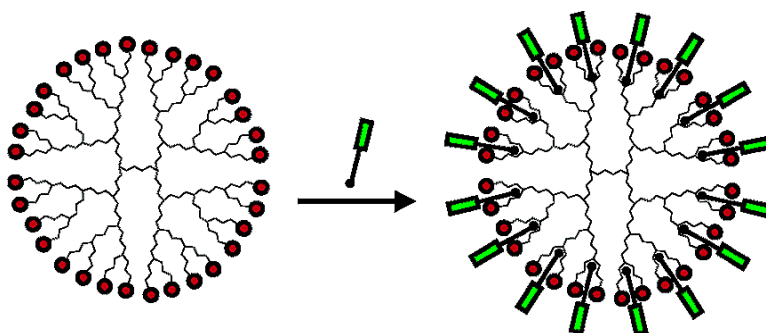Article

Highly Emissive Supramolecular Oligo(*p*-phenylene vinylene) Dendrimers

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Highly Emissive Supramolecular Oligo(*p*-phenylene vinylene) Dendrimers

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Abstract: π-Conjugated oligo(*p*-phenylene vinylene) (OPV) guest molecules for interaction with dendritic hosts were synthesized and fully characterized by NMR spectroscopy, MALDI-TOF−MS, elemental analysis and optical measurements. The binding properties of the five different OPV guests to a *N,N*-bis[[(3-adamantyl ureido) propyl] methylamine host have been investigated. The guests that contained an aryl urea glycine spacer were bound with the highest association constant. Subsequently, an adamantyl urea modified fifth generation poly(propylene imine) dendrimer was synthesized as a multivalent host which contains 32 *N,N*-bis[[(3-adamantyl ureido) propyl] amine binding sites. Size exclusion chromatography showed that 32 of the OPV guests strongly bind to the fifth generation adamantyl functionalized dendritic host. In the case of the supramolecular dendritic host/guest system smooth homogeneous thin films could be obtained by spin coating. The dendritic guest−host complexes showed a significantly higher emission upon binding then that of the individual molecules due to the three-dimensional orientation of the OPV guest molecules. In the solid state, this enhancement in luminescence was a factor of 10. The π-conjugated oligomers are less aggregated in the supramolecular assemblies presumably because of a shielding effect of the bulky adamantyl units present in the hosts.

Introduction

After the first report on electroluminescence in poly(*p*-phenylene vinylene) (PPV),[1] a variety of π-conjugated polymers and oligomers have been synthesized and applied in light emitting diodes (LEDs).[2] An impressive number of research groups have expended considerable effort in attempting to improve the performance of these materials.[3,4]

Aggregation of π-conjugated materials (especially H-type aggregates) is often observed resulting in low quantum efficiencies of luminescence.[5] Branching of π-conjugated systems can overcome this stacking phenomenon, for example, oligo(*p*-phenylene vinylene)s (OPVs) have been oriented in a tetrahedral framework minimizing intramolecular stacking.[6] These tetrahedral arrays do not crystallize and form stable amorphous phases.

Another route to obtain branched systems is the use of dendrimers. These macromolecules possess a covalent three-dimensional structure that permits spatial control of the active components and thus the electroluminescent properties.[7] Furthermore, the durability of LEDs can be enhanced by prevention of crystallization of the active component, leading to truly amorphous films. This is important because crystallization or melting, caused by heat or short-circuit currents, often results in device damage.[8] Dendrimers can be designed so that the core defines the color of the light emission, whereas the surface groups control the processing properties and the branching units act as charge transporting units.[9] An important feature of incorporating chromophores as cores is that it provides the chromophores in a solution processable form, and reducing


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Scheme 1. Concept of Supramolecular Anchoring of OPV Guest to a Dendritic Host

Dendritic host   **Host-Guest Complex**
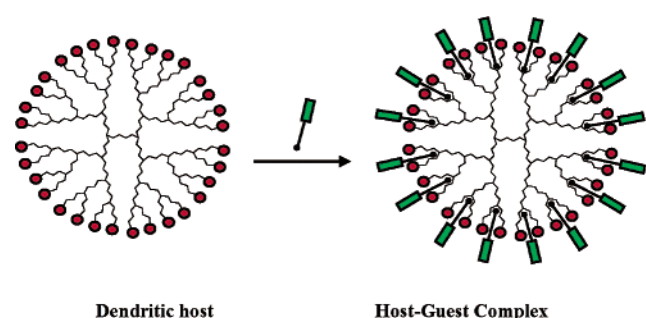
aggregation.[10] Moreover, light harversting and site-isolation of the chromophores is achieved.[11]

We have functionalized poly(propylene imine) dendrimers up to generation five with π-conjugated oligo(*p*-phenylene vinylene)s (OPVs).[12] These dendrimers proved to be good hosts for anionic dye molecules. Thin films prepared from these host–guest complexes showed efficient (>90%) energy transfer from the OPV units to the encapsulated dye molecules. By choosing the appropriate dye, the emission wavelength could be tuned. Preliminary experiments showed that it was possible to construct LEDs from the dye/dendrimer system, athough aggregation and, hence quenching of the luminescence was still observed even for the fifth generation dendrimer.

Recently, we published a supramolecular strategy for modifying the periphery of the poly(propylene imine) dendrimer (Scheme 1).[13,14] Adamantyl-urea modified dendrimers were used as a scaffold to reversibly bind glycine-urea funtionalized guests in organic media using hydrogen bond (between the urea linkages of dendrimer and the guest) and acid–base interactions (between COOH of the guest and amines of the host). We have also found that adamantyl dendrimers, noncovalently functionalized with catalytic sites, can be applied in a continuous flow membrane reactor. This system does not show leaching of the catalytic sites.[15]

Adamantyl dendrimers are known to adopt a persistent globular conformation similar to the dendritic box,[16] due to the three-dimensional dendritic scaffolding, resulting in the formation of amorphous films. Moreover, the existence of bulky and rigid adamantyl groups at the periphery of dendrimer reduces intermolecular distances, preventing aggregation.

Here, we report the design, synthesis, and optical properties of glycinyl-urea functionalized π-conjugated oligo(*p*-phenylene

vinylene) guests that bind to adamantyl urea modified dendritic hosts (Scheme 1). The resulting supramolecular assemblies are investigated with respect to their photophysical properties.

Recently, Holmes, Kraft and co-workers described the preparation of stilbene-carboxylic acids that form noncovalent complexes with tris(imidazoline) base derivatives.[17] These supramolecular complexes showed strong fluorescence in solution whereas in the solid-state photoluminescence was quenched.

Results and Discussion

Synthesis. The π-conjugated guests (**OPV1**, **OPV2**, **OPV3**, **OPV4**, **OPV5,** Scheme 2) are rationally designed and consist of a carboxylic acid and an urea moiety. **OPV1** and **OPV2** were synthesized from activated ester derivative **1**.[12] Reaction of **1** with *tert*-butyl *N*-(6-aminohexyl)carbamate hydrochloride yielded compound **2** which was deprotected to give amine **3**. After reaction with, respectively, ethyl isocyanatoacetate and ethyl 3-isocyanatopropionate and subsequent hydrolysis, **OPV1** and **OPV2** were obtained. **OPV3** and **OPV4** were synthesized from nitro derivative **7** that was formed in a Wittig–Horner reaction of diethyl(4-nitrobenzyl)phosphonate and aldehyde compound **6**.[18] Subsequent reduction of the nitro group yielded amine **8**. After reaction with ethyl isocyanatoacetate and ethyl 3-isocyanatopropionate and subsequent hydrolysis **OPV3** and **OPV4** were obtained, respectively. **OPV5** was prepared from isocyanate derivative **11**[19] after subsequent reaction with glycine methyl ester hydrochloride and hydrolysis. All five OPV guests were fully characterized including NMR spectroscopy, MALDI-TOF–MS and elemental analysis.

