N, 5.57. Found: C, 74.94; H, 9.49; N, 5.66.

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