

Supporting Information to

# White-Light Emitting Hydrogen-Bonded Supramolecular Copolymers Based on $\pi$ -Conjugated Oligomers

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## General Experimental

All chemicals were purchased from Acros, Belgium, unless stated otherwise. Concentrated hydrochloric and sulphuric acid was delivered by VWR International, Belgium. (S)-3,7-dimethyloct-6-en-1-ol was a grant from Takasago, fuming nitric acid, Pd on carbon (10 weight%), Na<sub>2</sub>SO<sub>4</sub>, and NaOH, KOH, and KI were obtained from Merck, Germany. 2-Isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (iPrOBPin), bispinacolatodiboron, and tetrakis(triphenylphosphino)palladium(0) were purchased from Aldrich, the Netherlands, silica gel (40 – 63  $\mu$ m, 60 Å) from Screening Devices, the Netherlands and Fluka, Germany. PEDOT/PSS aqueous solutions came from H. C. Starck GmbH, Germany and was filtrated prior to use. Non-deuterated solvents were purchased from Biosolve, the Netherlands, except for heptane, which came from Chempropack, Belgium. For reactions that involved n-butyllithium, THF was dried by reflux over molecular sieves and subsequent distillation. All other solvents and chemicals were used as received. Deuterated solvents were bought from Cambridge Isotope Laboratories, United States.

NMR spectra were recorded using a Varian Mercury NMR Spectrometer at 400 MHz for <sup>1</sup>H and 100 MHz for <sup>13</sup>C or on a Varian Gemini NMR Spectrometer at 300 MHz

for  $^1\text{H}$  and 75 MHz for  $^{13}\text{C}$ , DOSY spectra on a Varian AS 500 at 500 MHz for  $^1\text{H}$ . IR, UV-vis, and PL spectra were measured on a Perkin Elmer 1600 FT-IR, a Perkin Elmer Lambda 900 UV/VIS/NIR spectrometer and an Edinburgh Instruments FS920 spectrophotometer, respectively. Elemental analysis was performed using a Perkin Elmer 2400 Series II CHNS/O Analyzer. MALDI-TOF-MS spectra were measured on a Perseptive DE Voyager Mass Spectrometer with *a*-cyano-4-hydroxycinnamic acid as a matrix.

Analytical GPC was done on an apparatus consisting of a Shimadzu SIL-10AD VP Auto Injector, a Shimadzu LC-10AD VP Liquid Chromatograph, a PLgel 5  $\mu\text{m}$  Mixed C / Mixed D column set, and a SPD-M10A VP Diode Array Detector, using HPLC grade THF or  $\text{CHCl}_3$  as the eluent. Preparative GPC was performed using Biobeads SX1 column material bought from Bio Rad Laboratories, U.S. with THF as the eluent. For recGPC, an apparatus consisting of a Shimadzu LC-10AD VP Liquid Chromatograph, a Shimadzu SPD-10AV VP UV-vis detector, and two JAIGEL columns (2.5 H and 2 H) from Japan Analytical Industry was used with HPLC grade THF + 1 % TFA as the eluent. All analytical and recGPC traces for were recorded at the respective maximum absorption wavelength.. The viscosity measurements were done at 20  $^\circ\text{C}$  using an Ubbelohde viscosimeter supplied by Schott (AVS 350, thermostate CT 1650, capillary 538 10). The chloroform solutions were filtered through a 5  $\mu\text{m}$  Teflon syringe filter prior to the experiments.

For cyclic voltammetry the analyte was dissolved in a 0.1 M solution of tetrabutyl ammonium hexafluorophosphate in dry ODCB (ca. 5 mg/ml) and was measured using Pt electrodes and a Ag/AgCl reference electrode with  $\text{Fc}/\text{Fc}^+$  as the standard (0.43 V vs. Ag/AgCl) at a scan speed of 0.1 V/s. The experimental values were converted to vacuum by subtracting 5.23 eV. Thin films were spin coated on cleaned quartz or glass substrates using a Headway Research Spin coater from concentrated toluene, chlorobenzene, or ODCB solutions (10 – 15 mg/ml) which had been heated to 70  $^\circ\text{C}$  over night. Film thicknesses were determined using a Tencor P-10 Surface Profiler.

Electroluminescent devices were constructed on glass substrates with patterned indium tin oxide (ITO) electrodes with a 50 nm thick layer of PEDOT:PSS to planarise the surface topology of the ITO layer and improve hole injection into the device. After

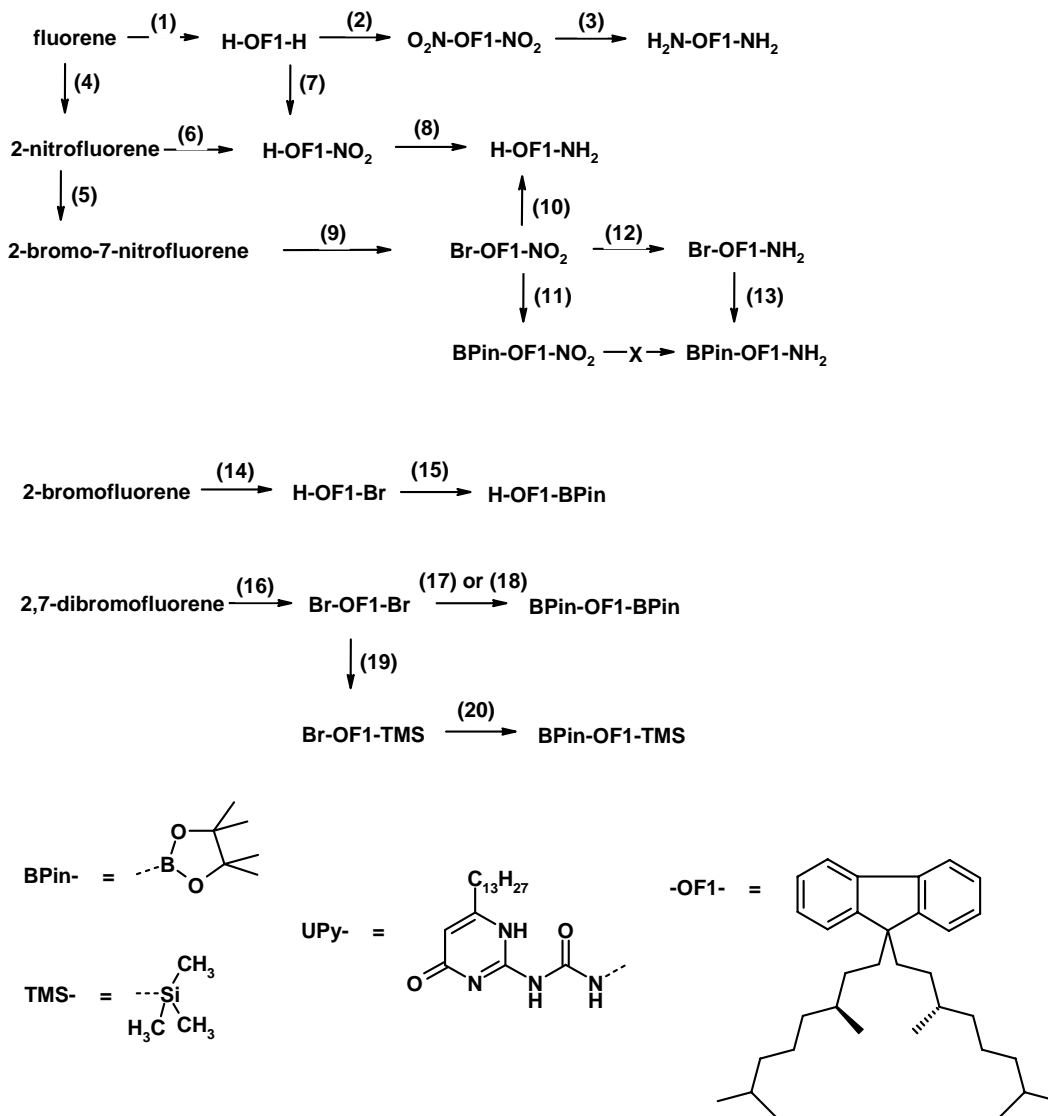
annealing in air at 180 °C for 1 min the active layer was spin coated under ambient conditions as a 10 – 15 mg/ml solution in OCDB (film thickness 45 – 55 nm; controlled by variation of concentration and spin speed). The metal cathode for electron injection was obtained by successively evaporating 5 nm of barium and 100 nm of aluminium. The current–voltage ( $I - V$ ) measurements were performed inside a glove box using a Keithley 2400 source meter. The electroluminescence spectra were recorded with a fiber optic

Avantes AVS USB 2000 spectrometer. The light intensity was measured with a Hamamatsu S9219 photodiode connected to a Keithley 2400 source meter. The photodiode was calibrated using a Minolta LS110 luminance meter.

AFM measurements were performed on thin polymer deposits obtained by spin coating on cleaned glass substrates. These surfaces are very flat, which precludes any influence of the substrate topography on the observed morphology. AFM images were recorded with a Nanoscope V microscope (Veeco Inc., Santa Barbara, CA) operated in Tapping mode at room temperature in air, using microfabricated cantilevers (spring constant of 30 N/m). The images were recorded with the 2048 pixels resolution in each direction and are shown as captured.

## Synthesis

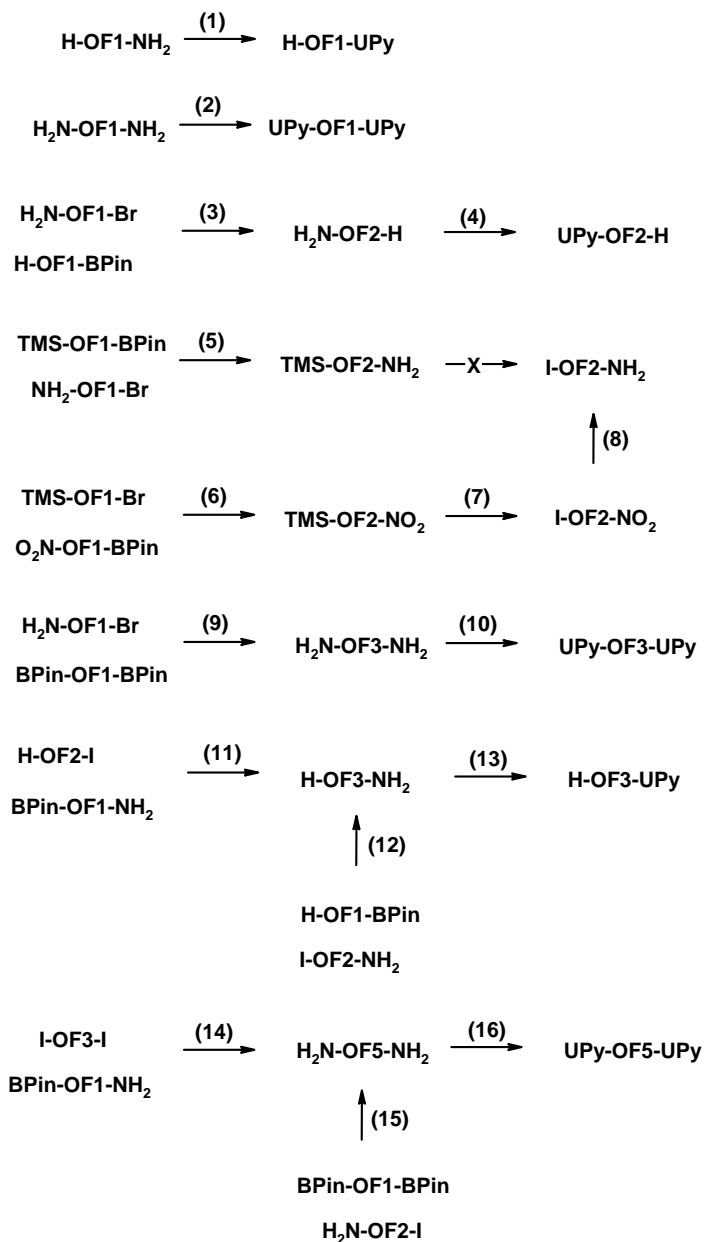
*Chart S1.* Synthetic procedure for the monomeric fluorene building blocks



(1, 6, 14, 16): (S)-3,7-dimethyloctylbromide, DMSO/aq. NaOH, benzyltriethyl ammonium bromide, over night (1, 14, 16), 2d (6), RT, 59 % (1), 41 % (6), 76 % (14), 74 – 95 % (16). (2): HNO<sub>3</sub> (fum.), HOAc (glac.), 2d, 0 °C – RT, 55 %. (3, 10) Pd/C, H<sub>2</sub> (4.8 bar), MeOH/CH<sub>2</sub>Cl<sub>2</sub>, over night, RT, 63 % (3), 66 % (10). (4) HNO<sub>3</sub> (fum.), SiO<sub>2</sub>/H<sub>2</sub>SO<sub>4</sub> (conc.), CH<sub>2</sub>Cl<sub>2</sub>, 4d, RT, 46 %. (5) Br<sub>2</sub>, CH<sub>2</sub>Cl<sub>2</sub>, over night, RT, 65 %. (7): HNO<sub>3</sub> (fum.),



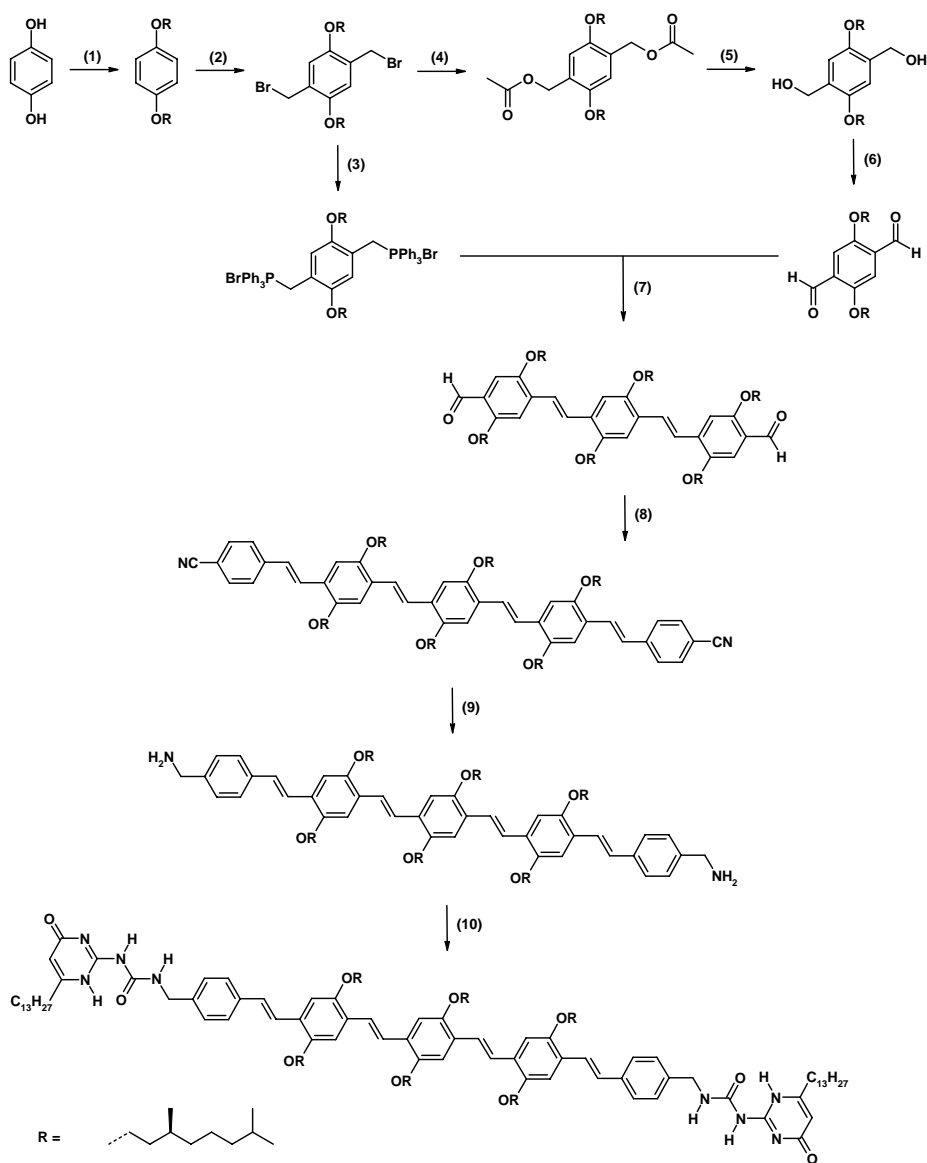
**Chart S3.** Synthetic procedure for the synthesis of UPy containing oligofluorenes



(1, 2) CDI activated tridecylisocytosine,  $\text{CHCl}_3$ , over night, reflux, 59 % (1), 67 % (2).  
 (3, 5, 6, 9, 11, 12, 14, 15):  $\text{Pd}(\text{PPh}_3)_4$ ,  $\text{Na}_2\text{CO}_3$  or  $\text{K}_2\text{CO}_3$ , dioxane/water or THF/water, Ar, 2d or longer, reflux or 90 – 100 °C, 70 % (3), 72 % (5), 92 % (6), 55 % (9), 50 % (11), 76 % (12), 30 % (14), 25 % (15). (4, 10, 13, 16): CDI activated tridecylisocytosine,

CHCl<sub>3</sub>, Ar, one night, reflux, 74 % (4), 78 % (10), 58 % (13), 56 % (16). (7): ICl, CH<sub>2</sub>Cl<sub>2</sub>, 30 min, 0 °C – RT, 60 %. (8): SnCl<sub>2</sub>, EtOH, EtOAc, 2 d, reflux, 77 %.