Binding Studies. The binding properties of OPV guests were first tested with *N,N*-bis[(3-adamantylureido)propyl]methylamine (**Pincer**, Figure 1a), which is the binding moiety in the fifth generation poly(propylene imine) dendrimer functionalized with urea adamantyl units at the periphery (**Dendr**, Figure 1b).[13] All pincer-guest complexes show fast exchange between the bound and free states on NMR time scale. For example treatment of **Pincer** with OPV-guest **OPV5** in CDCl$_3$ resulted in characteristic changes (Figure 1) of both NH protons of the guest **OPV5** ($\delta = 7.53$ to 8.45; and $\delta = 5.85$ to 7.0−7.6), as well as the urea hydrogen signal of the pincer ($\delta = 5.75$ to 6.57), indicating the formation of a hydrogen-bonded complex **Pincer·OPV5**. The urea NH resonances of **Pincer** as well as for the guests show a downfield shift for all the guests used, being in full agreement with the previous results.[13]

The binding constants were determined by following the urea hydrogen resonances of the **Pincer**. The guest molecules were bound as 1:1 inclusion complexes and the association constants are listed in Table 1. Although the differences in binding strength are relatively small, there are some significant trends. Increasing the spacer between the ureido and acid group (from methylene to ethylene) leads to a lowering of the association constant (**Pincer·OPV1** versus **Pincer·OPV2** and **Pincer·OPV3** versus **Pincer·OPV4**). Introduction of an aliphatic spacer induced a decrease in binding strength (**Pincer·OPV3** and **Pincer·OPV4** versus **Pincer·OPV1** and **Pincer·OPV2**). A decrease in as-

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Scheme 2
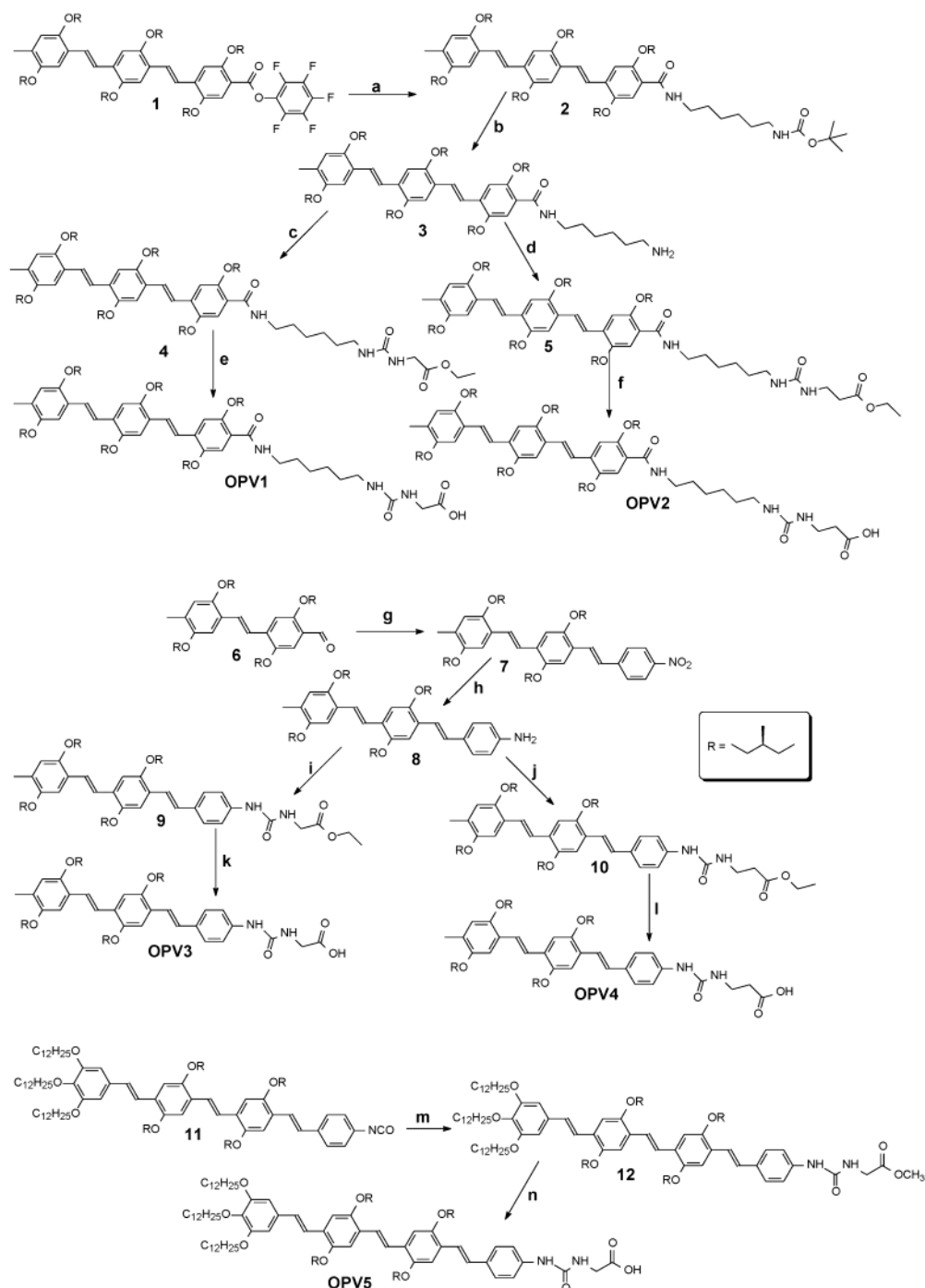
Reagents and conditions: (a) *tert*-butyl N−(6-aminohexyl)carbamate hydrochloride, NEt₃, rt; (b) TsOH in toluene, reflux, 2 h; (c) ethyl isocyanate acetate, rt, 30 min; (d) ethyl 3-isocyanateproprionate, 0 °C; (e, f, k, l, n) LiOH·H₂O, THF, rt; (g) diethyl(4-nitro benzyl) phosphonate, DMF, K*t*BuO, rt, 4h; (h) SnCl₂·2H₂O, EtOH/EtOAc, 75 °C, 5h; (i) ethyl isocyanate acetate, rt, 30 min; (j) ethyl 3-isocyanateproprionate, 0 °C; (m) Et₃N, glycine methyl ester hydrochloride, rt.

sociation constant of a factor of 2 is observed by comparing the association constant of complexes *Pincer*·**OPV3** with *Pincer*·**OPV5**.[20]

The properties of **OPV3** and **OPV5** were further investigated with fifth generation adamantyl functionalized propylene dendrimer *Dendr*, because these guests showed the highest as-

sociation constant with the *Pincer* host. In the ¹H NMR spectrum the urea-protons of the dendritic scaffold show a downfield shift for both guests, indicating binding at the periphery of the host. In both cases, a maximum of 32 guests were bound and this stoichiometry is preserved after repeated preparative size exclusion chromatography.[21] To confirm the complexation and location between host and guest, NOE

(20) A reasonable explanation for the differences in binding strength is difficult to give because of the many variables in the guest molecules. Moreover, some of the guests show self-association.

(21) We tried to determine the binding constant by microcalometry, but no reliable data were obtained for number of binding sites, see also ref 13.
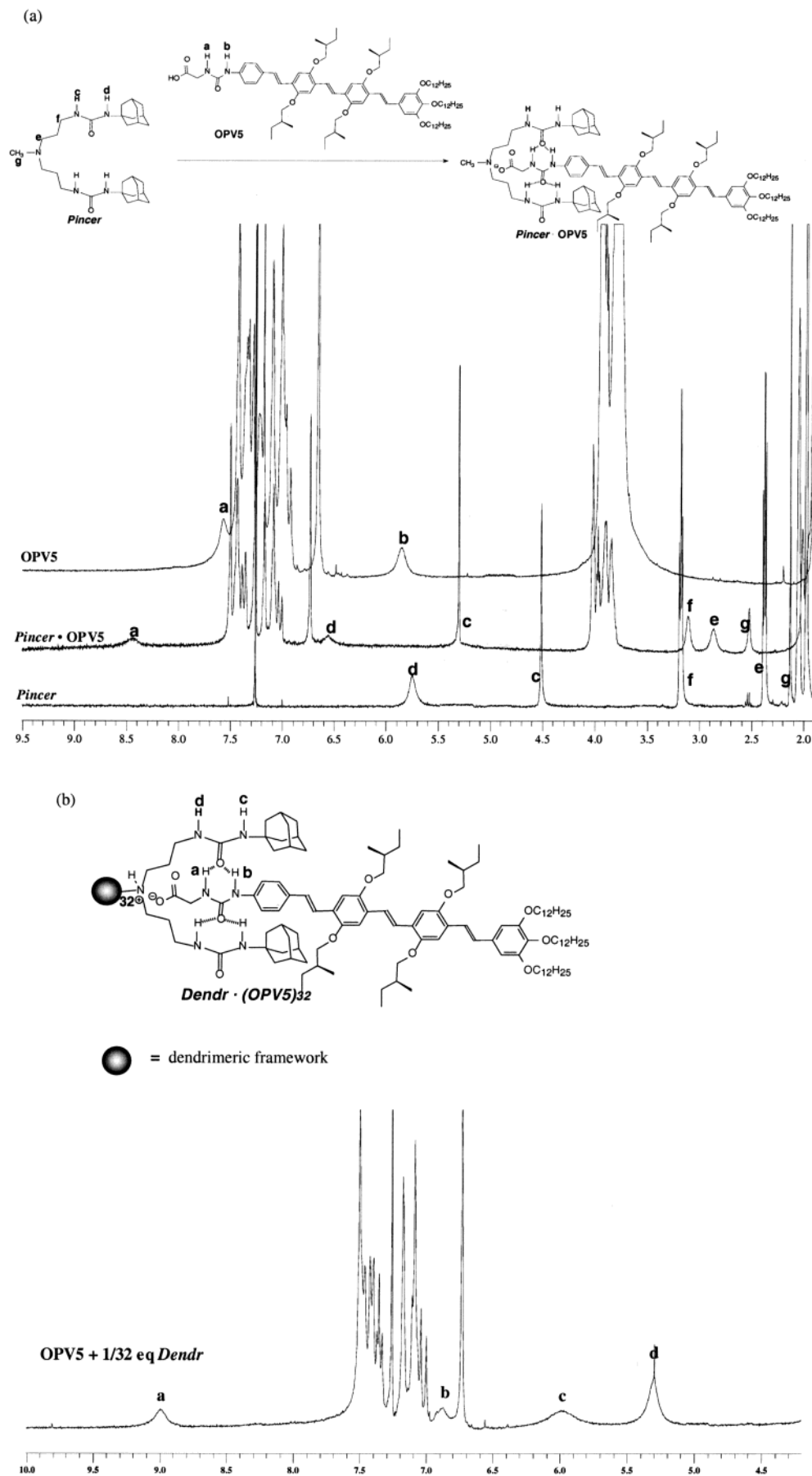
(a)

(b)

Figure 1. ¹H NMR of (a) **OPV5**, *Pincer*·**OPV5**, and *Pincer*; (b) *Dendr*·(**OPV5**)₃₂.

Table 1. Association Constants of the Different OPV-Guests with *Pincer*

complex	*Pincer* ·OPV1	*Pincer* ·OPV2	*Pincer* ·OPV3	*Pincer* ·OPV4	*Pincer* ·OPV5
K_a (M^{-1})	$(1.2 \pm 0.3) \times 10^3$	$(0.3 \pm 0.1) \times 10^3$	$(12.9 \pm 3.1) \times 10^3$	$(2.7 \pm 1.1) \times 10^3$	$(6.6 \pm 1.3) \times 10^3$
CIS (ppm)^a	1.5 ± 0.2	1.3 ± 0.2	1.0 ± 0.1	1.2 ± 0.1	0.8 ± 0.1

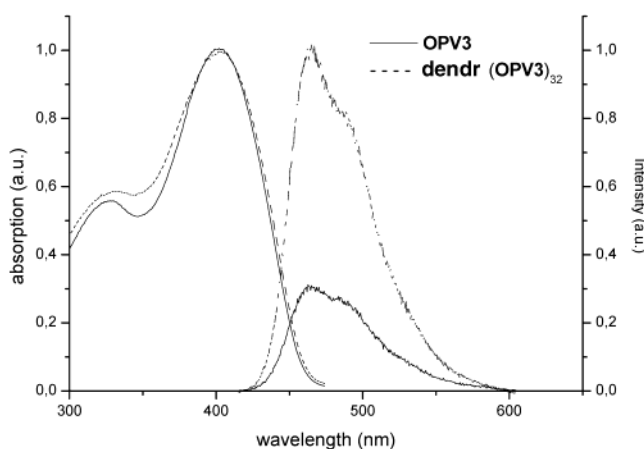^{a} CIS values of the urea hydrogen resonances of the pincer

Table 2. Absorption and Fluorescence Maxima of the Guests and Host−Guest Complexes in Solution and in Thin Film

	UV−vis λ_{max}(nm)		fluorescence $\lambda_{max,em}$ (nm)		
	solution	thin film	solution	thin film	thin film PL efficiency
OPV3	402	390	470	510	4%
Dendr·**(OPV3)₃₂**	402	395	470	511	37%
OPV5	434	405	500	550	2%
Dendr·**(OPV5)₃₂**	432	423	500	552	12%
Pincer ·**OPV5**	429	416	500	552	19%

experiments were performed in CDCl₃. Due to the overlap of signals in ¹H NMR spectrum of the complex **Dendr·(OPV3)₃₂** in CDCl₃, the solution structure of the complex was further investigated with the fifth generation adamantyl-functionalized dendrimer having amide linkages.[13] The ¹H−¹H NOESY spectrum of the complex showed NOE interactions between the CH₂ protons next to the urea group of the guest and the middle CH₂ of the outermost shell of the dendritic host, similar as observed previously.[13] These results reveal that the guest molecules are located at the periphery of the dendrimers.

Optical Studies. The optical properties of guests **OPV3**, **OPV5**, and the host−guest complexes **Pincer·OPV5**, **Dendr·(OPV3)₃₂**, and **Dendr·(OPV5)₃₂** were investigated by UV−vis and fluorescence spectroscopy. The absorption maximum of **OPV3** and **OPV5** (illustrated in Table 2) is located at $\lambda_{max} = 402$ nm and $\lambda_{max} = 434$ nm respectively, and can be attributed to the $\pi-\pi^*$ transition of an OPV trimer and tetramer.[22] The UV−vis spectrum of **Pincer·OPV5** shows an absorption maximum at $\lambda_{max} = 429$ nm, whereas the dendritic complexes show a absorption maximum at $\lambda_{max} = 402$ and 432 nm, respectively. Fluorescence measurements show an emission maximum at $\lambda_{max,em} = 470$ nm for both **OPV3** and **Dendr·(OPV3)₃₂** and $\lambda_{max,em} = 500$ nm for **OPV5**, **Pincer·OPV5** and **Dendr·(OPV5)₃₂**; values typical for OPV trimers and OPV tetramers. Interestingly, an increase in the intensity of the emission for the bound guest was observed: 3.3 times for **Dendr·(OPV3)₃₂** and 2 times for **Dendr·(OPV5)₃₂** (Figure 2). This behavior indicates that the guest molecules are not completely molecularly dissolved in solution. When no host is present, weak interactions between the π-conjugated oligomers are presumably present, and therefore, the fluorescence is slightly quenched. In the supramolecular complexes such interactions do not exist due to the bulky adamantyl groups.

In the case of the dendritic host−guest complexes (**Dendr·(OPV3)₃₂** and **Dendr·(OPV5)₃₂**) we obtained good quality thin films by spin coating from a toluene solution. The supramolecular system based on the **pincer** as host (**Pincer·OPV5**) showed an inhomogeneous yellow film indicating domain formation. Poor quality films were obtained in the case of the guest molecules alone. Tapping-mode atomic force micrcoscopy (AFM) confirmed this behavior, e.g. pure **OPV5** revealed a

(22) Peeters, E.; Janssen, R. A. J.; Meskers, S. C. J.; Meijer, E. W. *Polymer Preprint.* **1999**, *40*, 519.