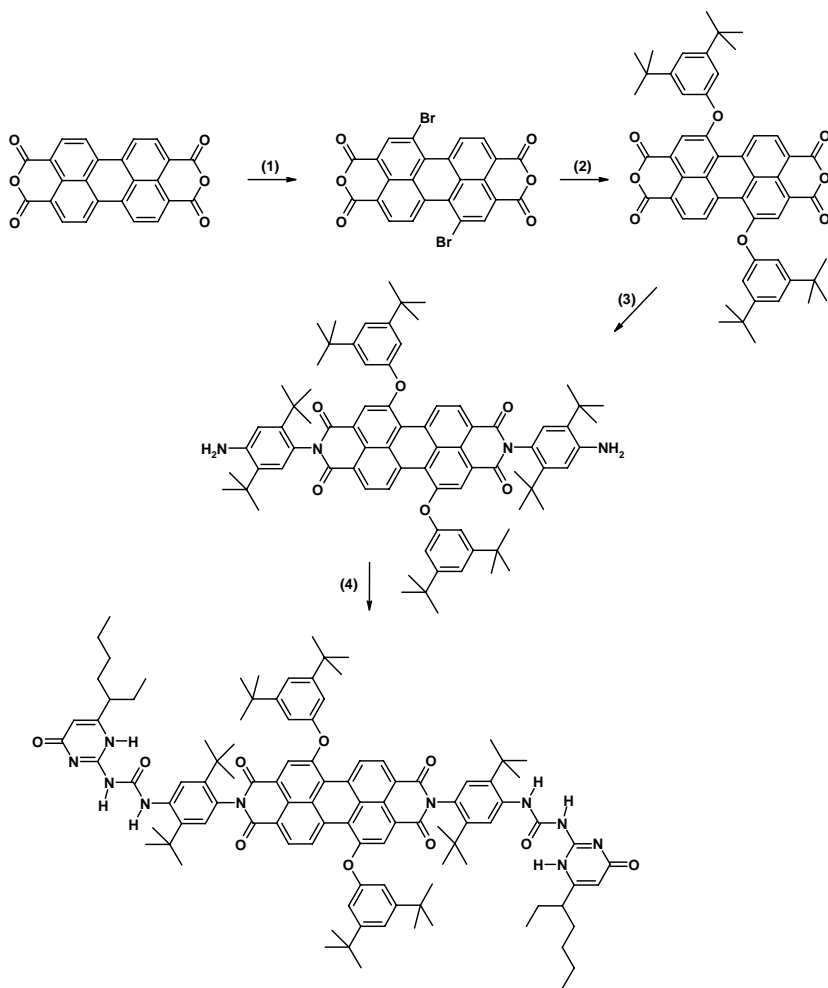
**Chart S4.** Synthesis of UPy-OPV5-UPy



(1) (S)-1-bromo-3,7-dimethyloctane, K<sub>2</sub>CO<sub>3</sub>, acetonitrile, reflux, 36 h. (2) paraformaldehyde, HBr, 60 °C, 2 h. (3) PPh<sub>3</sub>, toluene, reflux. (4) KOAc, Bu<sub>4</sub>NBr, acetonitrile, reflux, overnight. (5) LiAlH<sub>4</sub>, THF, RT, 2 h. (6) PCC, CH<sub>2</sub>Cl<sub>2</sub>, RT, 2 h. (7) a.

LiOEt, CH<sub>2</sub>Cl<sub>2</sub>, RT, 10 min; b. I<sub>2</sub>, CH<sub>2</sub>Cl<sub>2</sub>, RT, overnight. (8) KO<sup>t</sup>Bu, 4-cyanobenzyl-diethylphosphonate, DMF/THF, overnight, RT, 85 %. (9) LiAlH<sub>4</sub>, Et<sub>2</sub>O, overnight, RT, 90 %. (10) CDI activated tridecylisocytosine, CHCl<sub>3</sub>, reflux, overnight, 25 %.

**Chart S5. Synthesis of UPy-Pery-UPy**



(1) Br<sub>2</sub>, I<sub>2</sub>, conc. H<sub>2</sub>SO<sub>4</sub>, 55 – 85 °C, 2 d. (2) 3,5-di-*t*-butylphenol, Cs<sub>2</sub>CO<sub>3</sub>, DMF, 1 h, reflux. (3) 1,4-diamino-2,6-di-*t*-butylbenzene, Zn acetate, DMA, 190 °C, 3 h, 60 %. (4) CDI activated ethylhexylisocytosine, CHCl<sub>3</sub>, reflux, 18 h, 97 %.

## Synthetic procedures

The syntheses of Br-OF1-H, BPin-OF1-H, Br-OF1-Br, BPin-OF1-BPin, Br-OF1-TMS, BPin-OF1-TMS, TMS-OF2-H, I-OF2-H, TMS-OF3-TMS, I-OF3-I<sup>S1</sup>, bis(di-*t*-butylphenoxy)perylene bisanhydride,<sup>S2,S3</sup> 1,4-diamino-2,5-di-*t*-butylbenzene<sup>S4,S5</sup> tridecylisocytosine<sup>S6</sup> and CDI activated tridecylisocytosine<sup>S7</sup> have already been described elsewhere.

**General procedure for coupling of amino oligofluorenes with CDI activated isocytosine.** The amino oligofluorene is weighted into a flask and CDI activated isocytosine and dry CHCl<sub>3</sub> are added. The mixture is refluxed under a dry Ar atmosphere for one night and then in the case of bis UPy compounds, after cooling to room temperature, a small amount of TFA is added to dissolve formed solids. HCl (1 M) and CHCl<sub>3</sub> are added, giving a turbid mixture that only very slowly phase separates. The aqueous layer is extracted with CHCl<sub>3</sub> several times and the combined organic extracts are washed with NaHCO<sub>3</sub> solution (sat.), NaCl solution (sat.), and water and then dried over Na<sub>2</sub>CO<sub>3</sub> (bis UPy compounds) or Na<sub>2</sub>SO<sub>4</sub> (mono UPy compounds). Upon evaporation of the solvent, a brown solid film (bis UPy compounds) or a brown waxy solid (mono UPy compounds) is obtained that is dissolved in a small amount of CHCl<sub>3</sub> (plus some additional TFA for bis UPys) and purified by column chromatography. First, impurities are washed from the column with pure CHCl<sub>3</sub>, then the THF content of the solvent is gradually increased from 1 % to 10 %, leading to elution of the product. After removal of TFA (with Na<sub>2</sub>CO<sub>3</sub> for bis UPys) and evaporation of the solvents, an orange solid film (bis UPy compounds) or an orange waxy solid (mono UPy compounds) is obtained. Yields are given for these crude products, which are at least 95 % pure according to GPC and NMR analysis. Further purification on small scale is done by recycling GPC. The compounds are injected onto the column as solutions in THF/TFA mixtures (1 % TFA for mono UPys, higher for bis UPys). After recycling GPC, the pure fractions are concentrated by evaporation of the THF and the pure products are obtained by precipitation into aqueous MeOH (20 % water). The compounds are collected by

filtration, washed several times with aqueous MeOH and dried overnight in vacuo at 60 °C.

**General procedure for Suzuki couplings.** Halogenofluorene (bromo or iodo) and fluorene boronic ester were weighted in a two necked flask, base ( $\text{Na}_2\text{CO}_3$  or  $\text{K}_2\text{CO}_3$ ) was added and the flask was connected to a reflux condenser and equipped with a septum. Air was pumped out of the setup and replaced by Ar for several times, then  $\text{Pd}(\text{PPh}_3)_4$  was added under Ar counterflow and the degassed solvent mixture (dioxane/water 2 : 1 or THF/water 2 : 1) was added via the septum with a syringe. The reaction mixture was heated and stirred under Ar for at least two days, then poured into water and extracted several times with organic solvents (EtOAc,  $\text{CHCl}_3$  or  $\text{CH}_2\text{Cl}_2$ ). After washing the combined organic layers with NaCl solution (sat.) and water, they were dried over  $\text{Na}_2\text{SO}_4$  and the solvents evaporated. The resulting material was purified by column chromatography ( $\text{SiO}_2$ ), and sometimes also biobeads chromatography (THF) afterwards.

**General procedure for deprotection of TMS groups.** The TMS containing oligofluorene is dissolved in dry  $\text{CH}_2\text{Cl}_2$ , the solution is cooled to 0 °C in an ice bath and ICl is added drop wise as a solution in  $\text{CH}_2\text{Cl}_2$  (1 M) while stirring. After complete addition of ICl, the ice bath is removed and the reaction mixture is stirred at room temperature for at least 30 min. The reaction is stopped by addition of  $\text{Na}_2\text{S}_2\text{O}_3$  solution (sat.) and EtOAc, the organic phase is separated, washed again with  $\text{Na}_2\text{S}_2\text{O}_3$  solution (sat.), then with water. After drying over  $\text{Na}_2\text{SO}_4$ , the solvent is removed and the remaining material purified by column chromatography ( $\text{SiO}_2$ ).

**9,9-di((S)-3,7-dimethyloctyl)fluorene (H-OF1-H).** Fluorene (8.02 g, 48.25 mmol, 1.00 eq.) was added to a mixture of dimethylsulfoxide (80 ml) and an aqueous solution of NaOH (50 % w/w, 20 ml), resulting in an orange solution that quickly solidified. After addition of benzyltriethylammonium bromide (0.60 g, 2.62 mmol, 5 %) and (S)-1-bromo-3,7-dimethyloctane (28.8 g, 121.16 mmol, 2.51 eq.) the mixture was stirred for 18 h by means of a mechanical stirrer, resulting in a dark purple viscous mixture. It was poured into EtOAc and the resulting solution was washed twice with diluted hydrochloric acid (1

M) and water, leading to a colour change from dark purple to bright orange. After drying over  $\text{Na}_2\text{SO}_4$  the solvent was removed by vacuum evaporation and the resulting orange oil was dissolved in THF to which an excess of  $\text{KO}^t\text{Bu}$  was added, giving a deep red mixture which was stirred over night and then filtered through celite. Concentrated  $\text{NaCl}$  solution was added, leading to disappearance of the red colour. The organic layer was dried over  $\text{Na}_2\text{SO}_4$ , the solvent and subsequently excess alkyl bromide were removed by vacuum distillation. The resulting oil was purified by column chromatography ( $\text{SiO}_2$ , pentane), giving a clear colourless oil (12.62 g, 28.25 mmol, 59 %).  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ ):  $\delta$  7.66 (dd,  $^3\text{J} = 6.0$  Hz,  $^4\text{J} = 2.0$  Hz, 2 H), 7.29 – 7.32 (m, 2 H), 7.24 – 7.27 (m, 4 H), 1.70 – 2.02 (m, 4 H), 1.37 – 1.47 (m, 2 H), 0.96 – 1.16 (m, 12 H), 0.82 – 0.93 (m, 2 H), 0.79 (d,  $^3\text{J} = 6.5$  Hz, 12 H), 0.66 (d,  $^3\text{J} = 6.5$  Hz, 6 H), 0.55 – 0.66 (m, 2 H), 0.42 – 0.51 (m, 2 H).  $^{13}\text{C-NMR}$  ( $\text{CDCl}_3$ ):  $\delta$  150.31, 141.00, 126.78, 126.47, 122.50, 119.40, 54.59, 39.03, 37.42, 36.42, 32.68, 30.19, 27.73, 24.39, 22.50, 22.41, 19.36. MALDI TOF MS: calc.  $[\text{M}^+]$  446.39, found 446.28. IR ( $\text{cm}^{-1}$ ):  $\nu = 3066$  (w), 3374 (w), 3014 (w) 2953 (s), 2925 (s), 2868 (s), 1617 (s), 1449 (m), 1366 (w), 772 (w), 734 (vs). EA calc. for  $\text{C}_{33}\text{H}_5$ : 88.7 % C, 11.3 % H, 5.9 % N; found 88.8 % C, 11.2 % H. UV-vis ( $\text{CHCl}_3$ ):  $\lambda_{\text{max}}$  ( $\log \epsilon$ ) = 266 nm (4.20), 294 nm (3.83), 305 nm (3.99). PL ( $\text{CHCl}_3$ )  $\phi$  ca. 5 % (2-aminopyridine).

**2,7-dinitro-9,9-di((S)-3,7-dimethyloctyl)fluorene ( $\text{O}_2\text{N-OF1-NO}_2$ ).** Alkylation of commercially available 2,7-dinitrofluorene analogous to the preparation of H-OF1-H was not successful. Therefore H-OF1-H (10.16 g, 22.74 mmol) was mixed with 18 ml of glacial acetic acid and the mixture was cooled to 0 °C, giving a white sludge to which fuming  $\text{HNO}_3$  (18 ml) was added drop wise under cooling and stirring. After removal of the ice bath, the mixture was stirred for two days at room temperature and poured on ice. After extraction with EtOAc, the organic layers were washed with saturated aq.  $\text{NaHCO}_3$ , brine and water, and dried over  $\text{Na}_2\text{SO}_4$ . After evaporation of the solvent, the resulting dark orange oil was purified by column chromatography (heptane/ $\text{CHCl}_3$  2 : 1), to give a slightly impure yellow oil from which over night light yellow crystals separated out which were collected by decantation and washed with cold MeOH (6.69 g, 12.46 mmol, 55 %). Mp. 74 – 79 °C.  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ ):  $\delta$  8.34 (dd,  $^3\text{J} = 8.5$  Hz,  $^4\text{J} = 2.0$  Hz, 2 H), 8.26 (d,  $^4\text{J} = 2.0$  Hz, 2 H), 7.94 (d,  $^3\text{J} = 8.5$  Hz), 2.09 – 2.18 (m, 4 H), 1.39 – 1.42 (m, 2 H),

0.96 – 1.08 (m, 12 H), 0.81 – 0.88 (m, 2 H), 0.79 (dd,  $^3J = 6.5$  Hz,  $^4J = 1.5$  Hz, 12 H), 0.69 (d,  $^3J = 6.5$  Hz, 6 H), 0.50 – 0.53 (m, 2 H), 0.38 – 0.42 (m, 2 H).  $^{13}\text{C}$ -NMR ( $\text{CDCl}_3$ ):  $\delta$  153.14, 148.14, 144.43, 123.24, 121.21, 118.07, 55.99, 38.73, 36.82, 36.16, 32.37, 30.21, 27.54, 24.18, 22.25, 22.16, 19.01. MALDI TOF MS: calc.  $[\text{M}^+]$  536.36, found 536.28. IR ( $\text{cm}^{-1}$ ):  $\nu = 3097$  (w), 3063 (w), 2954 (m), 2926 (m), 2967 (m), 1516 (s), 1335 (s), 1072 (m), 898 (m), 832 (s), 740 (s). EA calc. for  $\text{C}_{33}\text{H}_{48}\text{N}_2\text{O}_4$ : 73.8 % C, 9.0 % H, 5.2 % N; found 74.0 % C, 9.1 % H, 5.2 % N.

**2,7-diamino-9,9-di((S)-3,7-dimethyloctyl)fluorene ( $\text{H}_2\text{N-OF1-NH}_2$ ).** 2,7-dinitro-9,9-di((S)-3,7-dimethyloctyl)fluorene (4.91 g, 9.15 mmol) was dissolved in a mixture of MeOH (40 ml) and  $\text{CH}_2\text{Cl}_2$  (40 ml). A stream of Ar was bubbled through the solution to remove oxygen, then Pd on carbon (10 %, 400 mg) was added and the mixture was reduced in a Parr reactor under hydrogen gas (70 psi) over night. The solids were removed by filtration through celite and the filtrate was washed with water and dried over  $\text{Na}_2\text{SO}_4$ . After evaporation a brown oil was obtained that was purified by column chromatography ( $\text{CHCl}_3/\text{EtOH}$  98 : 2), giving a brown oil that solidified into a dark solid (2.77 g, 63 %). Mp. 46 - 48 °C.  $^1\text{H}$ -NMR ( $\text{CDCl}_3$ ):  $\delta$  7.32 (dd,  $^3J = 7.5$  Hz,  $^4J = 1.5$  Hz, 2 H), 6.60 (d,  $^4J = 1.5$  Hz, 2 H), 6.59 (d,  $^3J = 7.5$  Hz, 2 H), 3.61 (br, 4 H), 1.77 – 1.90 (m, 4 H), 1.40 – 1.50 (m, 2 H), 1.02 – 1.18 (m, 12 H), 0.85 – 0.96 (m, 2 H), 0.82 (d,  $^3J = 6.5$  Hz, 12 H), 0.68 (d,  $^3J = 6.5$  Hz, 6 H), 0.60 – 0.66 (m, 2 H), 0.48 – 0.57 (m, 2 H).  $^{13}\text{C}$ -NMR ( $\text{CDCl}_3$ ):  $\delta$  151.54, 144.51, 133.19, 118.98, 113.82, 109.97, 54.38, 39.26, 38.11, 36.69, 33.05, 30.52, 27.93, 24.67, 22.71, 22.59, 19.50. MALDI TOF MS: calc.  $[\text{M}^+]$  476.41, found 476.53. IR ( $\text{cm}^{-1}$ ):  $\nu = 3461$  (w), 3374 (w), 3212 (w), 3004 (w), 2952 (s), 2925 (s), 2867 (s), 1617 (s), 1584 (m), 1467 (s), 1326 (m), 1297 (m), 1245 (m), 1133 (m), 857 (m), 808 (s). EA calc. for  $\text{C}_{33}\text{H}_{52}\text{N}_2$ : 83.1 % C, 11.0 % H, 5.9 % N; found 83.2 % C, 11.0 % H, 5.8 % N.

**2-nitrofluorene.** Commercially available fluorene was recrystallised from ethanol and nitrated according to literature procedures.<sup>S8</sup> Mp 154 °C.  $^1\text{H}$ -NMR ( $\text{CDCl}_3$ ):  $\delta$  8.34 (d,  $^4J = 1.5$  Hz, 1 H), 8.24 (dd,  $^3J = 8.5$  Hz,  $^4J = 1.5$  Hz, 1 H), 7.83 (m, 1 H), 7.80 (d,  $^3J = 8.5$  Hz, 1 H), 7.58 (m, 1 H), 7.42 (m, 2 H), 3.94 (s, 2 H).  $^{13}\text{C}$ -NMR ( $\text{CDCl}_3$ )  $\delta$ , GC MS: calc.

[M<sup>+</sup>] 211.06, found 211.15, 165.10 (M<sup>+</sup> - NO<sub>2</sub>). IR (cm<sup>-1</sup>): ν = 3097 (w), 3078 (w), 3013 (w), 1624 (m), 1592 (s), 1517 (s), 1471 (m), 1394 (m), 1331 (s), 1185 (m), 1073 (m), 912 (m), 842 (m), 803 (m), 779 (s), 739 (s). EA calc. for C<sub>13</sub>H<sub>9</sub>NO<sub>2</sub>: 73.9 % C, 4.3 % H, 6.6 % N; found 73.8 % C, 4.1 % H, 6.5 % N.