Figure 2. UV−vis (left) and fluorescence (right) spectrum of **OPV3** (2.16 × 10⁻⁶ M) and **Dendr·(OPV3)₃₂** (6.75 × 10⁻⁸ M).

rough surface with a typical roughness of >50 nm. In the case of the dendritic host−guest systems, a homogeneous surface was obtained (a roughness of < 10 nm for surfaces on 20 μm scale), whereas in the case of the **pincer** as host an inhomogeneous film was observed even on a scale less than 5 μm.

The films show a hypsochromic shift of the absorption maximum when comparing with the solution spectra (for example **OPV5**: $\Delta\lambda_{max} = 29$ nm, **Pincer·OPV5**: $\Delta\lambda_{max} = 13$ nm, **Dendr·(OPV5)₃₂**: $\Delta\lambda_{max} = 9$ nm) indicating aggregation of the π-systems (Table 2). This blue shift is larger in the free guest than in the case of the host−guest systems. Presumably, the bulky adamantyl units prevent the OPV units from $\pi-\pi$ stacking. Fluorescence spectra of these films show an emission at $\lambda_{max,em} = 510$ nm for the OPV trimers and $\lambda_{max,em} = 552$ nm for the OPV tetramers. The thin film of host−guest complexes show brilliant yellow fluorescence while in the case of the guest itself the fluorescence is highly quenched. To quantify this observation, external quantum efficiencies of the films were measured using an integrated sphere (Table 2).[23] In the case of host−guest systems, the PL efficiencies are a factor of 10 higher. There is almost no difference between the pincer and dendritic host which illustrates that the high emission is the result of the bulky adamantly unit sealing the chromophores from aggregation. The supramolecular approach shows clearly that chromophores can be isolated in the solid state, whereas dendritic hosts give rise to films of good quality.

Conclusions

In conclusion, we have studied the binding and optical properties of π-conjugated guests to *N, N*-bis[(3-adamantyl ureido) propyl] methylamine, and to a adamantyl urea modified fifth generation poly(propylene imine) dendritic hosts that contain 32 of these binding sites. Guests consisting of urea glycine moiety are bound most strongly. The reversible nature of this binding opens the way toward dynamic multicomponent assemblies that are of interest for electron and energy transfer reactions.

Furthermore, we have demonstrated that the conjugated guests show improved emission upon binding. In the solid state this enhancement is 10 times higher than the guest itself. The π-conjugated oligomers are most likely less aggregated in the supramolecular assemblies because of shielding effect of the bulky adamantyl units present in the host. In the case of the dendrimer system, smooth homogeneous thin films could be obtained by spin coating. It shows that the dendritic host/guest complexes are the most promising ones in applying this supramolecular concept in LEDs and work along this line is in progress.

Experimental. General Methods. ^{1}H NMR and ^{13}C NMR spectra were recorded at room temperature on a Varian Gemini 300 or 400 MHz spectrometer in deuterated chloroform and tetramethylsilane (TMS) was used as internal reference. Abbreviations used are s = singlet, d = doublet, t = triplet, m = multiplet, and b = broad. Preparative size exclusion chromatography was carried out with Biobeads S−X1 Beads (200−400 mesh) with a cutoff of 14 kD, and were obtained from Bio-Rad Laboratories; dichloromethane was used as eluent. Elemental analysis were performed on a Perkin-Elmer, Series II, 2400. The 2D NMR ^{1}H, ^{1}H NOESY experiments were carried out on a Varian Inova 500 spectrometer operating at 500.618 MHz and equipped with a 5 mm 500 SW/PFG probe. The spectra were obtained at 25 °C. The 2D NMR spectra were acquired using nonspinning 5 mm samples with deuterium field-frequency locking. For the ^{1}H, ^{1}H NOESY spectra, the following parameters were used: spectral width, 5086 Hz (f2) and 5086 Hz (f1); 256 increments and 16 scans per increment in t1; calibrating mixing time 0.1 s. The concentrations of the host−guest complexes were kept constant at 0.4 mM. The constancy of the equilibrium signal intensity was always investigated over the whole d2-array period.

Determination of the association constants (K_a) was carried out under Benesi-Hildebrand conditions at 25 °C in CDCl$_3$.[24] The concentration of the host was kept constant (1 mM), whereas the guests' concentrations were varying in the range 0.1−2 mM.

UV−vis spectra and fluorescence spectra were recorded on a Perkin-Elmer Lambda 40 Spectrometer and a Perkin-Elmer luminescence spectrometer LS 50 B instrument. Melting points were determined with a Buchi B-450 Melting point apparatus. Infrared spectra were recorded on a Perkin-Elmer Spectrum one with a ATR sampling accessory. Matrix assisted laser desorption ionization time-of-flight (MALDI-TOF) mass spectrometry were measured on a Perspective Biosystems Voyager- DE PRO instrument in reflector mode, using α-cyano-4-hydroxy-cinnamic acid as the matrix. Spin-coated thin films were prepared by spin-casting from THF solutions using a Headway Research Spin-coat apparatus. For measuring thin-film PL quantum efficiency an integrating sphere was used.[23]

Atomic Force Microscopy measurements were carried out at room temperature with an AFM (Digital Instruments) equipped with a Nanoscope IIIa controller (Digital Instruments) in the Tapping Mode.

(E,E)-6-{-4-{4-(4-Methyl-2,5-bis[(S)-2-methylbutoxy]styryl)-2,5-bis[(S)-2-methylbutoxy]styryl}-2,5-bis[(S)-2-methylbutoxy]-benzoylamino}hexylcarbamic acid t-butyl ester (2). To a CH$_2$Cl$_2$ suspension (10 mL) of *tert*-butyl *N*-(6-aminohexyl)carbamic hydrochloride (378 mg 1.5 mmol) and triethyamine (151 mg 1.5 mmol) was added (E,E)-4-{4-(4-Methyl-2,5-bis[(S)-2-methylbutoxy]styryl)-2,5-bis[(S)-2-methylbutoxy]styryl}-2,5-bis[(S)-2-methylbutoxy]benzoic acid pentafluoro- phenyl ester (1)[12] (900 mg 0.88 mmol) in CH$_2$Cl$_2$. After half hour the mixture was washed with a saturated K$_2$CO$_3$ solution. The organic layer was dried, filtered, and concentrated. After crystallization from heptane pure 2 was obtained (927 mg, 100%). Mp: 144

°C. IR (UATR) ν 3366, 2959, 2930, 2874, 1687, 1633, 1603, 1507, 1464, 1414, 1389, 1342, 1249, 1201, 1173, 1043, 965, 851 cm^{-1}. ^{1}H NMR (CDCl$_3$): δ 0.9−1.1 (m, 36H), 1.3−2.0 (m, 26H), 1.44 (s, 9H), 2.24 (s, 3H), 3.11 (dt, br, 2H), 3.46 (dt, br, 2H) 3.74−4.04 (m, 12H), 4.54 (s, 1H), 6.73 (s, 1H), 7.10 (s, 1H), 7.17 (s, 1H), 7.19 (s, 1H), 7.21 (s, 1H), 7.45 (d, 1H), 7.49 (d, 1H,), 7.51 (d, 1H), 7.57 (d, 1H), 7.77 (s, 1H), 8.15 (t, br, 1H). ^{13}C NMR (CDCl$_3$): δ 11.28, 11.36, 11.43, 11.46, 16.4, 16.69, 16.73, 16.79, 16.82, 26.24, 26.33, 26.35, 26.51, 26.81, 28.37, 28.40, 29.62, 30.02, 34.93, 34.95, 35.03, 39.68, 40.50, 73.37, 74.00, 74.10, 74.22, 74.28, 74.64, 108.37, 109.54, 109.82, 110.26, 115.63, 116.27, 120.68, 121.58, 121.85, 123.37, 124.97, 125.07, 126.42, 127.70, 128.26, 131.12, 150.47, 150.75, 150.92, 151.24, 151.67, 155.96, 165.13. UV−vis (CH$_2$Cl$_2$): 419 (49000), 322 (20000). MALDI-TOF−MS (MW = 1055.53) m/z = 1055.48.

(E,E)-N-{-4-{4-(4-Methyl-2,5-bis[(S)-2-methylbutoxy]styryl)-2,5-bis[(S)-2-methyl butoxy]styryl}-2,5-bis[(S)-2-methylbutoxy]benzoyl}-hexyldiamine (3). Compound 2 (700 mg 0.66 mmol) and *p*-toluenesulfonic acid (506 mg 2.6 mmol) were dissolved in toluene (50 mL) and heated to reflux for 2 h. The solution was cooled, concentrated, dissolved in chloroform, and washed with a K$_2$CO$_3$ saturated solution. The organic layer was dried, filtered and concentrated. After crystallization from heptane 3 (590 mg, 93%) was obtained as a yellow solid. Mp: 111 °C. IR (UATR) ν 3403, 2961, 2928, 2875, 1655, 1602, 1501, 1464, 1415, 1386, 1201, 1042, 774 cm^{-1}. ^{1}H NMR (CDCl$_3$): δ 0.9−1.1 (m, 36H), 1.3−2.0 (m, 26H), 2.24 (s, 3H), 2.72 (s, 2H), 3.46 (dt, br, 2H), 3.74−4.04 (m, 14H), 6.73 (s, 1H), 7.10 (s, 1H), 7.17 (s, 1H), 7.19 (s, 1H), 7.21 (s, 1H), 7.45 (d, 1H), 7.49 (d, 1H), 7.51 (d, 1H), 7.57 (d, H), 7.77 (s, 1H), 8.15 (t, br, 1H). ^{13}C NMR (CDCl$_3$): δ 11.28, 11.35, 11.42, 11.45, 16.40, 16.68, 16.73, 16.78, 16.81, 26.24, 26.32, 26.34, 26.53, 26.93, 29.62, 33.05, 34.93, 34.94, 35.03, 35.09, 39.70, 41.86, 73.36, 74.00, 74.10, 74.22, 74.28, 74.64, 108.36, 109.53, 109.81, 110.25, 115.62, 116.27, 120.68, 121.57, 121.84, 123.36, 124.96, 125.07, 126.42, 127.69, 128.25, 131.11, 150.46, 150.74, 150.92, 151.24, 151.67, 165.12. UV−vis (CH$_2$Cl$_2$): 419 (33000), 320 (24000). MALDI-TOF−MS (MW = 955.41) m/z=955.54.

(E,E)-6-{-4-{4-(4-Methyl-2,5-bis[(S)-2-methylbutoxy]styryl)-2,5-bis[(S)-2-methyl butoxy]styryl}-2,5-bis[(S)-2-methylbutoxy]benzoylamino}-hexyl ureido-acetic acid ethyl ester (4). To a CHCl$_3$ solution (5 mL) of 3 (153 mg 0.16 mmol) was added ethyl isocyanateacetate (51 mg 0.39 mmol) in CHCl$_3$ (2 mL). After 30 min, the solvent was evaporated, toluene was added and evaporated several times to remove the excess of isocyanate. After crystallization from heptane 4 was obtained as a yellow solid (173 mg, 100%). Mp: 125 °C. IR (UATR) ν 3346, 3058, 2959, 2928, 2859, 1748, 1687, 1636, 1603, 1592, 1538, 1507, 1464, 1414, 1389, 1375, 1343, 1251, 1200, 1113, 1043, 966, 852 cm^{-1}. ^{1}H NMR (CDCl$_3$): δ 0.9−1.11 (m, 36H), 1.25−2.0 (m, 26H), 1.27 (t, 3H), 2.24 (s, 3H), 3.19 (dt, br, 2H), 3.48 (dt, br, 2H), 3.74−4.04 (m, 14H), 4.19 (q, 2H), 5.16 (t, br., 1H), 5.36 (t, br., 1H), 6.73 (s, 1H), 7.10 (s, 1H), 7.17 (s, 1H), 7.19 (s, 1H), 7.21 (s, 1H), 7.44 (d, 1H), 7.48 (d, 1H), 7.52 (d, 1H), 7.58 (d, 1H), 7.76 (s, 1H), 8.20 (t, br, 1H). ^{13}C NMR (CDCl$_3$): δ 11.29, 11.36, 11.45, 14.14, 16.40, 16.69, 16.73, 16.82, 25.86, 26.09, 26.26, 26.33, 29.56, 34.94, 35.04, 35.09, 39.21, 40.07, 42.25, 61.21, 73.40, 74.01, 74.11, 74.24, 74.30, 74.66, 108.42, 109.59, 109.84, 110.28, 115.94, 116.29, 120.56, 121.60, 121.82, 123.42, 125.10, 126.41, 127.73, 128.32, 131.28, 150.49, 150.80, 150.95, 151.27, 151.69, 157.88, 165.40, 171.23. UV−vis (CH$_2$Cl$_2$): 420 (43000), 323 (18000). MALDI-TOF−MS (MW = 1084.53) m/z = 1084.61. Anal.Calcd. for C$_{65}$H$_{101}$N$_3$O$_{10}$: C 71.99, H 9.39, N 3.87. Found: C 71.09, H 9.26, N 3.84.

(E,E)-3-[-6-{-4-{4-(4-Methyl-2,5-bis[(S)-2-methylbutoxy]styryl)-2,5-bis[(S)-2-methylbutoxy]styryl}-2,5-bis[(S)-2-methylbutoxy]-benzoylamino}hexylureido] propionic acid ethyl ester (5). To a chloroform solution (5 mL) of 3 (153 mg 0.16 mmol) at 0°C was added ethyl 3-isocyanatepropionate (51 mg 0.39 mmol in CHCl$_3$ (2 mL). After 30 min HCl (1M) was added and the organic layer was further washed

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with brine, dried, filtrated and concentrated. After crystallization from heptane (95 mg, 100%) **5** was obtained as a yellow solid. Mp: 136 °C. IR (UATR) v 3373, 2960, 2929, 2875, 1735, 1633, 1535, 1508, 1464, 1416, 1389, 1346, 1251, 1200, 1043, 967, 852 cm^{-1}. ^{1}H NMR (CDCl$_3$): δ 0.9−1.11 (m, 36H), 1.25 (t, 3H), 1.33−2.0 (m, 26H), 2.24 (s, 3H), 2.53 (t, 2H) 3.15 (dt, br., 2H), 3.47 (m, br., 4H), 3.74−4.04 (m, 12H), 4.14 (q, 2H), 4.60 (s, br., 1H), 5.02 (t, br., 1H), 6.73 (s, 1H), 7.10 (s, 1H), 7.17 (s, 1H), 7.19 (s, 1H), 7.21 (s, 1H), 7.44 (d, 1H), 7.48 (d, 1H), 7.52 (d, 1H), 7.58 (d, 1H), 7.76 (s, 1H), 8.17 (t, br., 1H). ^{13}C NMR (CDCl$_3$): δ 11.29, 11.36, 11.45, 14.17, 16.40, 16.69, 16.73, 16.82, 26.15, 26.24, 26.32, 26.35, 29.57, 29.79, 34.88, 34.92, 34.95, 35.03, 35.09, 35.85, 39.39, 40.2, 60.57, 73.37, 74.01, 74.09, 74.21, 74.28, 74.64, 108.37, 109.56, 109.81, 110.25, 115.58, 116.27, 120.59, 121.57, 121.80, 123.39, 125.03, 125.07, 126.39, 127.71, 128.28, 131.22, 150.47, 150.76, 150.93, 151.25, 151.67, 158.08, 165.27, 173.02. UV−vis (CH$_2$Cl$_2$): 420 (44 000), 320 (20000). MALDI−TOF−MS (MW = 1098.55) m/z = 1098.66. Anal.Calcd. for C$_{66}$H$_{103}$N$_3$O$_{10}$: C 72.16, H 9.45, N 3.82. Found: C 72.06, H 9.38, N 3.71.