**2-bromo-7-nitrofluorene.** 2-nitrofluorene was brominated according to literature procedures.<sup>S9</sup> Mp. 233 - 238 °C. <sup>1</sup>H-NMR (DMSO-d<sub>6</sub>): δ 8.51 (d, <sup>4</sup>J = 2.0 Hz, 1 H), 8.35 (dd, <sup>3</sup>J = 8.5 Hz, <sup>4</sup>J = 2.0 Hz, 1 H), 8.22 (d, <sup>3</sup>J = 8.5 Hz, 1 H), 8.09 (d, <sup>3</sup>J = 8.0 Hz), 7.96 (d, <sup>4</sup>J = 1.5 Hz, 1 H), 7.72 (dd, <sup>3</sup>J = 8.0 Hz, <sup>4</sup>J = 8.0 Hz, 1 H), 4.16 (s, 2 H). GC MS: calc. [M<sup>+</sup>] 289.0, found 290.1 (M-H<sup>+</sup>). IR (cm<sup>-1</sup>): ν = 3098 (w), 3076 (w), 1614 (m), 1593 (m), 1509 (s), 1331 (s), 1061 (m), 820 (s), 810 (s), 757 (s), 726 (s). EA calc. for C<sub>13</sub>H<sub>8</sub>BrNO<sub>2</sub>: 53.8 % C, 2.8 % H, 4.8 % N; found 53.7 % C, 2.6 % H, 4.7 % N.

**2-nitro-9,9-di((S)-dimethyloctyl)fluorene (O<sub>2</sub>N-OF1-H).** Method 1: Nitrofluorene (127 mg, 0.26 mmol, 1.00 eq.), dihydrocitronellyl bromide (200 mg, 0.90 mmol, 3.46 eq.) and benzyltriethylammonium chloride (15 mg, 0.06 mmol, 23 %) were stirred in a mixture of DMSO (2 ml) and aq. NaOH (50:50 weight %, 0.5 ml). After two days, the reaction mixture was neutralised by addition of diluted H<sub>2</sub>SO<sub>4</sub> and extracted with CH<sub>2</sub>Cl<sub>2</sub>. The organic extracts were washed with water, dried over Na<sub>2</sub>SO<sub>4</sub>, and after evaporation of the solvent, a dark oil was obtained that was purified by column chromatography (heptane/CHCl<sub>3</sub> 60:40), giving a yellow oil (52 mg, 0.106 mmol, 41 %).

Method 2: H-OF1-H (2.52 g, 5.64 mmol) was dissolved in CHCl<sub>3</sub> (5 ml), then HOAc (1 ml) was added. The reaction mixture was cooled to 0 °C, and then HNO<sub>3</sub> (fum., 0.3 ml) was added drop wise while stirring. After slowly warming up to room temp., the mixture was stirred for one night. TLC (heptane/CHCl<sub>3</sub> 60:40) did not show a lot of conversion, so more HNO<sub>3</sub> (0.5 ml) was added. After one more night at room temp., another portion of HNO<sub>3</sub> (0.5 ml) was added and the mixture stirred for three nights. Although TLC analysis showed that not all starting material was consumed yet, the reaction was stopped by addition of aq. NaHCO<sub>3</sub> (sat.). The aqueous layer was extracted with CHCl<sub>3</sub>, the combined organic extracts were washed with NaCl solution (conc.) and water, dried over Na<sub>2</sub>SO<sub>4</sub>, and the solvent was evaporated. From the remaining oil, unreacted starting

material was recovered by column chromatography (heptane), and the product was obtained by changing the eluent to  $\text{CHCl}_3$ /heptane 40:60. Yellow oil (890 mg, 1.81 mmol, 32 %).  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ ):  $\delta$  8.26 (dd,  $3J = 8.5$  Hz,  $4J = 2.0$  Hz, 1 H), 8.21 (d,  $4J = 2.0$  Hz, 1 H), 7.77 – 7.80 (m, 2 H), 7.38 – 7.42 (m, 3 H), 1.97 – 2.12 (m, 4 H), 1.35 – 1.46 (m, 2 H), 0.94 – 1.19 (m, 12 H), 0.84 – 0.90 (m, 2 H), 0.78 – 0.80 (m, 12 H), 0.67 (dd,  $^3J = 6.5$  Hz,  $4J = 2.0$  Hz, 6 H), 0.50 – 0.58 (m, 2 H), 0.38 – 0.47 (m, 2 H).  $^{13}\text{C-NMR}$  ( $\text{CDCl}_3$ )  $\delta$  152.23, 151.91, 141.71, 147.18, 138.83, 129.28, 127.39, 123.25, 123.14, 121.18, 119.77, 118.14, 55.53, 39.15, 39.13, 37.34, 36.62, 36.48, 32.77, 30.45, 30.40, 27.91, 27.88, 24.55, 24.52, 22.64, 22.55, 19.52, 19.41. MALDI TOF MS: calc.  $[\text{M}^+]$  491.38, found 492.35 ( $\text{M-H}^+$ ). IR ( $\text{cm}^{-1}$ ):  $\nu = 3065$  (w), 2953 (s), 2926 (s), 2868 (s), 1612 (m), 1591 (m). 1522 (s), 1468 (s), 1336 (vs), 1077 (m), 908 (s), 839 (m), 774 (m), 738 (vs). EA calc. for  $\text{C}_{33}\text{H}_{49}\text{NO}_2$ : 80.6 % C, 10.0 % H, 2.8 % N; found 80.1 % C, 10.5 % H, 2.6 % N.

**2-amino-9,9-di((S)-dimethyloctyl)fluorene (H<sub>2</sub>N-OF1-H).** Method 1: Br-OF1-NO<sub>2</sub> (6.23 g, 10.92 mmol) was dissolved in a mixture of MeOH (80 ml) and  $\text{CH}_2\text{Cl}_2$  (40 ml), the solution was degassed by bubbling an Ar stream through it and then Pd on C (10 %, 0.25 g, 0.235 mmol, 2 %) was added. The reaction mixture was reduced in a Parr reactor under an atmosphere of hydrogen gas (70 psi) over night. The catalyst was removed by filtration through celite, giving a dark green filtrate, which after evaporation of the solvents left back a dark orange brown oil. This was purified by column chromatography ( $\text{SiO}_2$ , heptane/EtOAc gradient from 9:1 to 4:1), leading to an orange oil (3.35 g, 7.25 mmol, 66 %).

Method 2: H-OF1-NO<sub>2</sub> (870 mg, 1.77 mmol) and  $\text{SnCl}_2$  (2.68 g, 14.14 mmol, 8.0 eq.) were dissolved in a degassed mixture of EtOH and EtOAc (15 ml, 50:50). The reaction mixture was refluxed under Ar for 3 d and after cooling down, aq. NaOH (1 M) was added. The formed precipitates were filtrated off, extracted thoroughly with EtOAc, and the combined organic extracts were washed with aq. NaOH (1 M), aq. HCl (1 M), and water, then dried over  $\text{Na}_2\text{SO}_4$ . After evaporation of the solvent, the remaining dark oil was purified by column chromatography (gradient heptane/ $\text{CHCl}_3$  from 60:40 to 40:60) to obtain an orange oil (496 mg, 1.07 mmol, 60 %).  $^1\text{H-NMR}$  ( $\text{CD}_2\text{Cl}_2$ ):  $\delta$  7.57 (dd,  $^3J =$

7.5 Hz,  $^4J = 0.5$  Hz, 1 H), 7.50 (d,  $^3J = 7.5$  Hz, 1 H), 7.26 – 7.31 (m, 2 H), 7.21 (dd,  $^3J = 7.5$  Hz,  $^4J = 1.5$  Hz, 1 H), 6.69 (d,  $^4J = 1.5$  Hz, 1 H), 6.66 (dd,  $^3J = 8.0$  Hz,  $^4J = 2.0$  Hz, 1 H), 3.81 (br, 2 H), 1.89 – 2.04 (m, 4 H), 1.46 – 1.52 (m, 2 H), 1.07 – 1.19 (m, 12 H), 0.88 – 0.94 (m, 2 H), 0.86 (dd,  $^3J = 6.5$  Hz,  $^4J = 0.5$  Hz, 12 H), 0.73 (d,  $^3J = 6.5$  Hz, 6 H), 0.50 – 0.79 (m, 4 H).  $^{13}\text{C-NMR}$  ( $\text{CDCl}_3$ )  $\delta$  152.56, 149.70, 146.11, 141.78, 132.53, 126.68, 125.42, 122.56, 120.52, 118.38, 113.98, 109.63, 54.64, 39.37, 39.35, 38.03, 37.94, 36.81, 36.72, 33.07, 33.05, 30.56, 30.54, 28.03, 24.78, 24.69, 22.84, 22.74, 19.72, 19.63. MALDI TOF MS: calc.  $[\text{M}^+]$  461.40, found 461.58. IR ( $\text{cm}^{-1}$ ):  $\nu = 3475$  (w), 3388 (w), 3009 (w), 2953 (s), 2926 (s), 2868 (m), 1619 (s), 1455 (s), 907 (s), 817 (m), 731 (vs). EA calc. for  $\text{C}_{33}\text{H}_{51}\text{N}$ : 85.8 % C, 11.1 % H, 3.0 % N; found 85.6 % C, 10.8 % H, 3.1 % N.

**2-bromo-7-nitro-9,9-di((S)-3,7-dimethyloctyl)fluorene (Br-OF1-NO<sub>2</sub>).** 2-bromo-7-nitrofluorene (40.4 g, 139.25 mmol) was added to a mixture of DMSO (350 ml), powdered KOH (30 g) and potassium iodide (3.3 g), which gave a viscous, dark green reaction mixture. (S)-1-bromo-3,7-dimethyloctan (74 g, 334.54 mmol) was added and the mixture stirred over night at room temperature. Water and  $\text{CH}_2\text{Cl}_2$  were added and the aqueous phase was extracted with  $\text{CH}_2\text{Cl}_2$  several times. After drying the combined organic layer over  $\text{Na}_2\text{SO}_4$  and removal of the solvent, a black oil was obtained from which excess alkylbromide was removed by vacuum distillation. Column chromatography (heptane/chloroform 4 : 1) gave an orange oil that slowly solidified into yellow crystal plates (46.1 g, 58 %). Mp. 46 – 48 °C.  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ ):  $\delta$  8.27 (dd,  $^3J = 8.5$  Hz,  $^4J = 2.0$  Hz, 1 H), 8.19 (d,  $^4J = 2.0$  Hz, 1 H), 7.77 (d,  $^3J = 8.5$  Hz, 1 H), 7.65 (d,  $^3J = 8.5$  Hz, 1 H), 7.53 – 7.55 (m, 2 H), 1.93 – 2.17 (m, 4 H), 1.40 – 1.44 (m, 2 H), 0.94 – 1.04 (m, 12 H), 0.84 – 0.88 (m, 2 H), 0.79 – 0.81 (m, 12 H), 0.67 (dd,  $^3J = 6.5$  Hz,  $^4J = 2.0$  Hz, 6 H), 0.34 – 0.64 (m, 4 H).  $^{13}\text{C-NMR}$  ( $\text{CDCl}_3$ ):  $\delta$  154.32, 151.55, 147.40, 146.50, 137.78, 130.74, 126.50, 123.69, 123.42, 122.46, 119.95, 118.19, 69.23, 39.10, 37.28, 37.22, 36.50, 36.47, 32.71, 30.39, 27.89, 27.87, 24.54, 24.48, 22.63, 22.60, 22.53, 19.40, 19.38. MALDI TOF MS: calc.  $[\text{M}^+]$  569.29, found 569.23. IR ( $\text{cm}^{-1}$ ):  $\nu = 2954$  (s), 2925 (s), 2868 (m), 1523 (s), 1456 (m), 1338 (vs), 1138 (w), 1079 (m), 1063 (m), 817 (s), 737 (s). EA calc. for  $\text{C}_{33}\text{H}_{48}\text{BrNO}_2$ : 69.5 % C, 8.5 % H, 2.5 % N; found 69.4 % C, 8.4 % H, 2.3 % N.

**2-nitro-7-pinacoyl-9,9-di((S)-3,7-dimethyloctyl)fluorene boronic ester (O<sub>2</sub>N-OF1-BPin).** Br-OF1-NO<sub>2</sub> (8.65 g 15.16 mmol) was boronated according to literature procedures<sup>S10</sup> using DMF (60 ml), bispinacoyldiboron (5.00 g, 19.69 mmol, 1.30 eq.), Pd(dppf)Cl<sub>2</sub> (0.662 mg, 0.81 mmol, 0.05 eq.), and KOAc (4.46 g, 45.45 mmol, 3.00 eq.). Workup was performed by pouring the black reaction mixture into EtOAc, washing with HCl (1 M), NaCl solution (sat.), and water, drying of the organic layer over Na<sub>2</sub>SO<sub>4</sub>, and evaporation of the solvent. Column chromatography (SiO<sub>2</sub>, chloroform/heptane 1 : 1) gave a yellowish oil (6.35 g, 10.28 mmol, 68 %). <sup>1</sup>H-NMR (CDCl<sub>3</sub>): δ 8.25 (dd, <sup>3</sup>J = 8.5 Hz, <sup>4</sup>J = 2.0 Hz, 1 H), 8.21 (d, <sup>3</sup>J = 2.0 Hz, 1 H), 7.77 – 7.89 (m, 4 H), 1.99 – 2.14 (m, 4 H), 1.41 – 1.46 (m, 2 H), 1.39 (s, 12 H), 0.80 – 1.20 (m, 14 H), 0.79 (d, <sup>3</sup>J = 6.5 Hz, 12 H), 0.66 (d, <sup>3</sup>J = 6.5 Hz, 6 H), 0.28 – 0.58 (m, 4 H). <sup>13</sup>C-NMR (CDCl<sub>3</sub>): δ 152.48, 151.38, 157.48, 147.40, 141.52, 134.12, 129.11, 123.15, 120.35, 120.20, 118.20, 83.94, 55.60, 39.10, 37.25, 37.18, 36.51, 36.47, 32.76, 32.73, 30.41, 30.37, 27.87, 24.90, 24.52, 24.49, 22.63, 22.60, 22.53, 19.43. MALDI TOF MS: calc. [M<sup>+</sup>] 616.46, found 616.45. IR (cm<sup>-1</sup>): ν = 2955 (s), 2926 (s), 2870 (m), 1526 (m), 1463 (m), 1357 (s), 1338 (vs), 1265 (w), 1144 (s), 1082 (m), 963 (w), 827 (m), 739 (m), 692 (m). EA calc. for C<sub>39</sub>H<sub>60</sub>BNO<sub>4</sub>: 75.8 % C, 9.8 % H, 2.3 % N; found 76.1 % C, 9.8 % H, 2.2 % N.

**2-bromo-7-amino-9,9-di((S)-3,7-dimethyloctyl)fluorene (Br-OF1-NH<sub>2</sub>).** 2-bromo-7-nitro-9,9-di((S)-3,7-dimethyloctyl)fluorene (15.40 g, 26.99 mmol) was added to a degassed mixture of ethanol and ethyl acetate (1 : 1 v/v). Then anhydrous SnCl<sub>2</sub> (45.0 g, 236.34 mmol) was added and the mixture was refluxed under Ar for 3 d, resulting in a clear yellow solution. Upon addition of 1 M NaOH (aq.), a white precipitate formed which was removed by vacuum filtration and thoroughly washed with EtOAc. The combined organic phases were washed with 1 M NaOH, water and brine, and dried over Na<sub>2</sub>SO<sub>4</sub>. Filtration and evaporation of the solvent resulted in an orange oil that was purified by column chromatography (chloroform/heptane 4 : 1). A yellow oil was obtained that solidified over night into beige crystal needles (13.50 g, 27.97 mmol, 93 %). Mp. 50 – 52 °C. <sup>1</sup>H-NMR (CDCl<sub>3</sub>): δ 7.30 – 7.36 (m, 4 H), 6.53 – 6.55 (m, 2 H), 3.73 (br, 2 H), 1.71 – 1.90 (m, 4 H), 1.38 – 1.43 (m, 2 H), 0.92 – 1.10 (m, 12 H), 0.78 – 0.83 (m, 2 H), 0.73 (d, 3J = 6.5 Hz, 12 H), 0.61 (d, 3J = 6.5 Hz, 6 H), 0.10 – 0.37 (m, 4 H).

$^{13}\text{C-NMR}$  ( $\text{CDCl}_3$ ):  $\delta$  152.24, 152.01, 146.42, 140.75, 131.34, 129.69, 125.75, 120.63, 119.63, 119.04, 114.06, 109.45, 54.92, 39.26, 39.23, 37.85, 37.72, 36.65, 36.61, 32.92, 32.89, 30.39, 27.96, 24.67, 24.58, 22.73, 22.65, 22.64, 19.53. MALDI TOF MS: calc.  $[\text{M}^+]$  539.31, found 539.32. IR ( $\text{cm}^{-1}$ ):  $\nu$  = 3402 (w), 3303 (w), 3210 (w), 2952 (s), 2924 (s), 2867 (m), 1611 (m), 1459 (s), 1444 (s), 1270(m), 1061 (m), 864 (m), 814 (s), 736 (s), 701 (s). EA calc. for  $\text{C}_{33}\text{H}_{50}\text{BrN}$ : 73.3 % C, 9.3 % H, 2.6 % N; found 73.2 % C, 9.3 % H, 2.5 % N.