(*E*,*E*)-4-{4-(4-Methyl-2,5-bis[(*S*)-2-methylbutoxy]styryl)-2,5-bis[(*S*)-methyl butoxy]styryl}nitrobenzene (7). To a solution of diethyl-(4-nitrobenzyl) phosphonate (1.20 g, 4.40 mmol) in anhydrous DMF (20 mL) under argon was added K*t*BuO (0.59 g, 5.20 mmol) at room temperature. After stirring for 15 min, a solution of aldehyde **6**[18] (2.27 g, 4.00 mmol) in 30 mL DMF was added dropwise. The solution was stirred for 4 h and subsequently poured onto a mixture of 100 g crushed ice and 45 mL HCl (6 N) was added. The mixture was extracted three times with CH$_2$Cl$_2$ and the collected organic fractions were washed with 3N HCl and dried over MgSO$_4$. After evaporation of the solvent the compound was recrystallized twice from hexane to afford 2.24 g (82%) of **7** as small deep red crystals. Mp: 137 °C. IR (UATR) v 3053, 2958, 2920, 2874, 1626, 1587, 1506, 1464, 1424, 1333, 1256, 1243, 1203, 1108, 1043, 964, 857, 749, 691 cm^{-1}. ^{1}H NMR (CDCl$_3$): δ 0.89−1.19 (m, 24H), 1.20−1.48 (m, 4H), 1.50−1.78 (m, 4H), 1.82−2.06 (m, 4H), 2.25 (s, 3H), 3.70−3.97 (m, 8H), 6.76 (s, 1H), 7.12 (s, 1H), 7.13 (s, 1H), 7.21 (d, 1H), 7.23 (s,1H), 7.49 (d, 1H), 7.58 (d,1H), 7.62 (d,2H), 7.66 (d, 1H), 8.22 (d, 2H). ^{13}C NMR (CDCl$_3$): δ 11.37, 11.47, 11.51, 16.43, 16.68, 16.79, 16.85, 26.22, 26.33, 34.91, 35.07, 35.10, 73.30, 73.85, 74.43, 74.51, 108.20, 109.32, 111.12, 116.17, 121.21, 123.92, 124.12, 124.77, 125.83, 126.56, 127.94, 128.28, 129.35, 144.73, 146.36, 150.72, 151.62, 151.77. UV−vis (CH$_2$Cl$_2$): 442 (39000), 332 (23000). MALDI−TOF−MS (MW = 685.43) m/z = 685.59 [M$^+$]. Anal.Calcd. for C$_{43}$H$_{59}$NO$_6$: C 75.29, H 8.67, N 2.04. Found: C 74.91, H 8.80, N 1.99.

(*E*,*E*)-4-{4-(4-Methyl-2,5-bis[(*S*)-2-methylbutoxy]styryl)-2,5-bis[(*S*)-2-methyl butoxy]styryl}aniline (8). Under an argon atmosphere, **7** (988 mg 1.44 mmol) was suspended in a mixture of 10 mL ethanol and 8 mL ethyl acetate and 2.6 g (11.52 mmol) of SnCl$_2$ · 2H$_2$O was added. The reaction mixture was heated to 75°C, stirred for 5 h, cooled to room temperature and subsequently poured into crushed ice. The aqueous phase was extracted with diethyl ether and the organic layer dried over MgSO$_4$, filtrated, and the solvent remove in vacuo. Purification by column flash chromatography using hexane/ethyl acetate 3:1 (v/v) as eluent yielded 660 mg (70%) of **8** as an orange solid. Mp: 106 °C. IR (UATR) v 3388, 3045, 2959, 2916, 2873, 1618, 1506, 1461, 1412, 1388, 1342, 1253, 1197, 1040, 964, 852, 815, 713 cm^{-1}. ^{1}H NMR (CDCl$_3$): δ 0.89−1.19 (m, 24H), 1.20−1.48 (m, 4H), 1.50−1.78 (m, 4H), 1.82−2.06 (m, 4H), 2.25 (s, 3H), 3.70−3.97 (m, 8H), 6.70 (d, 2H), 6.84 (s, 1H), 7.19 (d, 1H), 7.22 (s, 1H), 7.25 (s, 1H), 7.32 (s, 1H), 7.43 (d, 1H), 7.44 (d, 2H), 7.60 (d, 1H), 7.66 (d, 1H). ^{13}C NMR (CDCl$_3$): δ 11.54, 11.57, 11.67, 11.72, 16.55, 16.88, 16.97, 17.00, 17.03, 26.46, 26.54, 26.58, 34.17, 35.20, 35.39, 73.47, 74.21, 74.62, 74.77, 108.33, 109.70, 110.75, 115.31, 116.50, 119.88, 121.86, 122.77, 125.47, 127.14, 127.40, 127.56, 128.65, 128.93, 146.45, 150.63, 151.14, 151.21, 151.90. UV−vis (CH$_2$Cl$_2$): 408 (39000), 329 (20000). MALDI−TOF−MS (MW = 655.46) m/z = 655.60 [M$^+$].

(*E*,*E*)-3-[4-{4-(4-Methyl-2,5-bis[(*S*)-2-methylbutoxy]styryl)-2,5-bis[(*S*)-methyl butoxy]styryl}phenyl]ureido acetic acid ethyl ester (9). To a chloroform solution (5 mL) of **8** (124 mg 0.19 mmol) was added ethyl isocyanatoacetate (65 mg 0.5 mmol) in CHCl$_3$ (2 mL). After 30 min the solvent was evaporated and toluene was added and evaporated several times to remove the excess isocyanate. After crystallization from heptane **9** (149 mg, 100%) was obtained as a yellow solid. Mp: 126 °C. IR (UATR) v 3349, 3057, 2962, 2922, 2875, 1748, 1704, 1654, 1594, 1543, 1512, 1464, 1413, 1202, 1044 cm^{-1}. ^{1}H NMR (CDCl$_3$): δ 0.85−1.11 (m, 24H), 1.29 (t, 3H), 1.25−1.39 (m, 4H), 1.57−1.68 (m, 4H), 1.87−1.97 (m, 4H), 2.24 (s, 3H), 3.73−3.93 (m, 8H), 4.07 (d, 2H), 4.22 (q, 2H), 5.83 (s, br., 1H), 6.73 (s, 1H), 6.89 (s, br., 1H), 7.08 (d, 1H), 7.09 (s, 1H), 7.10 (s, 1H), 7.17 (s, 1H), 7.34 (d, 2H), 7.40 (d, 1H), 7.44 (d, 1H), 7.45 (d, 2H), 7.5 (d, 1H). ^{13}C NMR (CDCl$_3$): δ 11.36, 11.46, 11.50, 14.04, 14.13, 16.38, 16.69, 16.80, 16.85, 22.32, 26.26, 26.35, 34.11, 34.97, 35.12, 35.16, 42.16, 61.56, 73.39, 74.05, 74.53, 74.68, 108.33, 109.60, 110.84, 116.33, 121.40, 121.63, 122.86, 123.08, 125.186, 126.34, 127.35, 127.61, 127.68, 127.77, 134.20, 137.26, 150.46, 150.88, 151.26, 151.71, 155.43, 171.03. UV−vis (CH$_2$Cl$_2$): 405 (34000), 321 (21000). MALDI−TOF−MS (MW = 785.07) m/z = 785.14.

(*E*,*E*)-3-{3-[4-{4-(4-Methyl-2,5-bis[(*S*)-2-methylbutoxy]styryl)-2,5-bis[(*S*)-methyl butoxy]styryl}phenyl]ureido} propionic acid ethyl ester (10). To a chloroform solution (5 mL) of **8** (186 mg 0.28 mmol) at 0°C was added ethyl 3-isocyanatopropionate (47 mg 0.31 mmol) in CHCl$_3$ (2 mL). After 30 min HCl (1M) was added and the organic layer washed with brine, dried, filtrated, and concentrated. After crystallization from heptane **10** (210 mg, 75%) was obtained as a yellow solid. Mp: 114 °C. IR (UATR) v 3318, 2959, 2922, 2874, 1731, 1643, 1588, 1555, 1509, 1462, 1412, 1375, 1341, 1309, 1239, 1200, 1043, 964, 851 cm^{-1}. ^{1}H NMR (CDCl$_3$): δ 0.95−1.11 (m, 24H), 1.25 (t, 3H), 1.25−1.39 (m, 4H), 1.57−1.68 (m, 4H), 1.87−1.97 (m, 4H), 2.24 (s, 3H), 2.59 (t, 2H), 3.55 (dt, br., 2H), 3.73−3.94 (m, 8H), 4.14 (q, 2H), 5.59 (s, br., 1H), 6.73 (s, 1H), 6.89 (s, br., 1H), 7.09 (d, 1H), 7.10 (s, 1H), 7.14 (s, 1H), 7.18 (s, 1H), 7.31 (d, 2H), 7.41 (d, 1H), 7.44 (d, 1H), 7.45 (d, 2H), 7.51 (d, 1H). ^{13}C NMR (CDCl$_3$): δ 11.47, 11.56, 11.61, 14.24, 16.49, 16.78, 16.92, 22.32, 26.35, 26.44, 34.74, 35.06, 35.20, 35.24, 35.88, 60.89, 73.46, 74.14, 74.61, 74.76, 108.39, 109.68, 110.88, 116.41, 120.89, 121.71, 122.67, 123.11, 125.27, 126.49, 127.40, 127.61, 127.68, 127.80, 127.86, 133.79, 137.83, 150.53, 150.96, 151.30, 151.78, 155.65, 171.22. UV−vis (CH$_2$Cl$_2$): 407 (51000), 329 (26000). MALDI−TOF−MS (MW = 799.10) m/z = 799.29. Anal.Calcd. for C$_{48}$H$_{68}$N$_2$O$_7$: C 73.44, H 8.73, N 3.57. Found: C 73.16, H 8.87, N 3.33.

(*E*,*E*,*E*)-4-[4-{3,4,5-Tridodecyloxystyryl)-2,5-bis[(*S*)-2-methylbutoxy]styryl}-2,5-bis[(*S*)-2-methylbutoxy]styryl}phenyl]ureido acetic acid methyl ester (12). To a stirred solution of (*E*,*E*,*E*)-4-[4-{3,4,5-Tridodecyloxystyryl)-2,5-bis[(*S*)-2-methylbutoxy]styryl}-2,5 -bis[(*S*)-2-methylbutoxy]styryl] phenyl isocyanate (**11**)[19] in dry CH$_2$Cl$_2$ (3 mL) was added Et$_3$N (0.4 mL) and glycine methyl ester hydrochloride (53 mg, 1.1 equiv). The mixture was stirred overnight at room temperature. The product was washed with diluted aqueous hydrochloride solution (0.2 M) and a saturated solution of NaCl. The organic layer was dried over Na$_2$SO$_4$, filtrated and concentrated in vacuo to yield 0.4 g of 12 (80% yield) as a yellow solid. Mp: 134 °C. IR (UATR) v 3340, 3054, 2957, 2920, 2852, 1746, 1705, 1673, 1621, 1579, 1505, 1466, 1422, 1387, 1340, 1245, 1203, 1119, 1046, 963, 851, 721 cm^{-1}. ^{1}H NMR (CDCl$_3$): δ 0.80−1.18 (m, 33H), 1.18−1.92 (m, 68H), 1.92−2.05 (m, 4H), 3.7 (s, 3H), 3.75 (d, 2H), 3.78−4.08 (m, 14H), 5.85 (t, 1H), 6.64 (d, 2H), 6.75 (s, 2H), 7.04 (d, 1H), 7.07 (d, 1H), 7.10 (s, 1H), 7.11 (s, 1H), 7.19 (s, 1H), 7.21 (s, 1H), 7.31(d, 1H), 7.34 (d, 2H), 7.41(d, 1H), 7.49 (s, 2H), 7.53 (s, br., 1H). ^{13}C NMR (CDCl$_3$): δ 11.53, 11.63, 11.67, 14.25, 16.92, 17.00, 22.84, 26.29, 26.51, 29.52, 29.55, 29.59, 29.82, 29.86, 29.89, 29.91, 30.51, 32.08, 35.14, 35.24, 35.31, 41.20, 53.11, 69.20, 73.66, 74.21, 74.29, 74.58, 105.18, 109.74, 109.93, 110.62, 115.31, 119.94, 122.27, 122.70, 122.86, 126.76, 126.88, 127.63, 127.75,

127.83, 128.59, 128.78, 128.93, 133.43, 138.25, 146.23, 151.14, 151.19, 151.33, 153.39, 158.70, 176.50. UV−vis (CH₂Cl₂): 433 (56000), 333 (28000). MALDI-TOF−MS (MW = 1412.098) m/z = 1412.105 [M]⁺. Anal.Calcd. for $C_{90}H_{142}N_2O_{10}$: C 76.55, H 10.14, N 1.98. Found: C 76.74, H 10.39, N 2.22.

General Procedure for the Hydrolysis of the Ester Derivatives to Obtain the OPV Guests. To a solution of ester (1 equiv) in THF was added 7 equiv of LiOH·H₂O. The solution was stirred overnight (15 h) and the acid was precipitated by acidification with HCl 1M (pH = 2). The resulting solid was filtered off, dried under high vacuum and then washed with hexane at room temperature. Conjugated guests **OPV1**, **OPV2**, **OPV3**, **OPV4**, and **OPV5** were obtained with quantitative yield as a yellow solid.

(*E,E*)-6-{-4-{4-(4-Methyl-2,5-bis[(*S*)-2-methylbutoxy]styryl)-2,5-bis[(*S*)-2-methyl butoxy]styryl}-2,5-bis[(*S*)-2-methylbutoxy]benzoylamino}-hexyl ureido-acetic acid (OPV1). Mp; 166 °C. IR (UATR) v 3353, 3056, 2959, 2925, 2858, 1712, 1635, 1593, 1547, 1506, 1464, 1415, 1388, 1342, 1250, 1197, 1045, 965, 851, 668 cm⁻¹. ¹H NMR (CDCl₃): δ 0.9−1.11 (m, 36H), 1.25−2.0 (m, 26H), 2.24 (s, 3H), 3.2 (dt, br., 2H), 3.47 (dt, br., 2H), 3.74−4.04 (m, 14H), 5.70 (s, br., 1H), 5.85 (s, br., 1H), 6.73 (s, 1H), 7.10 (s, 1H), 7.16 (s, 1H), 7.18 (s, 1H), 7.21 (s, 1H), 7.44 (d, 1H), 7.47 (d, 1H), 7.51 (d, 1H), 7.58 (d, 1H), 7.69 (s, 1H), 8.34 (t, br., 1H). ¹³C NMR (CDCl₃): δ 11.28, 11.36, 11.46, 16.40, 16.69, 16.73, 16.80, 25.34, 25.73, 26.25, 26.33, 26.35, 29.16, 29.41, 29.68, 34.89, 34.94, 34.96, 35.02, 35.03, 35.10, 39.27, 39.83, 43.27, 73.38, 74.02, 74.09, 74.24, 74.28, 74.65, 108.38, 109.53, 109.81, 110.25, 115.43, 116.27, 119.82, 121.56, 121.64, 123.45, 125.06, 125.32, 126.38, 127.74, 128.4, 131.74, 150.48, 150.77, 150.93, 151.28, 151.40, 151.68, 159.62, 165.92, 173.35. MALDI-TOF−MS (MW = 1056.47) m/z = 1056.26. UV−vis (CH₂Cl₂): 421 (36000), 322 (11900). Anal. Calcd. for $C_{63}H_{97}N_3O_{10}$ (MW = 1056.47): C 71.62, H 9.25, N 3.98. Found: C 71.61, H 9.23, N 3.97.