**2-amino-7-pinacoyl-9,9-di((S)-3,7-dimethyloctyl)fluorene boronic ester ( $\text{H}_2\text{N-OF1-BPin}$ ).** Br-OF1- $\text{H}_2\text{N}$  (6.00 g, 11.10 mmol), was lithiated and boronated according to literature procedures<sup>S11</sup> using THF (50 ml), nBuLi (11.1 ml, 2.5 M in hexanes, 2.5 eq.), and iPrOBPin (4.5 ml, 4.10 g, 22.06 mmol, 1.99 eq.). To the turbid red reaction mixture water was added, and after stirring for 30 min, it was extracted with a mixture of EtOAc and  $\text{CHCl}_3$ . The organic layers were washed with NaCl solution (sat.) and water, dried over  $\text{Na}_2\text{SO}_4$ , and after evaporation of the solvent, a black oil was obtained. Purification by column chromatography (toluene/ $\text{CHCl}_3$  1 : 1) gave a dark oil (4.20 g, 7.15 mmol, 64 %). The compound could not be obtained from BPin-OF1- $\text{NO}_2$  by reduction of the nitro group.  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ ):  $\delta$  7.77 (d,  $^3\text{J} = 7.5$  Hz, 1 H), 7.70 (s, 1 H), 7.52 (d,  $^3\text{J} = 7.5$  Hz, 1 H), 7.46 (d,  $^3\text{J} = 8.0$  Hz, 1 H), 6.61 (d,  $^4\text{J} = 2.0$  Hz, 1 H), 6.58 (dd,  $^3\text{J} = 8.0$  Hz,  $^4\text{J} = 2.0$  Hz, 1 H), 3.72 (br, 2 H), 1.84 – 2.00 (m, 4 H), 1.40 – 1.45 (m, 2 H), 1.35 (s, 12 H), 0.95 – 1.22 (m, 12 H), 0.83 – 0.90 (m, 2 H), 0.80 (dd,  $^3\text{J} = 7.0$  Hz,  $^4\text{J} = 3.0$  Hz, 12 H), 0.67 (d,  $^3\text{J} = 6.0$  Hz, 6 H), 0.58 – 0.64 (m, 2 H), 0.47 – 0.52 (m, 2 H).  $^{13}\text{C-NMR}$  ( $\text{CDCl}_3$ )  $\delta$  153.26, 148.88, 146.63, 144.89, 133.87, 132.17, 128.59, 121.02, 117.64, 113.90, 109.45, 83.47, 54.63, 39.29, 39.26, 37.86, 37.69, 36.70, 36.61, 32.98, 32.95, 30.45, 30.38, 27.94, 24.98, 24.69, 24.59, 22.79, 22.73, 22.70, 22.67, 19.63, 19.61. MALDI TOF MS: calc.  $[\text{M}^+]$  586.43, found 586.49. IR ( $\text{cm}^{-1}$ ):  $\nu$  = 3478 (w), 3376 (w), 3215 (w), 2953 (s), 2926 (s), 2868 (m), 1606 (s), 1466 (m), 1353 (vs), 1301 (m), 1263 (w), 1145 (s), 1081 (m), 963 (w), 852 (w), 815 (w), 691 (w). EA calc. for  $\text{C}_{39}\text{H}_{62}\text{BNO}_2$ : 79.7 % C, 10.6 % H, 2.4 % N; found 79.8 % C, 10.7 % H, 2.2 % N.

**2-(4-(2-ureido-6-(1-tridecyl)-4[1H]-pyrimidinone)-9,9-di((S)-dimethyloctyl)fluorene (UPy-OF1-H).** H<sub>2</sub>N-OF1-H (402 mg, 0.87 mmol), CDI-activated isocytosine (410 mg, 1.06 mmol, 1.22 eq.), CHCl<sub>3</sub> (6 ml). Yield 450 mg (0.58 mmol, 67 %). <sup>1</sup>H-NMR (CDCl<sub>3</sub>): δ 13.03 (s, 1 H), 12.39 (s, 1 H), 12.21 (s, 1 H), 7.98 (br s, 1 H), 7.60 – 7.66 (m, 3 H), 7.21 – 7.35 (m, 3 H), 5.75 (s, 1 H), 1.98 – 2.19 (m, 6 H), 1.36 – 1.50 (m, 4 H), 0.98 – 1.36 (m, 32 H), 0.49 – 0.98 (m, 30 H). <sup>13</sup>C-NMR (THF-d<sub>8</sub> + TFA-d<sub>1</sub>) δ 155.58, 155.05, 152.28, 151.37, 142.38, 139.45, 137.90, 127.73, 127.33, 123.61, 120.60, 120.13, 119.77, 115.42, 196.15, 56.03, 40.36, 40.33, 38.86, 38.73, 37.87, 34.17, 34.05, 33.49, 33.04, 31.70, 30.81, 30.77, 30.75, 30.68, 30.48, 30.44, 30.06, 29.04, 29.01, 27.74, 23.72, 23.22, 23.14, 23.10, 20.39, 20.08, 14.60. MALDI TOF MS: calc. [M<sup>+</sup>] 780.63, found 781.51 (M-H<sup>+</sup>), 803.49 (M-Na<sup>+</sup>). IR (cm<sup>-1</sup>): ν = 3039 (w), 2953 (s), 2923 (s), 2853 (s), 1702 (s), 1660 (s), 1622 (m), 1600 (s), 1580 (s), 1492 (s), 1454 (s), 1315 (m), 1262 (m), 1230 (s), 1024 (w), 843 (w), 833 (w), 758 (m), 736 (s). EA calc. for C<sub>51</sub>H<sub>80</sub>N<sub>4</sub>O<sub>2</sub>: 78.4 % C, 10.3 % H, 7.2 % N; found 78.0 % C, 10.0 % H, 7.1 % N. UV-vis (CHCl<sub>3</sub>): λ<sub>max</sub> (logε) = 300 nm (4.49), 320 (4.50). PL (CHCl<sub>3</sub>): φ ca. 2 % (naphthalene).

**2,7-bis(4-(2-ureido-6-(1-tridecyl)-4[1H]-pyrimidinone)-9,9-di((S)-dimethyloctyl)fluorene (UPy-OF1-UPy).** H<sub>2</sub>N-OF1-NH<sub>2</sub> (2.30 g, 4.82 mmol, 1.00 eq), CDI activ. isocytosine (4.45 g, 11.48 mmol, 2.38 eq.), CHCl<sub>3</sub> (35 ml). Beige solid. Yield 3.15 g (2.82 mmol, 59 %). <sup>1</sup>H-NMR (TFA + CDCl<sub>3</sub>): δ 7.82 (d, <sup>3</sup>J = 8.0 Hz, 2 H), 7.54 (s, 2 H), 7.40 (d, <sup>3</sup>J = 8.0 Hz, 2 H), 6.47 (s, 2 H), 2.86 (t, <sup>3</sup>J = 7.5 Hz, 4 H), 2.06 – 2.22 (m, 4 H), 1.77 – 1.87 (m, 4 H), 1.28 – 1.57 (m, 42 H), 1.05 – 1.28 (m, 12 H), 0.88 – 1.05 (m, 8 H), 0.84 (dd, <sup>3</sup>J = 6.5 Hz, <sup>4</sup>J = 2.0 Hz, 12 H), 0.78 (d, <sup>3</sup>J = 6.0 Hz, 6 H), 0.67 – 0.80 (m, 2 H), 0.50 – 0.64 (m, 2 H). <sup>13</sup>C-NMR (TFA + CDCl<sub>3</sub>): δ 159.57, 152.88, 151.96, 151.27, 139.61, 132.94, 121.33, 120.42, 116.96, 115.81, 113.31, 105.56, 55.75, 38.85, 37.29, 36.27, 32.79, 32.64, 31.59, 30.33, 29.27, 29.22, 29.14, 29.00, 28.94, 28.67, 28.44, 27.58, 26.94, 24.29, 22.17, 21.40, 21.29, 18.20, 12.66. MALDI TOF MS: calc. [M<sup>+</sup>] 1114.86, found 1115.88 (M-H<sup>+</sup>), 1137.86 (M-Na<sup>+</sup>), 1153.90 (M-K<sup>+</sup>). IR (cm<sup>-1</sup>): ν = 2923 (s), 2853 (s), 1699 (m), 1656 (s), 1581 (s), 1564 (s), 1468 (s), 1309 (w), 1238 (s), 1215 (s), 1024 (w), 847 (m), 821 (m), 761 (m). EA calc. for C<sub>69</sub>H<sub>110</sub>N<sub>8</sub>O<sub>4</sub>: 74.3 % C, 9.9 % H, 10.0 % N;

found 72.6 % C, 9.5 % H, 9.8 % N. UV-vis (CHCl<sub>3</sub>):  $\lambda_{\text{max}}$  (log $\epsilon$ ) = 332 nm (4.71). PL (CHCl<sub>3</sub>):  $\phi$  ca. 2 % (2-aminopyridine).

**2-amino-9,9,9',9'-tetra((S)-3,7-dimethyloctyl)bisfluorene (H<sub>2</sub>N-OF2-H).** Br-OF1-NH<sub>2</sub> (0.72 g, 1.33 mmol, 1.02 eq.), H-OF1-BPin (0.75 g, 1.31 mmol, 1.00 eq.), Na<sub>2</sub>CO<sub>3</sub> (0.46 g, 4.34 mmol, 3.3 eq.), Pd(PPh<sub>3</sub>)<sub>4</sub> (80 mg, 0.069 mmol, 0.05 eq.), dioxane/water (2 ml), 2 d at 90 °C, extraction with EtOAc, column with heptane/THF 85 : 15. Orange oil (0.83 g, 0.92 mmol, 70 %). <sup>1</sup>H-NMR (CDCl<sub>3</sub>):  $\delta$  7.81 (d, <sup>3</sup>J = 8.0 Hz, 1 H), 7.78 (d, <sup>3</sup>J = 6.5 Hz, 1 H), 7.56 – 7.69 (m, 6 H), 7.35 – 7.41 (m, 3 H), 6.71 – 6.74 (m, 2 H), 3.80 (br, 2 H), 1.86 – 2.11 (m, 8 H), 1.36 – 1.49 (m, 4 H), 0.96 – 1.22 (m, 24 H), 0.84 – 0.96 (m, 4 H), 0.81 – 0.87 (m, 24 H), 0.51 – 0.80 (m, 20 H). <sup>13</sup>C-NMR (CDCl<sub>3</sub>):  $\delta$  152.82, 151.23, 150.83, 150.37, 146.39, 141.06, 141.03, 140.94, 140.09, 138.81, 131.93, 126.91, 126.80, 125.94, 122.80, 121.27, 121.17, 120.55, 119.80, 119.64, 118.44, 113.93, 109.55, 54.92, 54.68, 39.31, 39.29, 39.26, 37.92, 37.88, 37.62, 36.78, 36.69, 36.66, 33.02, 32.98, 32.92, 32.90, 30.61, 30.54, 27.95, 27.94, 24.76, 24.69, 24.66, 22.73, 22.71, 22.63, 19.65, 19.60, 19.58, 19.53. MALDI TOF MS: calc. [M<sup>+</sup>] 905.78, found 905.62. IR (cm<sup>-1</sup>):  $\nu$  = 3481 (w), 3387 (w), 3006 (w), 2953 (s), 2925 (s), 2868 (s), 1619 (m), 1467 (s), 1448 (m), 1366 (m), 1262 (m), 910 (s), 812 (s), 735 (vs). EA calc. for C<sub>66</sub>H<sub>99</sub>N: 87.4 % C, 11.0 % H, 1.5 % N; found 87.2 % C, 10.7 % H, 1.4 % N.

**2-(4-(2-ureido-6-(1-tridecyl)-4[1H]-pyrimidinone)-9,9,9',9'-tetra((S)-3,7**

**dimethyloctyl)bisfluorene (UPy-OF2-H).** H-OF2-NH<sub>2</sub> (520 mg, 0.57 mmol, 1.00 eq.), CDI activated isocytosine (291 mg, 0.75 mmol, 1.3 eq.), CHCl<sub>3</sub> (10 ml). Column: CHCl<sub>3</sub>/THF gradient from 100:0 to 90:10. Yield: 509 mg (0.42 mmol, 74 %). <sup>1</sup>H-NMR (CDCl<sub>3</sub>):  $\delta$  13.14 (s, 1 H), 12.36 (s, 1 H), 12.26 (s, 1 H), 7.66 – 7.80 (m, 5 H), 7.65 – 7.65 (m, 5 H), 7.27 – 7.37 (m, 3 H), 2.55 (t, 3J = 7.5 Hz, 2 H), 1.95 – 2.15 (m, 8 H), 1.68 – 1.77 (m, 2 H), 1.23 – 1.48 (m, 24 H), 0.97 – 1.23 (m, 24 H), 0.83 – 0.97 (m, 8 H), 0.50 – 0.83 (m, 43 H). <sup>13</sup>C-NMR (THF-d<sub>8</sub>)  $\delta$  174.24, 156.58, 156.15, 154.73, 153.18, 152.83, 152.79, 152.36, 142.97, 142.35, 142.22, 141.50, 140.40, 138.08, 128.59, 128.47, 127.69, 127.64, 124.39, 122.65, 121.47, 121.33, 120.99, 120.49, 116.13, 107.34, 56.79, 56.62, 41.04, 40.98, 40.95, 39.42, 39.32, 39.24, 38.52, 38.50, 38.44, 38.41, 34.82, 34.74, 43.71,

33.70, 32.52, 32.42, 32.34, 32.27, 31.49, 31.47, 31.34, 31.15, 31.13, 30.72, 29.69, 29.66, 26.44, 26.40, 26.38, 26.36, 26.26, 26.22, 26.02, 24.39, 23.94, 23.91, 23.87, 23.84, 23.80, 20.99, 20.81, 20.76, 15.30. MALDI TOF MS: calc.  $[M^+]$ , found. IR ( $\text{cm}^{-1}$ ):  $\nu = 2952$  (s), 2923 (s), 2853 (s), 1701 (m), 1660 (s), 1581 (s), 1467 (s), 1451 (m), 1314 (m), 1229 (s), 1025 (w), 885 (w), 818 (s), 758 (m), 738 (s). EA calc. for  $\text{C}_{84}\text{H}_{128}\text{N}_4\text{O}_2$ : 82.3 % C, 10.5 % H, 4.6 % N; found 81.6 % C, 10.2 % H, 4.4 % N. UV-vis ( $\text{CHCl}_3$ ):  $\lambda_{\text{max}}$  ( $\log \epsilon$ ) = 344 nm (4.84). PL ( $\text{CHCl}_3$ ): 381 nm, 402 nm,  $\phi = 50 - 60$  % (9,10-diphenylanthracene).

**2-amino-7'-trimethylsilyl-9,9,9',9'-tetra((S)-3,7-dimethyloctyl)bisfluorene (H<sub>2</sub>N-OF2-TMS).** Br-OF1-NH<sub>2</sub> (138 mg, 0.255 mmol, 1.01 eq.), TMS-OF1-BPin (163 g, 0.253 mmol, 1.00 eq.), Na<sub>2</sub>CO<sub>3</sub> (111 mg, 1.05 mmol, 4.2 eq.), Pd(PPh<sub>3</sub>)<sub>4</sub> (13 mg, 0.011 mmol, 0.04 eq.), THF/water (2 ml), 2 d at 90 °C, extraction with EtOAc, column with heptane/CHCl<sub>3</sub> 50 : 50. Greenish, highly viscous oil (179 mg, 0.183 mmol, 72 %). <sup>1</sup>H-NMR (CDCl<sub>3</sub>):  $\delta$  7.80 (d, <sup>3</sup>J = 8.0 Hz, 1 H), 7.75 (d, <sup>3</sup>J = 7.5 Hz, 1 H), 7.54 – 7.66 (m, 8 H), 6.74 (s, 1 H), 6.70 (d, <sup>3</sup>J = 8.0 Hz, 1 H), 1.92 – 2.18 (m, 8 H), 1.42 – 1.55 (m, 4 H), 0.90 – 1.28 (m, 28 H), 0.89 (dd, <sup>3</sup>J = 6.5 Hz, <sup>4</sup>J = 2.0 Hz, 24 H), 0.56 – 0.80 (m, 20 H), 0.42 (s, 9 H). <sup>13</sup>C-NMR (CDCl<sub>3</sub>)  $\delta$  152.97, 151.54, 150.48, 150.10, 145.84, 141.75, 141.11, 140.97, 140.12, 139.02, 138.80, 132.40, 131.87, 127.68, 126.01, 125.98, 121.45, 121.28, 120.62, 119.99, 119.00, 118.57, 114.19, 109.89, 54.92, 54.78, 39.34, 39.31, 39.30, 37.96, 37.47, 36.82, 36.72, 36.68, 33.07, 33.03, 32.95, 32.92, 30.70, 30.65, 28.00, 27.96, 24.80, 24.74, 22.79, 22.78, 22.70, 19.74, 19.70, 19.59, -0.76. MALDI TOF MS: calc.  $[M^+]$  977.82, found 977.84. IR ( $\text{cm}^{-1}$ ):  $\nu = 3480$  (w), 3385 (w), 2952 (s), 2925 (s), 2868 (m), 1619 (m), 1461 (s), 1383 (m), 1248 (m), 1093 (m), 862 (s), 837 (s), 811 (vs), 754 (s), 691 (m).

**2-nitro-7'-trimethylsilyl-9,9,9',9'-tetra((S)-3,7-dimethyloctyl)bisfluorene (O<sub>2</sub>N-OF2-TMS).** Br-OF1-TMS (1.70 g, 2.84 mmol, 1.00 eq.), O<sub>2</sub>N-OF1-BPin (1.90 g, 3.08 mmol, 1.08 eq.), Na<sub>2</sub>CO<sub>3</sub> (1.09 g, 10.29 mmol, 3.6 eq.), Pd(PPh<sub>3</sub>)<sub>4</sub> (164 mg, 0.14 mmol, 0.05 eq.), dioxane/water (20 ml), 3 d at 90 °C, extraction with CHCl<sub>3</sub>, column with heptane/acetone 95 : 5. Yellow-orange, highly viscous oil (2.64 g, 2.62 mmol, 92 %). <sup>1</sup>H-NMR (CDCl<sub>3</sub>):  $\delta$  8.21 (dd, <sup>3</sup>J = 8.5 Hz, <sup>4</sup>J = 2.0 Hz, 1 H), 8.16 (d, <sup>4</sup>J = 2.0 Hz, 1 H), 7.77

(d,  $^3J = 8.0$  Hz, 1 H), 7.74 (d,  $^3J = 8.5$  Hz, 1 H), 7.71 (d,  $^3J = 7.5$  Hz, 1 H), 7.64 (d,  $^3J = 7.5$  Hz, 1 H), 7.61 (dd,  $^3J = 8.0$  Hz,  $^4J = 1.5$  Hz, 1 H), 7.52 – 7.57 (m, 3 H), 7.16 – 7.45 (m, 2 H), 1.90 – 2.11 (m, 8 H), 1.28 – 1.39 (m, 4 H), 0.85 – 1.15 (m, 12 H), 0.75 – 0.85 (m, 4 H), 0.70 (dd,  $^3J = 6.5$  Hz,  $^4J = 2.5$  Hz, 24 H), 0.62 – 0.64 (m, 12 H), 0.38 – 0.62 (m, 8 H), 0.24 (s, 9 H).  $^{13}\text{C}$ -NMR ( $\text{CDCl}_3$ )  $\delta$  152.79, 151.90, 151.46, 149.82, 147.19, 146.91, 142.76, 141.15, 140.83, 139.74, 139.02, 137.67, 131.71, 127.42, 126.57, 126.02, 123.16, 121.40, 121.31, 121.23, 119.93, 119.50, 118.96, 117.98, 55.42, 54.74, 39.02, 38.99, 38.93, 37.14, 36.48, 36.43, 36.36, 36.28, 35.28, 32.58, 31.71, 30.34, 27.75, 27.67, 26.24, 26.12, 24.48, 24.45, 24.39, 22.48, 22.43, 22.38, 22.36, 19.54, 19.47, 19.36, 19.33, 19.24, -1.07. MALDI TOF MS: calc.  $[\text{M}^+]$  1007.79, found 1007.76. IR ( $\text{cm}^{-1}$ ):  $\nu = 2952$  (s), 2925 (s), 2867 (m), 1610 (w), 1591 (w), 1523 (s), 1456 (s), 1336 (vs), 1261 (w), 1078 (w), 837 (w), 813 (vs), 756 (vs), 739 (s). EA calc. for  $\text{C}_{69}\text{H}_{105}\text{NO}_2\text{Si}$ : 82.2 % C, 10.5 % H, 1.4 % N; found 82.1 % C, 10.5 % H, 1.5 % N.

**2-iodo-7'-nitro-9,9',9'-tetra((S)-3,7-dimethyloctyl)bisfluorene (O<sub>2</sub>N-OF2-I).** O<sub>2</sub>N-OF2-TMS (2.63 g, 2.61 mmol),  $\text{CH}_2\text{Cl}_2$  (10 ml), ICl solution (3.0 ml), reaction time 30 min. Column with heptane/acetone 95:5, then second column with cyclohexane/ $\text{CHCl}_3$  95 : 5. Yellow film (1.67 g, 1.57 mmol, 60 %).  $^1\text{H}$ -NMR ( $\text{CDCl}_3$ ):  $\delta$  8.20 (dd,  $^3J = 8.5$  Hz,  $^4J = 2.0$  Hz, 1 H), 8.16 (d,  $^4J = 2.0$  Hz, 1 H), 7.76 (d,  $^3J = 8.0$  Hz, 1 H), 7.73 (d,  $^3J = 8.0$  Hz, 1 H), 7.67 (d,  $^4J = 1.5$  Hz, 1 H), 7.52 – 7.61 (m, 3 H), 7.49 (s, 1 H), 7.39 (d,  $^3J = 8.0$  Hz, 1 H), 1.84 – 2.11 (m, 8 H), 1.25 – 1.41 (m, 4 H), 0.88 – 1.14 (m, 12 H), 0.74 – 0.88 (m, 4 H), 0.66 – 0.74 (m, 24 H), 0.51 – 0.66 (m, 16 H), 0.38 – 0.51 (m, 4 H).  $^{13}\text{C}$ -NMR ( $\text{CDCl}_3$ )  $\delta$  153.40, 153.10, 153.06, 152.19, 150.98, 147.46, 147.36, 147.26, 147.21, 142.77, 140.69, 140.41, 140.05, 138.13, 137.95, 132.22, 126.85, 123.44, 121.70, 121.53, 120.24, 119.81, 118.27, 92.85, 55.71, 55.37, 39.33, 39.22, 37.42 (mult. C), 36.37, 36.57, 32.86 (mult. C), 32.05, 32.00, 30.64 (mult. C), 30.56, 29.15, 28.01, 27.99, 27.97, 27.94, 24.73, 24.69, 22.80, 22.73 – 22.78 (mult. C), 22.71 (mult. C), 22.64, 19.68, 19.63, 19.56, 19.50, 14.22. MALDI TOF MS: calc.  $[\text{M}^+]$  1061.65, found 1061.63. IR ( $\text{cm}^{-1}$ ):  $\nu = 2953$  (s), 2925 (s), 2867 (m), 1611 (w), 1522 (s), 1456 (s), 1336 (vs), 1216 (w), 812 (s), 755 (vs). EA calc. for  $\text{C}_{66}\text{H}_{96}\text{INO}_2$ : 74.6 % C, 9.1 % H, 1.3 % N; found 75.8 % C, 9.3 % H, 1.2 % N.

**2-amino-7''-iodo-9,9,9',9'-tetra((S)-3,7-dimethyloctyl)bisfluorene (H<sub>2</sub>N-OF2-I).** O<sub>2</sub>N-OF2-I (0.60 g, 0.565 mmol) and SnCl<sub>2</sub> (anh.) were dissolved in a degassed mixture of EtOAc and EtOH (50 : 50), which was subsequently refluxed under an atmosphere of Ar. After two days, more EtOAc was added and the mixture was poured into aqueous NaOH (1 M) under stirring. The white solids, which formed were filtered off and washed thoroughly with EtOAc. The combined filtrates were washed with aqueous NaOH (1 M), aq. HCl (1 M), NaCl solution (sat.), and water. After drying over Na<sub>2</sub>SO<sub>4</sub>, the solvents were removed by evaporation, and the remaining oil was purified by column chromatography (SiO<sub>2</sub>, CHCl<sub>3</sub>/heptane 1 : 2), giving an orange oil (0.45 g, 0.436 mmol, 77 %). NMR, MALDI-TOF MS and GPC analysis showed that this product was not pure. <sup>1</sup>H-NMR (CDCl<sub>3</sub>): δ 7.37 – 7.76 (m, 10 H), 6.58 – 6.67 (m, 2 H), 1.88 – 2.08 (m, 8 H), 1.37 – 1.48 (m, 4 H), 0.97 – 1.21 (m, 24 H), 0.85 – 0.96 (m, 4 H), 0.75 – 0.83 (m, 24 H), 0.49 – 0.75 (m, 20 H). <sup>13</sup>C-NMR (CDCl<sub>3</sub>) δ 153.42, 152.96, 150.78, 150.51, 146.17, 141.67, 140.73, 139.07, 138.70, 135.98, 132.26, 132.15, 126.21, 126.01, 125.60, 121.45, 121.34, 121.28, 120.66, 120.04, 118.58, 114.11, 109.77, 92.36, 55.28, 54.77, 39.34, 37.92, 37.62, 37.49, 36.83, 36.75, 36.71, 36.60, 33.05, 32.99, 32.92, 30.68, 30.60, 30.45, 28.00, 24.80, 24.75, 22.82, 22.73, 19.71, 19.60. MALDI TOF MS: calc. [M<sup>+</sup>] 1031.67, found 1031.62. IR (cm<sup>-1</sup>): ν = 3472 (w), 3387 (w), 2952 (s), 2924 (s), 2867 (s), 1618 (m), 1455 (s), 1382 (w), 1365 (m), 1261 (m), 1093 (w), 1025 (w), 809 (vs), 737 (m).

**2,7''-diamino-9,9,9',9'',9''-hexa((S)-3,7-dimethyloctyl)terfluorene (H<sub>2</sub>N-OF3-NH<sub>2</sub>).** H<sub>2</sub>N-OF1-Br (4.47 g, 8.27 mmol, 2.14 eq.), BPin-OF1-BPin (2.69 g, 3.85 mmol, 1.00 eq.), Na<sub>2</sub>CO<sub>3</sub> (3.73 g, 35.2 mmol, 9.1 eq.), Pd(PPh<sub>3</sub>)<sub>4</sub> (0.245 g, 0.21 mmol, 0.05 eq.), dioxane/water (75 ml), 2 d at 90 °C, extraction with EtOAc, column with heptane/THF 75 : 25. Dark orange glassy solid (2.89 g, 2.12 mmol, 55 %). <sup>1</sup>H-NMR (CDCl<sub>3</sub>): δ 7.78 (d, <sup>3</sup>J = 8.0 Hz, 2 H), 7.56 – 7.64 (m, 10 H), 7.50 (d, <sup>3</sup>J = 8.0 Hz, 2 H), 6.68 (s, 2 H), 6.64 (d, <sup>3</sup>J = 8.0 Hz, 2 H), 3.72 (br, 4H), 1.88 – 2.15 (m, 12 H), 1.37 – 1.49 (m, 6 H), 0.95 – 1.23 (m, 36 H), 8.86 – 0.95 (m, 6 H), 0.77 – 0.83 (m, 36 H), 0.72 – 0.75 (m, 18 H), 0.54 – 0.70 (m, 12 H). <sup>13</sup>C-NMR (CDCl<sub>3</sub>): δ 152.98, 151.65, 150.49, 146.11, 141.00, 140.84, 139.93, 138.97, 132.25, 126.06, 125.99, 121.46, 121.30, 120.62, 119.86, 118.55, 114.08, 109.79, 55.07, 54.77, 39.01, 37.61, 37.34, 36.50, 36.44, 36.39, 32.75, 32.72, 32.68,

30.49, 30.37, 27.67, 27.64, 24.48, 24.43, 22.47, 22.37, 19.38, 19.32, 19.27. MALDI TOF MS: calc.  $[M^+]$  1365.16, found 1365.17. IR ( $\text{cm}^{-1}$ ):  $\nu = 3642$  (w), 3475 (w), 3383 (w), 3005 (w), 2952 (s), 2924 (s), 2867 (s), 1618 (s), 1585 (w), 1460 (s), 1349 (w). 1272 (w), 1135 (w), 885 (w), 859 (w), 810 (s), 736 (m). EA calc. for  $\text{C}_{84}\text{H}_{128}\text{N}_4\text{O}_2$ : 82.3 % C, 10.5 % H, 4.6 % N; found 81.6 % C, 10.2 % H, 4.4 % N.

**2,7''-bis(4-(2-ureido-6-(1-tridecyl)-4[1H]-pyrimidinone)-9,9,9',9'',9''-hexa((S)-3,7-dimethyloctyl)terfluorene (UPy-OF3-UPy).**  $\text{H}_2\text{N-OF3-NH}_2$  (1.34 g, 0.98 mmol, 1.00 eq.), CDI activ. isocytosine (0.83 g, 2.13 mmol, 2.17 eq.),  $\text{CHCl}_3$  (30 ml). Orange film, yield 1.52 g (0.76 g, 78 %).  $^1\text{H-NMR}$  ( $\text{TFA-d}_1 + \text{THF-d}_8$ ):  $\delta$  7.30 – 7.50 (m, 16 H), 7.11 (d,  $3J = 8.5$  Hz, 2 H), 6.07 (s, 2 H), 2.45 (t,  $^3J = 7.5$  Hz, 4 H), 1.70 – 1.95 (m, 12 H), 1.38 – 1.48 (m, 4 H), 0.23 – 1.16 (m, 160 H).  $^{13}\text{C-NMR}$  ( $\text{THF-d}_8 + \text{TFA-d}_1$ )  $\delta$  167.00, 160.06, 159.85, 159.28, 159.15, 158.94, 148.25, 148.10, 147.91, 147.38, 147.29, 142.48, 133.62, 128.84, 128.69, 127.29, 112.94, 111.74, 62.84, 62.62, 46.66, 46.63, 46.55, 45.04, 44.85, 44.62, 44.08, 44.03, 40.34, 40.23, 40.15, 40.03, 39.27, 38.13, 38.07, 37.94, 37.00, 36.98, 36.96, 36.89, 36.69, 36.41, 36.07, 35.30, 35.25, 43.41, 32.07, 32.04, 31.90, 31.80, 29.89, 29.32, 29.31, 29.27, 29.23, 29.21, 29.17, 26.51, 26.39, 26.18, 20.55. MALDI TOF MS: calc.  $[M^+]$  2003.62, found 2003.45. IR ( $\text{cm}^{-1}$ ):  $\nu = 2952$  (m), 2923 (s), 2853 (m), 1699 (m), 1658 (s), 1583 (s), 1459 (s), 1312 (m), 1229 (s), 1023 (w), 846 (w), 813 (s), 760 (m), 746 (m). EA calc. for  $\text{C}_{135}\text{H}_{206}\text{N}_8\text{O}_4$ : 80.9 % C, 10.4 % H, 5.6 % N; found 80.5 % C, 10.1 % H, 5.4 % N. UV-vis ( $\text{CHCl}_3$ ):  $\lambda_{\text{max}}$  ( $\log \epsilon$ ) = 291 nm (4.25), 364 nm (4.91). PL ( $\text{CHCl}_3$ ): 407 nm, 429 nm,  $\phi = 50 - 55$  % (9,10-diphenylanthracene).

**2-amino--9,9,9',9'',9''-hexa((S)-3,7-dimethyloctyl)terfluorene (H-OF3-NH<sub>2</sub>).**

Method 1: H-OF2-I (236 mg, 0.23 mmol, 1.00 eq.),  $\text{H}_2\text{N-OF1-BPin}$  (143 mg, 0.24 mmol, 1.04 eq.),  $\text{Na}_2\text{CO}_3$  (82 mg, 0.77 mmol, 3.35 eq.),  $\text{Pd}(\text{PPh}_3)_4$  (13 mg, 0.011 mmol, 5 %), solvent: THF/water (4.5 ml, 2:1), reaction time 2 d. Column: heptane/ $\text{CHCl}_3$  gradient from 50:50 to 40:60. Highly viscous, dark orange oil. Yield 154 mg (0.11 mmol, 50 %).

Method 2:  $\text{H}_2\text{N-OF2-I}$  (910 mg, 0.88 mmol, 1.01 eq.), H-OF1-BPin (500 mg, 0.97 mmol, 1.00 eq.),  $\text{Na}_2\text{CO}_3$  (330 mg, 3.11 mmol, 3.6 eq.),  $\text{Pd}(\text{PPh}_3)_4$  (50 mg, 0.043 mmol, 5 %), solvent: dioxane/water (15 ml, 2:1), reaction time 2 d. Column: heptane/ $\text{CHCl}_3$  gradient

from 50:50 to 40:60. Highly viscous, dark orange oil. Yield 890 mg (0.66 mmol, 76 %).  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ ):  $\delta$  7.76 - 7.90 (m, 4 H), 7.56 - 7.76 (m, 10 H), 7.33 - 7.46 (m, 3 H), 6.74 - 6.83 (m, 2 H), 4.20 (br, 2 H), 1.94 - 2.25 (m, 12 H), 1.42 - 1.56 (m, 6 H), 1.04 - 1.40 (m, 36 H), 0.58 - 1.04 (m, 66 H).  $^{13}\text{C-NMR}$  ( $\text{CDCl}_3$ )  $\delta$  152.96, 151.70, 151.66, 151.40, 150.96, 150.49, 146.20, 141.14, 141.09, 141.05, 141.00, 140.72, 140.59, 140.47, 140.27, 139.85, 138.93, 132.20, 127.10, 126.90, 126.24, 126.15, 126.02, 122.91, 121.57, 121.49, 121.30, 120.64, 119.94, 119.80, 118.57, 114.06, 109.73, 55.12, 55.03, 54.78, 39.35, 37.95, 37.69, 36.84, 36.76, 36.72, 33.08, 33.05, 33.00, 30.80, 30.69, 30.61, 28.00, 24.81, 24.76, 24.73, 22.80, 22.71, 19.73, 19.67, 19.62. MALDI TOF MS: calc.  $[\text{M}^+]$  1350.15, found 1350.17. IR ( $\text{cm}^{-1}$ ): 3480 (w), 3386 (w), 3006 (w), 2952 (s), 2925 (s), 2867 (s), 1617 (m), 1463 (s), 1383 (m), 1366 (m), 1261 (m), 1084 (br), 1025 (br), 885 (w), 812 (s), 739 (s). EA calc. for  $\text{C}_{99}\text{H}_{147}\text{N}$ : 88.0 % C, 11.0 % H, 1.0 % N; found 87.7 % C, 11.2 % H, 1.1 % N.

**2-(4-(2-ureido-6-(1-tridecyl)-4[1H]-pyrimidinone)-9,9,9',9'',9'''-hexa((S)-3,7-dimethyloctyl)terfluorene (H-OF3-UPy).** H-OF3-NH<sub>2</sub> (352 mg, 0.26 mmol, 1.00 eq.), CDI activated isocytosine (121 mg, 0.31 mmol, 1.2 eq.),  $\text{CHCl}_3$  (6 ml). Column:  $\text{CHCl}_3/\text{THF}$  gradient from 100:0 to 90:10. Yield: 247 mg (0.15 mmol, 58 %).  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ ):  $\delta$  13.14 (s, 1 H), 12.37 (s, 1 H), 12.29 (s, 1 H), 7.61 - 7.82 (m, 15 H), 7.31 - 7.37 (m, 4 H), 5.96 (s, 1 H), 2.53 (t,  $^3\text{J} = 7.5$  Hz, 2 H), 2.00 - 2.20 (m, 12 H), 1.66 - 1.77 (m, 2 H), 0.53 - 1.52 (m, 137 H).  $^{13}\text{C-NMR}$  ( $\text{THF-d}_8$ ):  $\delta$  172.39, 157.76, 154.72, 154.26, 152.87, 151.29, 150.98, 150.52, 140.96, 140.47, 140.40, 140.35, 140.19, 140.05, 139.64, 138.53, 136.22, 126.76, 126.61, 125.82, 122.52, 120.96, 120.88, 119.70, 119.62, 119.48, 119.15, 118.65, 114.29, 105.49, 54.93, 54.91, 54.76, 39.17, 39.12, 39.09, 37.54, 37.37, 36.66, 36.62, 36.57, 36.54, 32.64, 32.85, 31.83, 30.59, 30.47, 30.40, 29.61, 29.57, 29.46, 29.28, 28.85, 27.83, 27.78, 24.61, 24.57, 24.54, 24.51, 24.49, 24.41, 24.28, 24.26, 24.12, 24.10, 24.01, 23.94, 22.51, 22.08, 22.06, 22.01, 21.99, 21.96, 21.92, 19.13, 18.95, 18.91, 13.44. MALDI TOF MS: calc.  $[\text{M}^+]$  1669.38, found 1669.10, 1692.09 ( $\text{M-Na}^+$ ). IR ( $\text{cm}^{-1}$ ):  $\nu =$  2952 (s), 2924 (s), 2854 (s), 1699 (m), 1658 (s), 1583 (s), 1462 (s), 1365 (w), 1314 (w), 1230 (s), 1169 (w), 1024 (w), 1002 (w), 885 (m), 815 (s), 738 (s). EA calc. for  $\text{C}_{117}\text{H}_{176}\text{N}_4\text{O}_2$ : 84.1 % C, 10.6 % H, 3.4 % N; found 84.6 % C, 10.3 % H, 3.3 % N. UV-

vis (CHCl<sub>3</sub>):  $\lambda_{\max}$  (log $\epsilon$ ) = 359 nm (5.01). PL (CHCl<sub>3</sub>): 402 nm, 425 nm,  $\phi$  ca. 95 % (9,10-diphenylanthracene).