(*E,E*)-3-[-6-{-4-{4-(4-Methyl-2,5-bis[(*S*)-2-methylbutoxy]styryl)-2,5-bis[(*S*)-2-methylbutoxy]styryl}-2,5-bis[(*S*)-2-methylbutoxy]-benzoylamino}hexylureido] propionic acid (OPV2). Mp: 172 °C. IR (UATR) v 3380, 3053, 2959, 2927, 2874, 1727, 1620, 1600, 1543, 1505, 1463, 1415, 1386, 1343, 1250, 1199, 1044, 965, 851, 668 cm⁻¹. ¹H NMR (CDCl₃): δ 0.9−1.11 (m, 36H), 1.33−2.0 (m, 26H), 2.24 (s, 3H), 2.58 (t, 2H) 3.17 (dt, br., 2H), 3.48 (m, br., 4H), 3.74−4.04 (m, 12H), 5.37 (s, br., 1H), 5.45 (s, br., 1H), 6.73 (s, 1H), 7.10 (s, 1H), 7.17 (s, 1H), 7.19 (s, 1H), 7.21 (s, 1H), 7.44 (d, 1H), 7.48 (d, 1H), 7.52 (d, 1H), 7.58 (d, 1H) 0.7.72 (s, 1H), 8.34 (t, br., 1H). ¹³C NMR (CDCl₃): δ 11.28, 11.37, 11.47, 16.41, 16.70, 16.76, 16.79, 16.80, 16.83, 25.69, 26.18, 26.26, 26.33, 26.36, 29.21, 29.75, 34.91, 34.95, 34.96, 35.02, 35.05, 35.10, 35.57, 39.23, 39.52, 40.15, 73.38, 74.09, 74.10, 74.24, 74.29, 74.65, 108.38, 109.51, 109.82, 110.26, 115.59, 116.28, 119.94, 121.56, 121.67, 123.45, 125.06, 125.28, 126.30, 127.74, 128.39, 131.66, 150.48, 150.75, 150.93, 151.28, 151.42, 151.68, 159.13, 165.78. UV−vis (CH₂Cl₂): 423 (45000), 325 (15000). MALDI-TOF−MS (MW = 1070.50) m/z= 1070.61. Anal. Calcd. for $C_{64}H_{99}N_3O_{10}$ (MW= 1070.50): C 71.81, H 9.32, N 3.93. Found: C 71.83, H 9.33, N 3.93.

(*E,E*)-3-[4-{4-(4-Methyl-2,5-bis[(*S*)-2-methylbutoxy]styryl)-2,5-bis[(*S*)-methyl butoxy]styryl}phenyl]ureido acetic acid (OPV3). Mp: 159 °C. IR (UATR) v 3338, 2959, 2918, 2875, 1739, 1698, 1641, 1590, 1555, 1510, 1463, 1412, 1389, 1342, 1309, 1236, 1203, 1045,

962, 849, 668 cm⁻¹. ¹H NMR (DMSO): δ 0.88−1.04 (m, 24H), 1.22−1.33 (m, 4H), 1.48−1.60 (m, 4H), 1.78−2.15 (m, 4H), 2.14 (s, 3H), 3.70−3.91 (m, 8H), 3.78 (d, 2H), 6.42 (s, br., 1H), 6.83 (s, 1H), 7.02 (s, 1H), 7.11 (s, 1H), 7.24 (d, 2H), 7.25 (s, 1H), 7.36 (d, 2H), 7.4−7.45 (m, 4H), 7.61 (s, br., 1H). −−

(*E,E*)-3-{3-[4-{4-(4-Methyl-2,5-bis[(*S*)-2-methylbutoxy]styryl)-2,5-bis[(*S*)-methyl butoxy]styryl}phenyl]ureido} propionic acid (OPV4). Mp: 150 °C. IR (UATR) v 3322, 3056, 2960, 2920, 2875, 1706, 1644, 1590, 1540, 1510, 1463, 1412, 1386, 1342, 1311, 1239, 1197, 1043, 964, 851, 668 cm⁻¹. ¹H NMR (CDCl₃): δ 0.94−1.11 (m, 24H), 1.26−1.37 (m, 4H), 1.56−1.67 (m, 4H), 1.87−1.97 (m, 4H), 2.23 (s, 3H), 2.54 (t, br., 2H), 3.47 (dt, br., 2H), 3.73−3.94 (m, 8H), 5.87 (s, br., 1H), 6.71 (s, 1H), 7.07 (s, 1H), 7.08(d, 1H), 7.09(s, 1H), 7.16 (s, 1H), 7.32 (d, 2H), 7.38 (d, 1H), 7.43 (d, 1H), 7.44 (d, 2H) 7.49 (d, 1H), 7.62 (s, br., 1H). ¹³C NMR (CDCl₃): δ 11.36, 11.46, 11.51, 16.38, 16.67, 16.78, 16.86, 26.23, 26.32, 34.92, 34.95, 35.09, 35.13, 35.72, 73.34, 74.03, 74.48, 74.65, 108.24, 109.52, 110.80, 116.29, 120.56, 121.56, 122.55, 122.98, 125.14, 126.34, 127.26, 127.57, 127.69, 127.76, 133.59, 137.64, 150.41, 150.85, 151.18, 151.67, 156.62, 176.99. UV−vis (CH₂Cl₂): 408 (44000), 329 (18000). MALDI-TOF−MS (MW = 771.05) m/z = 771.23. Anal. Calcd. for $C_{47}H_{66}N_2O_7$ (MW = 771.05): C 73.21, H 8.63, N 3.63. Found: C 73.23, H 8.64, N 3.65.

(E,E,E)-4-[4-{3,4,5-Tridodecyloxystyryl)-2,5-bis[(*S*)-2-methylbutoxy]styryl}-2,5-bis[(*S*)-2-methylbutoxy]styryl] ureido acetic acid (OPV5). Mp: 122 °C. IR (UATR) v 3341, 3053, 2957, 2921, 2853, 1649, 1590, 1545, 1504, 1466, 1421, 1386, 1340, 1238, 1202, 1117, 1045, 962, 851, 668 cm⁻¹. ¹H NMR (CDCl₃): δ 0.80−1.18 (m, 33H), 1.18−1.92 (m, 68H), 1.92−2.05 (m, 4H), 3.75 (d, 2H), 3.78−4.08 (m, 14H), 5.85 (t, 1H), 6.64 (d, 2H), 6.75 (s, 2H), 7.04 (d, 1H), 7.07 (d, 1H), 7.10 (s, 1H), 7.11 (s, 1H), 7.19 (s, 1H), 7.21 (s, 1H), 7.31(d, 1H), 7.34 (d, 2H), 7.41 (d, 1H), 7.49 (s, 2H), 7.53 (s, br., 1H). ¹³C NMR (CDCl₃): δ 11.53, 11.63, 11.67, 14.25, 16.92, 17.00, 22.84, 26.29, 26.51, 29.52, 29.55, 29.59, 29.82, 29.86, 29.89, 29.91, 30.51, 32.08, 35.14, 35.24, 35.31, 41.20, 69.20, 73.66, 74.21, 74.29, 74.58, 105.18, 109.74, 109.93, 110.62, 115.31, 119.94, 122.27, 122.70, 122.86, 126.76, 126.88, 127.63, 127.75, 127.83, 128.59, 128.78, 128.93, 133.43, 138.25, 146.23, 151.14, 151.19, 151.33, 153.39, 158.70, 176.50. UV−vis (CH₂Cl₂): 434 (54000), 336 (10000). MALDI-TOF−MS (MW = 1398.071) m/z = 1397.98 [M]⁺. Anal. Calcd. for $C_{89}H_{140}N_2O_{10}$ (MW = 1398.071): C 76.46, H 10.09, N 2.00. Found: C 76.45, H 10.10, N 1.98.