**2,7''''-diamino-9,9,9',9',9'',9'',9''',9''',9''''-deca((S)-3,7-dimethyloctyl)-pentafluorene (H<sub>2</sub>N-OF5-NH<sub>2</sub>).** Method 1: H<sub>2</sub>N-OF2-I (1.82 g, 1.76 mmol, 3.14 eq.), BPin-OF1-BPin (0.39 g, 0.56 mmol, 1.00 eq.), Na<sub>2</sub>CO<sub>3</sub> (0.46 g, 4.34 mmol, 7.75 eq.), Pd(PPh<sub>3</sub>)<sub>4</sub> (65 mg, 0.056 mmol, 10 %), dioxane/water (15 ml), reaction time 3 d. Column CHCl<sub>3</sub>/heptane 1:2. Dark orange glassy solid (326 mg, 0.14 mmol, 25 %).

Method 2: I-OF3-I (2.61 g, 1.64 mmol, 1.00 eq.), H<sub>2</sub>N-OF1-BPin (2.14g, 3.64 mmol, 2.22 eq.), Na<sub>2</sub>CO<sub>3</sub> (1.22 g, 11.51 mmol, 7.02 eq.), Pd(PPh<sub>3</sub>)<sub>4</sub> (190 mg, 10 %), dioxane/water (30 ml), reaction time 3d. Column chromatography heptane/EtOAc, gradient from 90:10 to 80:20. Brown glassy solid (1.11 g, 0.49 mmol, 30 %).

<sup>1</sup>H-NMR (CDCl<sub>3</sub>):  $\delta$  7.77 – 7.83 (m, 6 H), 7.50 – 7.69 (m, 20 H), 6.63 – 6.72 (m, 4 H), 3.78 (br, 4 H), 1.83 – 2.21 (m, 20 H), 1.34 – 1.51 (m, 10 H), 0.86 – 1.28 (m, 70 H), 0.51 – 0.86 (m, 110 H). <sup>13</sup>C-NMR (CDCl<sub>3</sub>)  $\delta$  152.95, 151.69, 151.68, 151.63, 150.47, 146.02, 140.95, 140.90, 140.63, 140.47, 140.21, 140.09, 138.88, 132.24, 126.17, 126.14, 126.03, 125.93, 121.53, 121.43, 121.25, 120.56, 119.24, 119.92, 119.86, 118.51, 109.79, 55.10, 55.06, 54.72, 39.30, 39.26, 37.88, 37.62, 36.78, 36.72, 36.66, 33.02, 33.00, 32.96, 30.78, 30.65, 29.95, 27.94, 27.92, 24.73, 24.71, 22.74, 22.72, 22.61, 19.62, 19.58, 19.52. MALDI TOF MS: calc. [M<sup>+</sup>] 2253.92, found 2253.97. IR (cm<sup>-1</sup>):  $\nu$  = 3477 (w), 3387 (w), 2952 (s), 2924 (s), 2867 (m), 1619 (m), 1459 (s), 1382 (w), 1365 (w), 1261 (w), 907 (w), 885 (w), 811 (s), 734 (s). EA calc. for C<sub>165</sub>H<sub>244</sub>N<sub>2</sub>: 87.8 % C, 10.9 % H 1.2 % N; found 87.6 % C, 10.8 % H, 1.2 % N.

**2,7''''-bis(4-(2-ureido-6-(1-tridecyl)-4[1H]-pyrimidinone)-9,9,9',9',9'',9'',9''',9''',9''''-deca((S)-3,7-dimethyloctyl)-pentafluorene (UPy-OF5-UPy).** H<sub>2</sub>N-OF5-NH<sub>2</sub> (326 mg, 0.145 mmol, 1.00 eq.), CDI activated isocytosine (142 mg, 0.37 mmol, 2.55 eq.), CHCl<sub>3</sub> (5 ml). Column chromatography CHCl<sub>3</sub>/THF gradient from 100:0 to 90:10. Orange solid (210 mg, 0.081 mmol, 56 %). <sup>1</sup>H-NMR (THF-d<sub>8</sub> + TFA-d<sub>1</sub>):  $\delta$  7.69 – 7.77 (m, 8 H), 7.65 – 7.69 (m, 20 H), 7.44 (d, 3J = 8.0 Hz, 4 H), 6.11 (s, 2 H), 2.61 (t, <sup>3</sup>J = 6.5 Hz, 4 H), 1.95 – 2.20 (m, 20 H), 0.90 – 1.38 (m, 110

H), 0.44 – 0.90 (m, 130 H).  $^{13}\text{C}$ -NMR (THF- $d_8$  + TFA- $d_1$ ):  $\delta$  153.14, 152.32, 151.62, 151.32, 150.99, 140.36, 140.14, 140.09, 140.04, 140.01, 137.32, 136.57, 125.85, 120.96, 120.83, 119.65, 119.30, 118.74, 114.39, 54.94, 54.88, 39.02, 38.97, 37.25, 36.51, 36.47, 32.77, 32.74, 32.71, 32.39, 31.67, 30.50, 30.41, 29.43, 29.40, 29.36, 29.20, 29.11, 28.95, 28.57, 27.67, 27.65, 26.94, 24.49, 24.45, 24.38, 24.33, 24.27, 24.17, 24.10, 24.01, 23.85, 23.69, 22.33, 21.83, 21.82, 21.78, 21.74, 21.71, 21.69, 18.82, 18.80, 18.70, 13.13. MALDI TOF MS: calc.  $[\text{M}^+]$  2894.63, found 2895.40. IR ( $\text{cm}^{-1}$ ):  $\nu$  = 2955 (m), 2918 (s), 2850 (s), 1717 (m), 1676 (s), 1660 (s), 1586 (s), 1567 (s), 1459 (m), 1412 (m), 1403 (m), 1308 (w), 1271 (s), 1226 (s), 1100 (m), 1022 (m), 970 (w), 885 (w), 813 (s), 772 (s), 722 (m). UV-vis ( $\text{CHCl}_3$ ):  $\lambda_{\text{max}}$  ( $\log \epsilon$ ) = 372 nm (5.01). PL ( $\text{CHCl}_3$ ): 413 nm, 437 nm,  $\phi$  = 40 - 50 % (9,10-diphenylanthracene).

**Hexa((S)-3,7-dimethyloctyl)terfluorene (H-OF3-H).** This compound was prepared according to the general procedure for Suzuki couplings described further above. BPin-OF1-BPin (1.06 g, 1.52 mmol, 1.00 eq.), H-OF1-Br (1.60 g, 3.04 mmol, 2.00 eq.),  $\text{Na}_2\text{CO}_3$  (0.97 g, 9.1 mmol, 6.0 eq.),  $\text{Pd}(\text{PPh}_3)_4$  (85 mg, 0.074 mmol, 0.05 eq.), dioxane/water (15 ml), 3 d at 90 °C, extraction with EtOA, column with heptane/acetone 95 : 5, then biobeads (THF) and finally recycling GPC ( $\text{CHCl}_3$ ) Clear light yellowish viscous oil (1.87 g, 1.40 mmol, 92 %).  $^1\text{H}$ -NMR ( $\text{CDCl}_3$ ):  $\delta$  7.90 (d,  $^3\text{J} = 8.5$  Hz, 2 H), 7.87 (d,  $^3\text{J} = 8.0$  Hz, 2 H), 7.83 (dd,  $^3\text{J} = 7.5$  Hz,  $^4\text{J} = 1.0$  Hz, 2 H), 7.73 – 7.77 (m, 8 Hz), 7.39 – 7.47 (m, 6 H), 2.08 – 2.29 (m, 12 H), 1.48 – 1.58 (m, 6 H), 1.09 – 1.36 (m, 36 H), 0.95 – 1.08 (m, 6 H), 0.87 – 0.92 (m, 36 H), 0.80 – 0.86 (m, 18 H), 0.63 – 0.80 (m, 6 H).  $^{13}\text{C}$ -NMR:  $\delta$  151.72, 151.41, 150.97, 140.99, 140.71, 140.68, 140.50, 140.15, 127.10, 126.89, 126.26, 126.14, 122.93, 121.59, 121.51, 119.99, 119.93, 119.79, 55.16, 55.03, 39.34, 39.32, 37.67, 36.76, 36.72, 33.00, 30.81, 30.69, 30.63, 28.00, 27.98, 24.80, 24.76, 24.73, 22.79, 22.70, 19.66. MALDI TOF MS: calc.  $[\text{M}^+]$  1385.14, found 1385.10. IR ( $\text{cm}^{-1}$ ):  $\nu$  = 2952 (s), 2924 (s), 2867 (s), 1466 (m), 1450 (m), 1382 (w), 1366 (w), 817 (s), 786 (s). EA calc. for  $\text{C}_{99}\text{H}_{146}$ : 89.0 % C, 11.0 % H; found 88.7 % C, 11.1 % H. UV-vis ( $\text{CHCl}_3$ ):  $\lambda_{\text{max}}$  ( $\log \epsilon$ ) = 351 nm (4.94). PL ( $\text{CHCl}_3$ ): 395 nm, 417 nm,  $\phi_{\text{PL}}$  ca. 80 % (anthracene).

**(E,E)-1,4'''-tri-*p*-(3,7-di(S)-dimethyloctyloxy-phenylene vinylene)-dialdehyde (OPV3-dialdehyde).** The synthesis of OPV3-dialdehyde was accomplished according to a modified literature procedure, where decyl chains were replaced by (S)-3,7-dimethyloctyl chains.<sup>S12</sup>

**(E,E,E,E)-1,4''''-Dicyanopenta-*p*-(3,7-di(S)-dimethyloctyloxy-phenylene vinylene) (NC-OPV5-CN).** In a 2-neck 50 ml round bottom flask, KO<sup>t</sup>Bu (224mgs, 2mmol) was added to a solution of 4-cyanobenzyl-diethylphosphonate in DMF (405mgs, 1.6 mmol in 15ml dry DMF). After 30 minutes, a THF solution of OPV3 dialdehyde (500mgs, 0.39 mmol in 10 ml dry THF) was added drop wise and the mixture was stirred overnight at room temperature. Chloroform (200ml) was added and the mixture was washed with diluted acid solution (0.1M, 2×100ml) then water (2×100ml) and brine (1×100ml). After drying with sodium sulphate, the solvent was evaporated under vacuum. Purification was achieved by column chromatography (SiO<sub>2</sub>, CHCl<sub>3</sub>) to yield a red-orange solid (490 mg, 85% yield). <sup>1</sup>H NMR (400MHz, CDCl<sub>3</sub>) 0.81-0.89 (m, 36H), 0.97-1.04 (m, 18H), 1.1-1.84 (m, 54H), 1.86-1.99 (m, 6H), 4.04-4.17 (m, 12H), 7.09-7.19 (m, 8H), 7.49-7.65 (m, 14H); <sup>13</sup>C NMR (100MHz, CDCl<sub>3</sub>) 19.98, 20.14, 20.16, 22.81, 22.9, 24.97, 25.06, 28.18, 28.21, 30.38, 30.45, 30.48, 36.70, 36.73, 36.78, 37.58, 37.62, 37.64, 39.46, 39.51, 67.74, 68.03, 68.22, 110.23, 110.32, 110.51, 111.09, 119.42, 123.25, 124.26, 125.49, 126.74, 126.97, 127.64, 127.62, 129.09, 132.67, 142.87, 151.11, 151.33, 151.76; MALDI-TOF Calculated 1474.13 Found 1474.00.

**(E,E,E,E)-1,4''''-Diaminomethylpenta-*p*-(3,7-di(S)-dimethyloctyloxy-phenylene vinylene) (NH<sub>2</sub>-OPV5-NH<sub>2</sub>).** In a 50ml round bottom flask, LiAlH<sub>4</sub> was dispersed in 20ml of dry ether. An ether solution of CN-OPV<sub>5</sub>-CN (300 mgs, 0.2 mmol in 5ml) is added to the suspension and the mixture is stirred overnight at room temperature. After careful quenching with water, 200ml of CHCl<sub>3</sub> were added and the organic phase was washed with water (3\*100ml) and brine (1\*100ml). After drying with sodium sulphate, the solvent was evaporated under vacuum. The product was purified using column chromatography (SiO<sub>2</sub>, 9/1 CHCl<sub>3</sub>/MeOH with 2% Et<sub>3</sub>N) leading to an orange solid (270mgs, 90%). <sup>1</sup>H NMR (400MHz, CDCl<sub>3</sub>) 0.8-0.88 (m, 36H), 0.98-1.03 (m, 18H), 1.1-

1.84 (m, 54H), 1.84-1.99 (m, 6H), 3.87-3.89 (m, 4H), 4.04-4.15 (m, 12H), 7.1-7.19 (m, 8H), 7.28-7.33 (d, 4H), 7.44-7.53 (m, 10H). <sup>13</sup>C NMR (100MHz, CDCl<sub>3</sub>) 19.99, 20.14, 20.18, 22.42, 22.83, 22.93, 24.98, 25.06, 28.20, 28.23, 30.34, 30.48, 36.80, 37.60, 37.64, 37.70, 39.52, 46.58, 67.87, 68.07, 68.23, 77.44, 110.42, 110.49, 110.80, 123.35, 123.51, 126.83, 126.91, 127.62, 127.86, 128.53, 136.94, 142.83, 151.21, 151.29, 151.36; MALDI-TOF calculated 1481.20 found 1481.25.

**(E,E,E,E)-1,4''''-Bis(2-ureido-6-(1-tridecyl)-4[1H]-pyrimidinone)penta-*p*-(3,7-di(S)-dimethyloctyloxy-phenylene vinylene) (UPy-OPV5-UPy).** In a 10 ml 2-neck round bottom flask under argon atmosphere, NH<sub>2</sub>-OPV<sub>5</sub>-NH<sub>2</sub> (100 mg, 0.0675 mmol) and N-(4-oxo-6-tridecyl-1,4-dihydropyrimidin-2-yl)-1H-imidazole-1-carboxamide (58mgs, 0.149 mmol) were dissolved in dry chloroform. The flask was equipped with a condenser and the mixture was refluxed overnight. After cooling to room temperature, the mixture was concentrated and then precipitated in MeOH. The bis-UPy functionalized oligomer was then purified by recycling GPC and obtained as an orange-yellow powder (35mgs, 25%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) 0.8-1.05 (60H, m), 1.05-1.8 (110H, m), 2.3-2.55 (4H, m), 3.8-4.2 (12H, m), 4.3-4.5 (4H, s), 5.75-5.9 (s, 2H), 7.0-7.6 (22H, m), 10.85 (2H, br), 12.05 (2H, br), 13.05 (2H, br); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) 14.34, 20.01, 20.14, 22.82, 22.91, 24.97, 27.22, 28.17, 29.10, 29.38, 29.58, 29.66, 29.85, 30.32, 30.45, 32.14, 32.93, 36.78, 37.62, 38.99, 39.50, 67.84, 68.22, 95.00, 106.19, 110.38, 110.78, 123.53, 126.90, 127.94, 128.57, 130.38, 151.28, 152.77, 154.88, 157.10, 173.44; MALDI-TOF: calc. 2119.65 found 2119.75. UV-vis (CHCl<sub>3</sub>): λ<sub>max</sub> (logε) = 314 nm (4.48), 445 nm (4.90). PL<sub>max</sub>: 520 nm, 554 nm, φ = 45 % (N,N'-bis(pentylhexyl) perylene bisimide).

**N,N'-bis(4'-amino-2,5-di-*t*-butylphenyl-1,7-bis(3',5'-di-*t*-butylphenoxy)perylene-3,4:9,10-bis-(dicarboximide) (H<sub>2</sub>N-Pery-NH<sub>2</sub>).** A one-necked flask was filled with bis(di-*t*-butylphenoxy)perylene bisanhydride (796 mg, 0.995 mmol, 1.00 eq.), 1,4-diamino-2,5-di-*t*-butylbenzene (869 mg, 3.98 mmol, 4.00 eq.) and zinc acetate (183 mg, 0.995 mmol, 1.00 eq.). 50 ml DMA were added and the mixture was heated to 190 °C and stirred under an atmosphere of Ar for 3 h, after which time the reaction was complete (TLC). The solvent was removed by vacuum evaporation and the crude product was

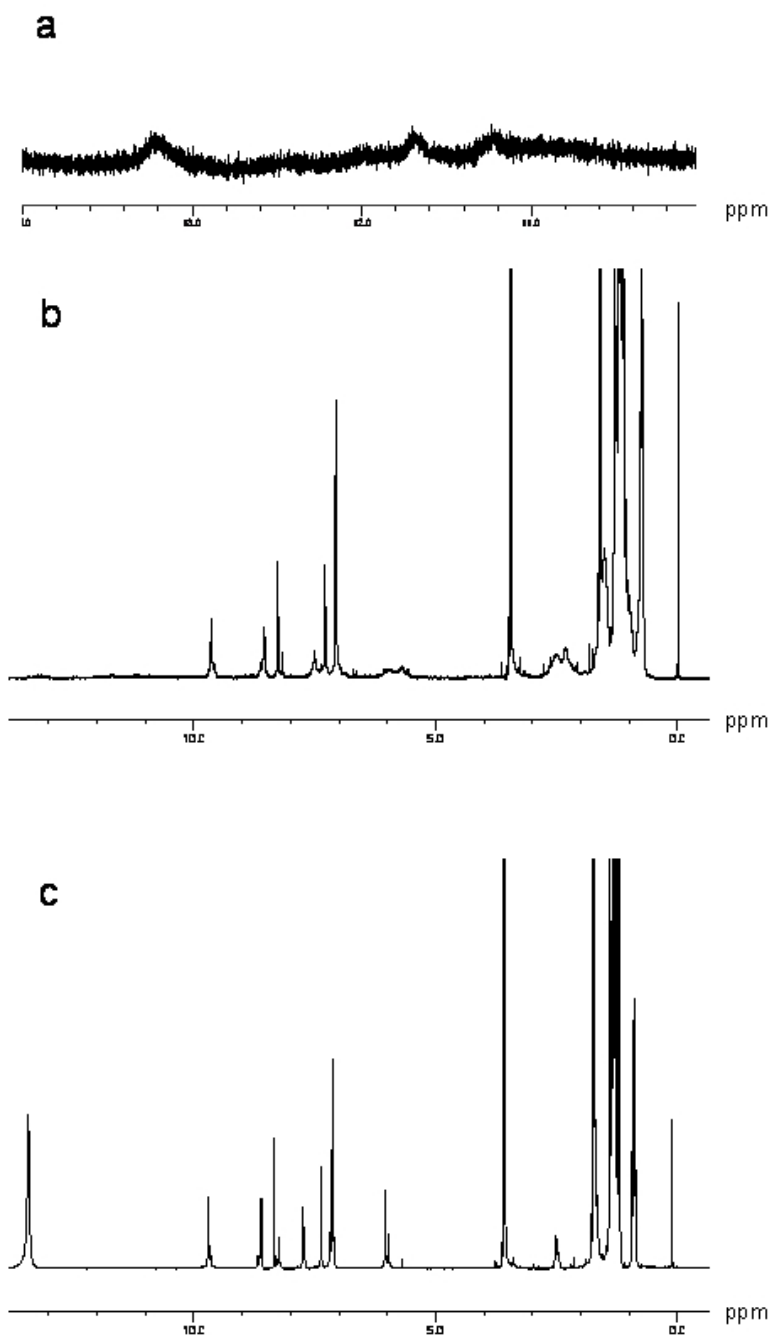
purified by column chromatography (SiO<sub>2</sub>, solvent gradient from 50:50 n-pentane: CH<sub>2</sub>Cl<sub>2</sub> to pure CH<sub>2</sub>Cl<sub>2</sub>). Ca. 15 % 1,6-isomer were present in the final product. Yield 727 mg (0.60 mmol, 60 %). <sup>1</sup>H-NMR (CDCl<sub>3</sub>): δ 9.74 (dd, 8.5 Hz, 2.0 Hz, 2 H), 8.72 (d, 8.5 Hz, 2 H), 8.44 (d, 2.0 Hz, 2 H), 7.35 – 7.32 (m, 2 H), 7.07 – 7.04 (m, 4 H), 6.84 (s, 2 H), 6.81 (s, 2 H), 3.93 (br s, 4 H), 1.48 – 1.16 (m, 72 H). <sup>13</sup>C-NMR (CDCl<sub>3</sub>): δ 164.68, 164.30, 155.80, 154.57, 153.58, 144.75, 133.78, 132.65, 130.33, 129.63, 129.09, 128.86, 125.16, 124.03, 123.67, 123.55, 123.40, 122.58, 119.25, 117.77, 114.09, 35.05, 35.00, 33.75, 31.43, 31.28, 29.42. MALDI TOF MS: calc. [M<sup>+</sup>] 1204.70, found 1204.56. IR (cm<sup>-1</sup>): ν = 3493 (w), 3382 (w), 2958 (s), 2872 (m), 1709 (s), 1670 (s), 1602 (s), 1589 (s), 1510 (m), 1480 (w), 1420 (m), 1404 (s), 1387 (m), 1345 (s), 1289 (m), 1257 (s), 1188 (m), 1223 (w), 1079 (w), 1010 (w), 965 (w), 946 (m), 859 (w), 812 (m), 707 (m). EA calc. for C<sub>80</sub>H<sub>92</sub>N<sub>4</sub>O<sub>6</sub>: 79.7 % C, 7.7 % H, 4.7 % N; found 77.5 % C, 7.9 % H, 4.3 % N.

**N,N'-bis(4-(2-ureido-6-(1-ethylpentyl)-4[1H]-pyrimidinone)-2,5-di-*t*-butylphenyl)-1,7-bis(3',5'-di-*t*-butylphenoxy)perylene-3,4:9,10-tetracarboxylic-bisimide (UPy-Pery-UPy).** H<sub>2</sub>N-Pery-NH<sub>2</sub> (100 mg, 0.083 mmol, 1.00 eq.) and CDI activated isocytosine (58 mg, 0.192 mmol, 2.20 eq.) were dissolved in dichloromethane (10 ml) and heated to reflux for 3 d in an atmosphere of argon. A red precipitate was formed that was soluble in chloroform. The reaction mixture was concentrated to dryness, redissolved in chloroform, and the resulting solution was washed with aq. HCl (1 M), aq. NaHCO<sub>3</sub> (3 M), and water. The aqueous layers were extracted with chloroform and the combined organic layers were concentrated and precipitated into heptane. After column chromatography (MeOH/CHCl<sub>3</sub> from 1:99 to 2.5:97.5), the product was obtained as a dark red solid containing ca. 10 % of the 1,6-isomer. Yield 136 mg (0.081 mmol, 97 %). <sup>1</sup>H-NMR (THF-d<sub>8</sub> + TFA-d<sub>1</sub>; main isomer): δ 9.65 (d, 8.5 Hz, 2 H), 8.55 (d, 8.5 Hz, 2 H), 8.28 (s, 2 H), 7.67 (d, 6.5 Hz, 2 H), 7.32 – 7.29 (m, 2 H), 7.13 – 7.04 (m, 6 H), 5.97 (s, 2 H), 2.45 – 2.32 (m, 2 H), 1.69 – 1.53 (m, 12 H), 1.32 – 1.06 (m, 72 H), 0.87 – 0.72 (m, 12 H). MALDI TOF MS: calc. [M<sup>+</sup>] 1674.97, found 1674.97. IR (cm<sup>-1</sup>): ν = 3161 (w), 2959 (s), 2931 (s), 2872 (m), 1708 (s), 1672 (s), 1657 (s), 1586 (vs), 1406 (s), 1338 (w), 1240 (vs), 1189 (m), 119 (w), 1081 (w), 1011 (w), 948 (m), 858 (m), 811 (m), 754 (m), 708 (w). EA calc. for C<sub>104</sub>H<sub>126</sub>N<sub>10</sub>O<sub>10</sub>: 74.5 % C, 7.6 % H, 8.4 % N; found 71.6 % C, 7.5 % H,

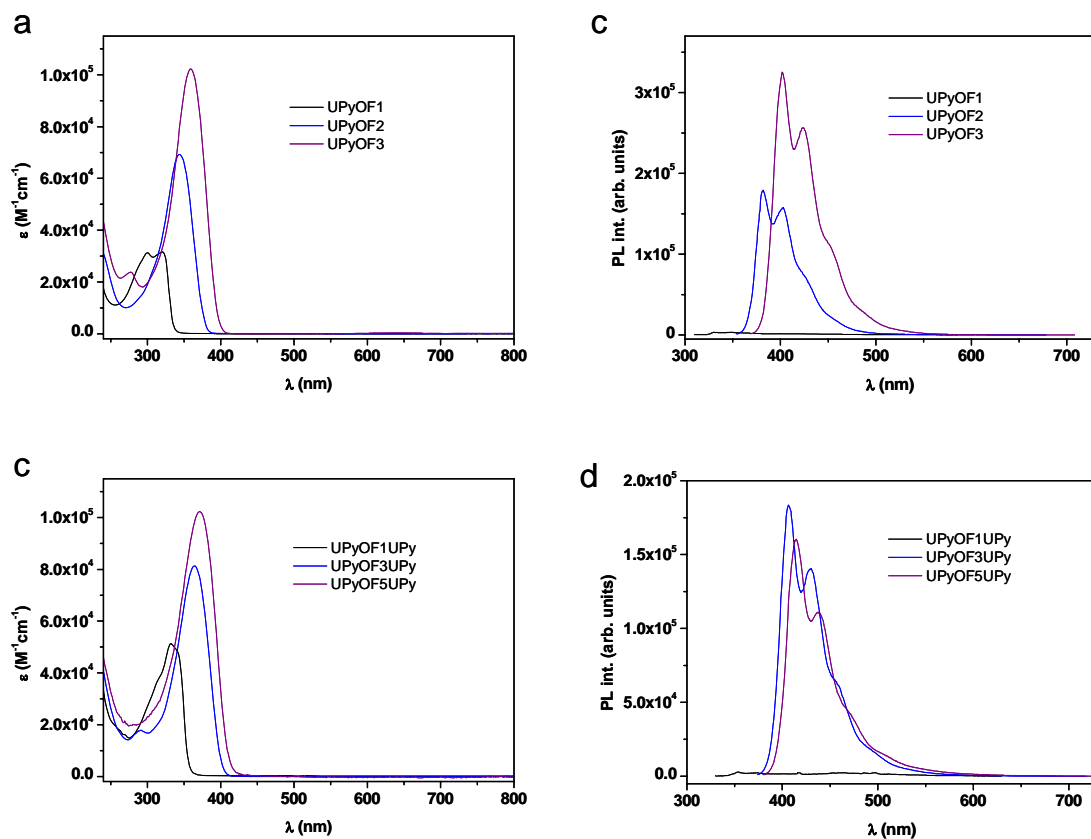
8.9 % N. UV-vis ( $\text{CHCl}_3$ ):  $\lambda_{\text{max}}$  ( $\log\epsilon$ ) = 406 nm (4.00), 513 nm (4.57), 550 nm (4.70).

PL<sub>max</sub>: 584 nm, 620 nm,  $\phi$  = 55 % (Rhodamine 101).

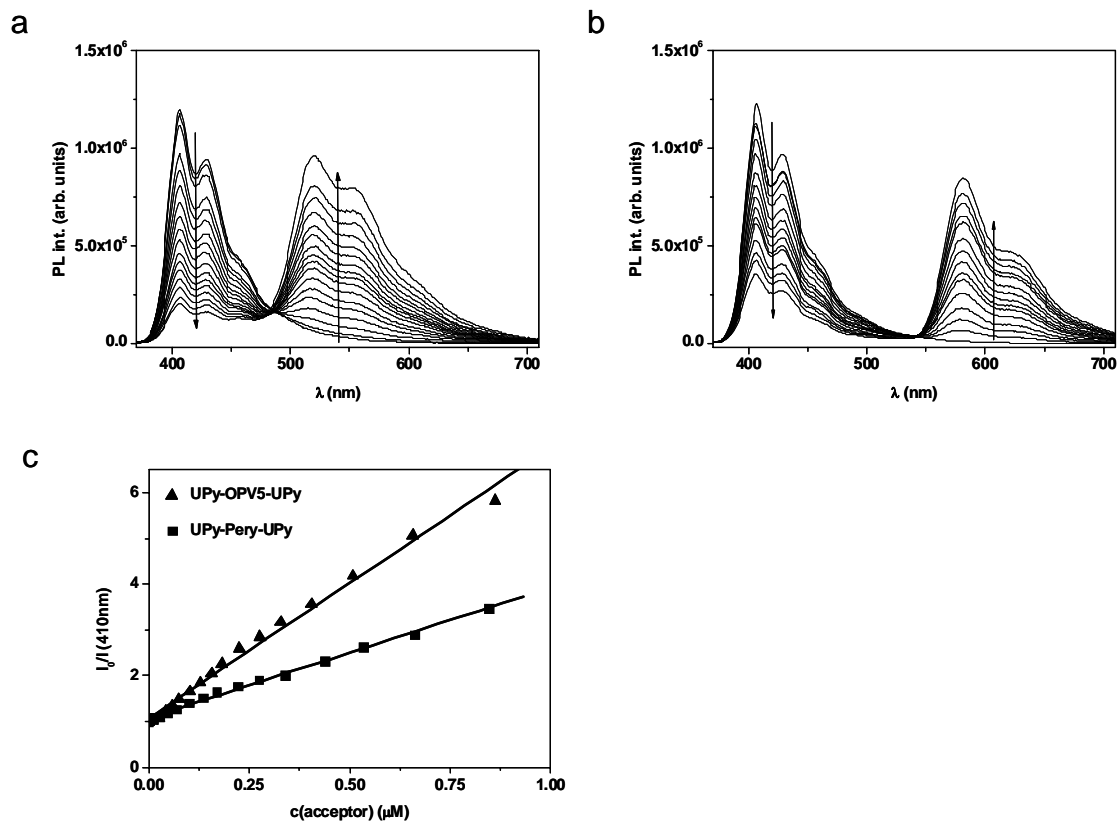
## Supporting Figures



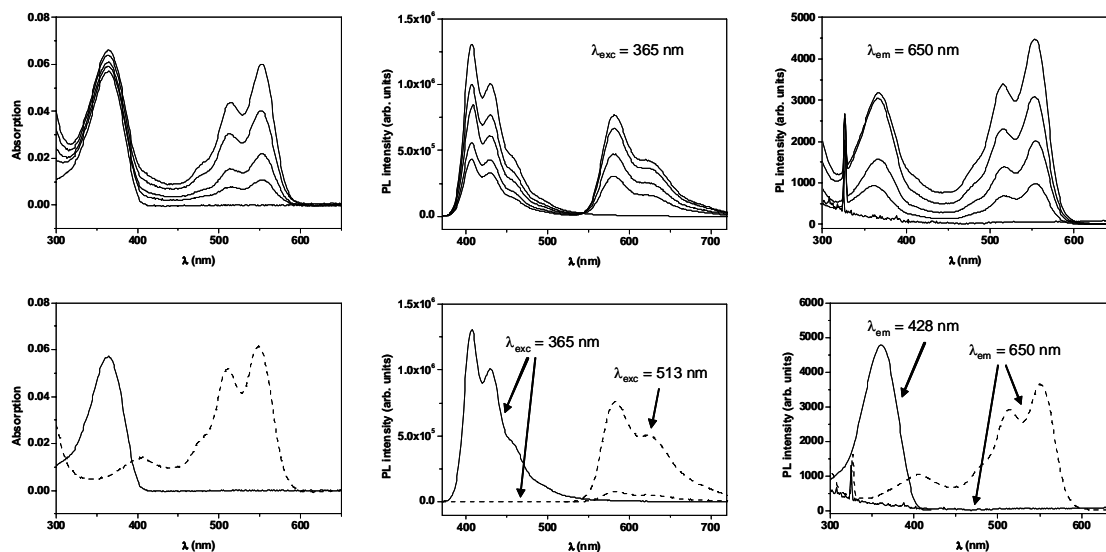
**Figure S1.**  $^1\text{H-NMR}$  spectra of UPy-Pery-UPy in THF- $d_3$ . (a) hydrogen bonding region, (b) complete spectrum, (c) after addition of ca. 15 % TFA- $d_1$ . The peak at ca. 13.5 ppm is due to TFA.



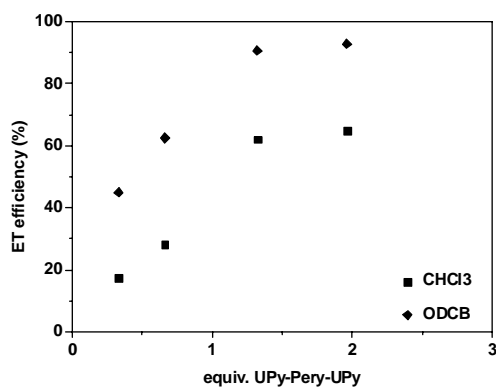
**Figure S2.** Absorption (a, c) and fluorescence (b, d) spectra of UPy-containing oligofluorenes in chloroform solution. The fluorescence spectra are weighted with the quantum yield of the compounds.



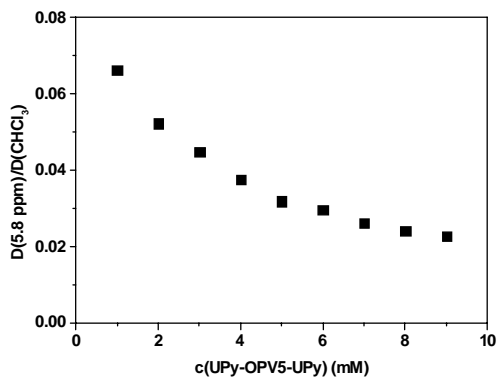
**Figure S3.** Fluorescence titration experiment with **UPy-OF3-UPy** as the donor ( $0.35 \cdot 10^{-6}$  M) and **UPy-OPV5-UPy** (a) and **UPy-Pery-UPy** (b) as the acceptor in chloroform solution. Excitation wavelength  $\lambda_{\text{exc}} = 365$  nm. Arrows indicate the spectral changes upon increasing the acceptor concentration. Stern-Volmer plot of both experiments (c).



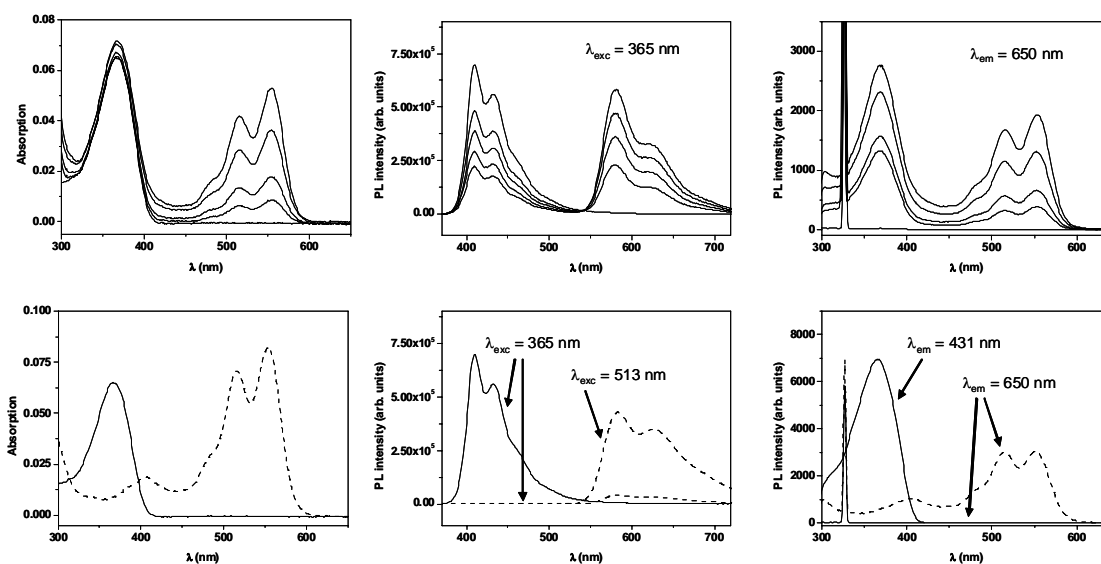
**Figure S4.** Absorption, emission and excitation spectra of mixtures of **UPy-OF3-UPy** (0.63  $\mu\text{M}$ ) with **UPy-Pery-UPy** (0.00, 0.21, 0.42, 0.83, 1.24  $\mu\text{M}$ ) (top) and of solutions of the pure compounds (**UPy-OF3-UPy** 0.63  $\mu\text{M}$  (solid line) and **UPy-Pery-UPy** 1.24  $\mu\text{M}$  (dashed line)) (bottom) in  $\text{CHCl}_3$ .



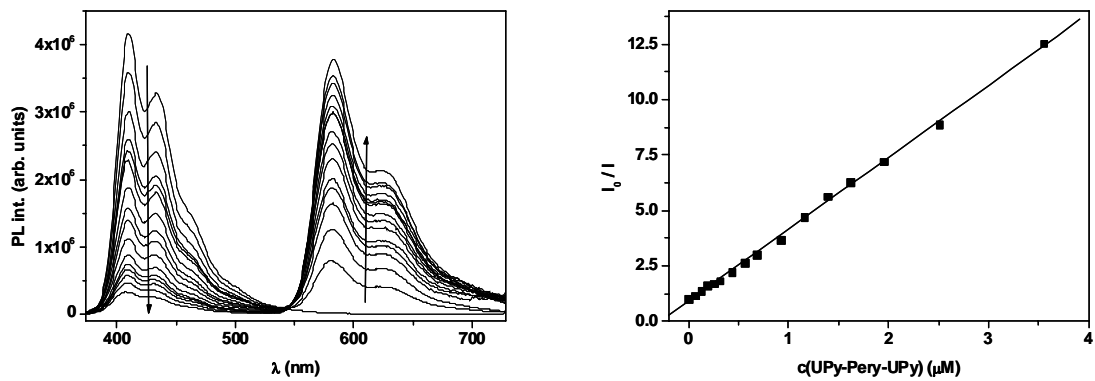
**Figure S5.** Energy transfer efficiency from **UPy-OF3-UPy** to **UPy-Pery-UPy** as extracted from a comparison of absorption and excitation spectra of mixed solutions in chloroform and ODCB.



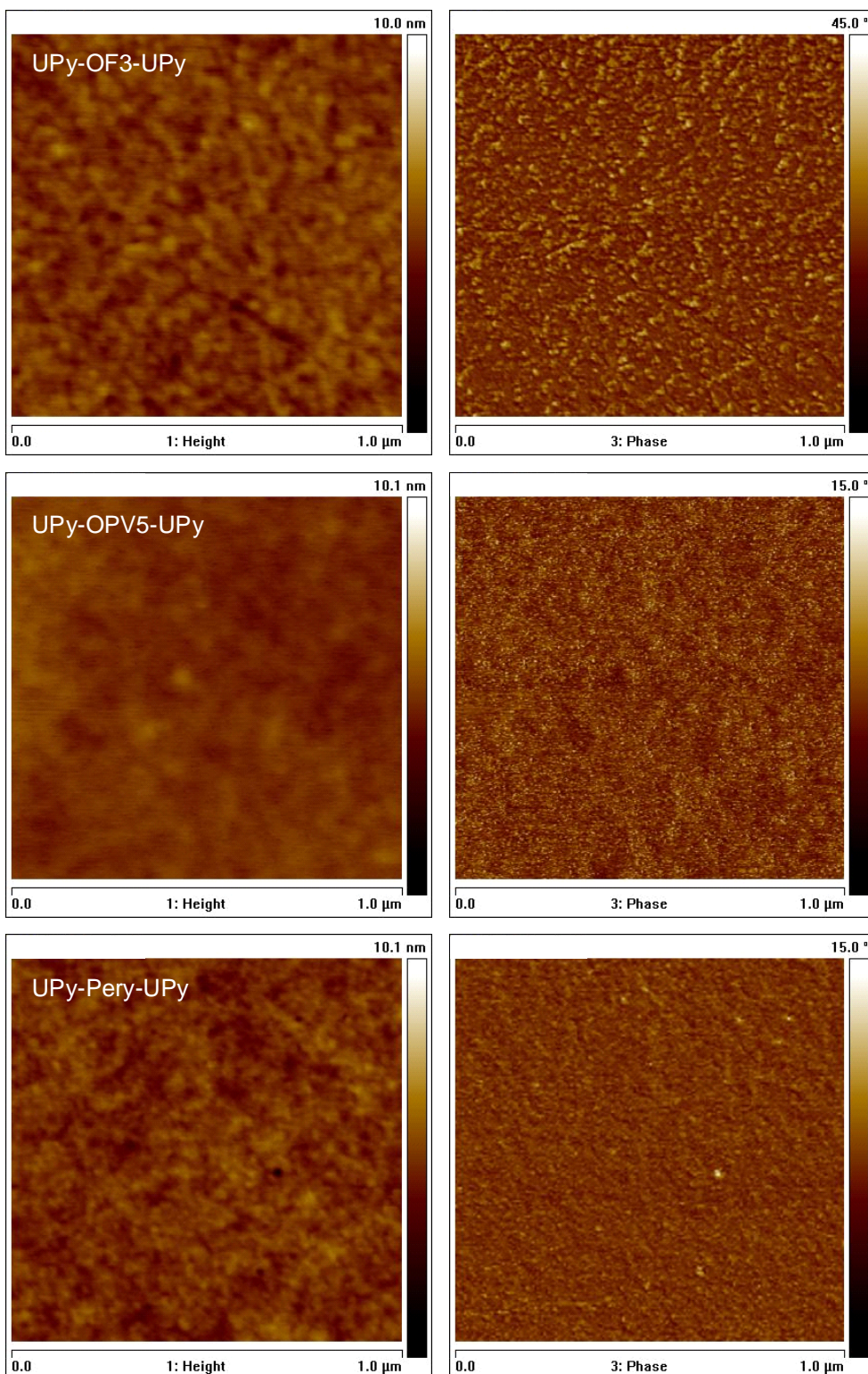
**Figure S6.** DOSY experiment in CDCl<sub>3</sub> showing the evolution of the UPy alkylidene singlet peak at ~ 5.8 ppm with concentration. The diffusion was normalized to the diffusion of CHCl<sub>3</sub>.



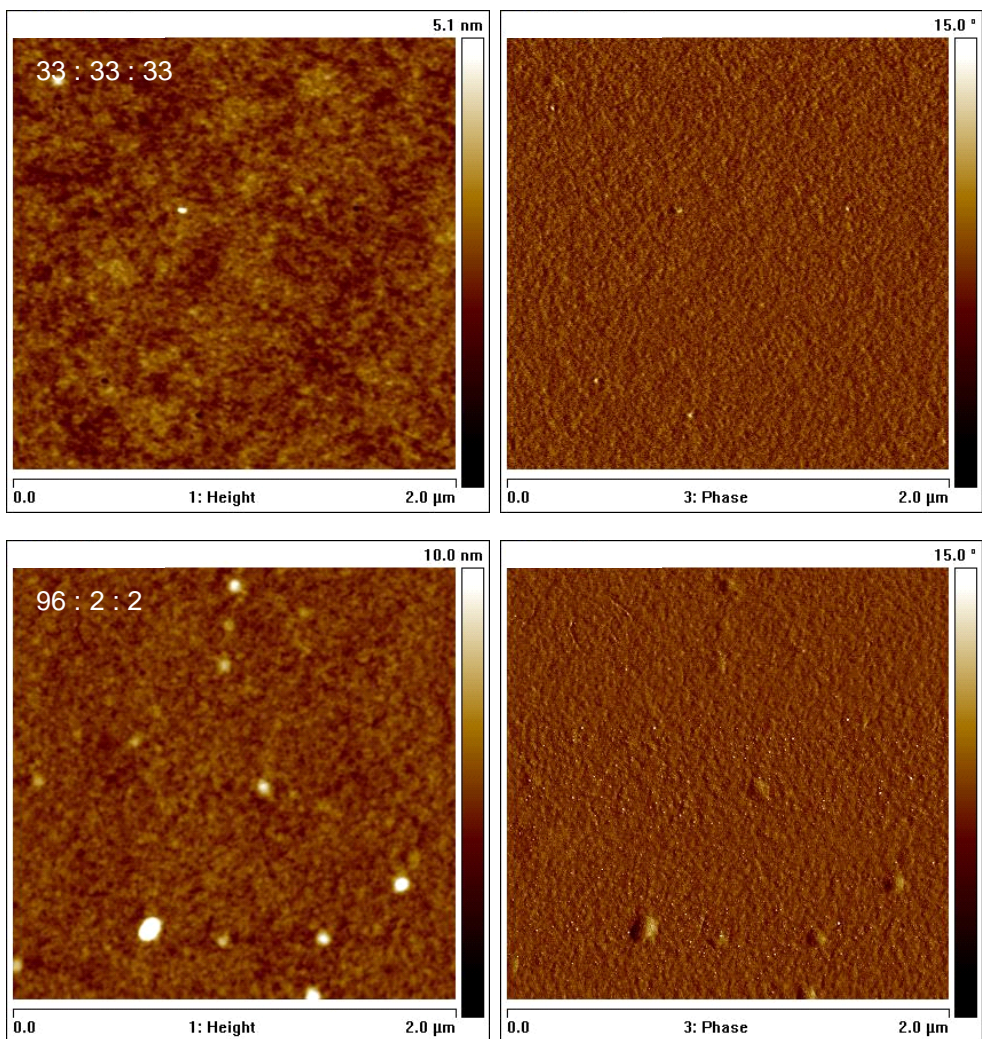
**Figure S7.** Absorption, emission and excitation spectra of mixtures of **UPy-OF3-UPy** (0.63 μM) with **UPy-Pery-UPy** (0.00, 0.21, 0.42, 0.83, 1.24 μM) (top) and of solutions of the pure compounds (**UPy-OF3-UPy** 0.63 μM (solid line) and **UPy-Pery-UPy** 1.24 μM (dashed line)) (bottom) in ODCB.



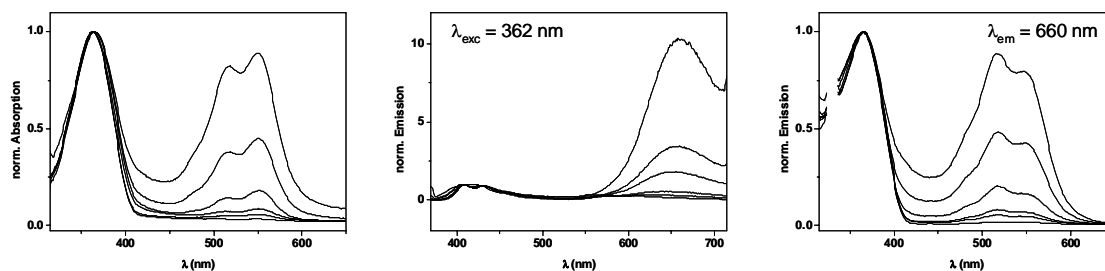
**Figure S8.** Fluorescence titration of UPy-OF3-UPy (0.35  $\mu\text{M}$ ) with UPy-Pery-UPy in ODCB and corresponding Stern-Volmer plot.



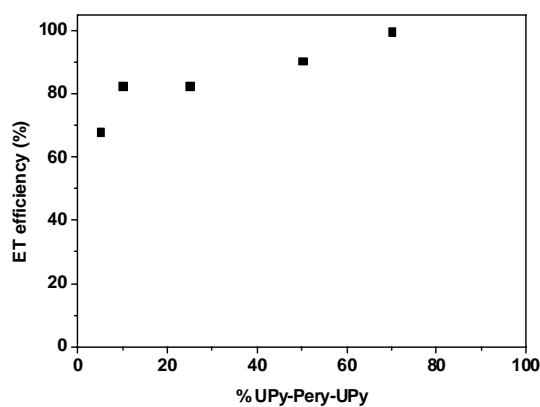
**Figure S9.** AFM height (left) and phase (right) images of thin film spin coated **UPy-OF3-UPy** (top), **UPy-OPV5-UPy** (centre) and **UPy-Pery-UPy** (bottom).



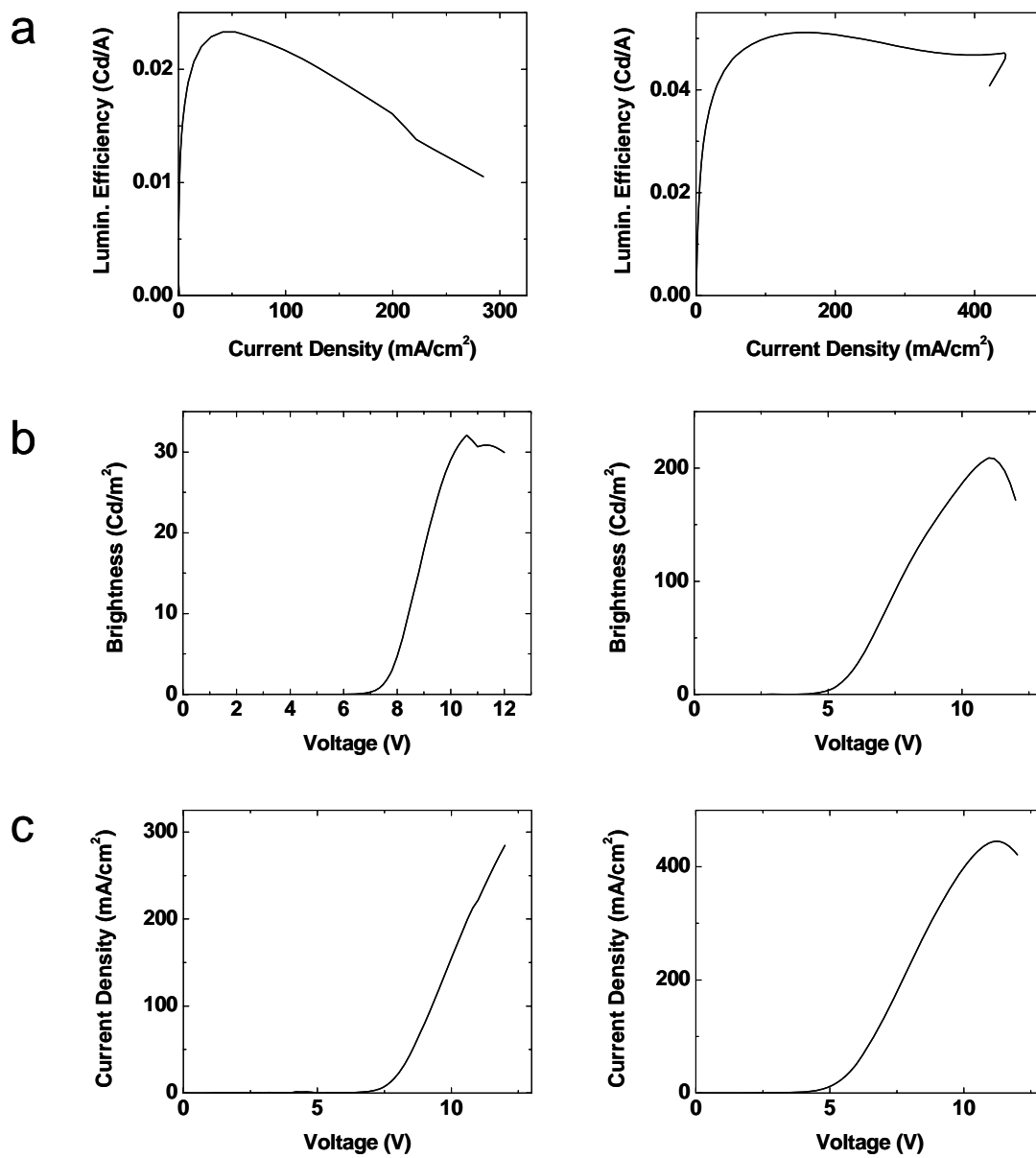
**Figure S10.** AFM height (left) and phase (right) images of thin film spin coated from a 33 : 33 : 33 mixture (top) and from a 96 : 2 : 2 mixture (bottom) of the three chromophores.



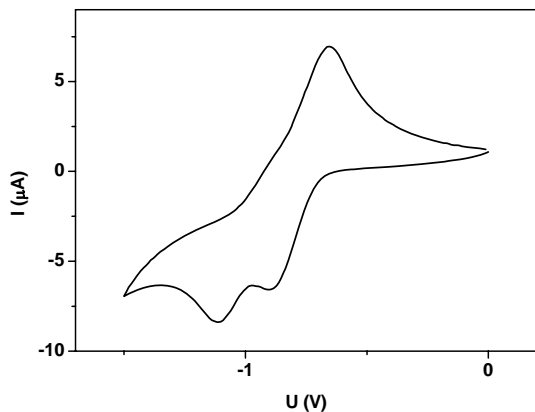
**Figure S11.** Normalised absorption, emission and excitation spectra of thin films of mixtures of **UPy-OF3-UPy** and **UPy-Pery-UPy** spin coated from ODCB solution (total chromophore concentration 15 mg/ml). **UPy-OF3-UPy** : **UPy-Pery-UPy** = 98:2, 95:5, 90:10, 75:25, 50:50, 30:70.



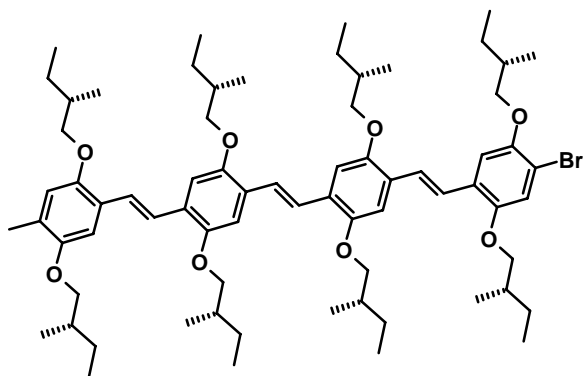
**Figure S12.** Energy transfer efficiency from **UPy-OF3-UPy** to **UPy-Pery-UPy** as extracted from a comparison of absorption and excitation spectra of mixed spin coated films.



**Figure S13.** Current Density – Efficiency (a), Voltage – Light Intensity (b), and Voltage – Current Characteristics (c) of OLEDs containing **UPy-OF3-UPy** (left) and **UPy-OPV5-UPy** (right).



**Figure S14.** Cyclic Voltammetry of **UPy-Pery-UPy** in a 0.1 M of tetrabutyl ammonium fluorophosphate solution in ODCB. As the solvent was not sufficiently stable to measure an oxidation peak, the HOMO energy was calculated from the first reduction peak using the optical band gap (2.13 eV).



**Figure S15.** Chemical structure of the control OPV4 acceptor molecule<sup>S13</sup> used in the experiment described in Fig. 4.

## References

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