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Synthesis of fluorescent fluorene–isoindole-containing mono- and oligomers

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ABSTRACT

Novel fluorene–isoindole-containing light-emitting mono- and oligomers were prepared. The synthesis of the monomers *N*-(4-bromo-phenyl)-2-(7-bromo-9,9-diethylfluoren-2-yl)-isoindole-1-carboxamide, *N*-(7-bromo-9,9-dibutylfluoren-2-yl)-2-(7-bromo-9,9-dibutylfluoren-2-yl)-isoindole-1-carboxamide, and *N*-[7-bromo-9,9-bis(2-ethylhexyl)-fluoren-2-yl]-2-[7-bromo-9,9-bis(2-ethylhexyl)-fluoren-2-yl]-isoindole -1-carboxamide was carried out by a three-component reaction of *ortho*-phthalaldehyde with the corresponding amine and isocyanide partners. The Ni(0) mediated polymerization reactions of the obtained monomers gave the corresponding mixture of oligomers from two up to twelve repeat units. The optical properties were also studied and it was found that the phenylene-containing oligomer emitted green light in dichloromethane solution, while both difluorene-containing oligomers, under the same conditions, proved to be blue light-emitters with good quantum efficiency.

1. Introduction

The development of organic light-emitting diodes (OLEDs) as base materials of future displays has attained much attention since the first report of electroluminescence from poly(*p*-phenylene vinylene)-based conjugated polymers by Burroughes et al. in 1990.[1] OLED based displays possess several advantages compared to their inorganic counterparts: they are flexible, transparent, light-weight and easily processable at lower temperatures. Blue light-emitting materials are the most important since blue light is easily converted to any other visible color.[2,3] The majority of efficient blue light-emitters contain polyaromatic backbones.[4] Fluorenes are considered important building blocks of polymers, which have the potential to act as both electroactive and photoactive materials.[5–8] The conjugation across the molecule allows for a reduced band gap the energy of which can be easily varied by the electron donating character of its substituents.[9]

The problem with polyfluorenes is that they often show both excimer and aggregate formation, which besides lowering the efficiency of the LEDs also causes a red shift in the emission spectrum.[10] These undesirable phenomena can be overcome in two ways (i) adding large substituents at the nine position of the fluorene unit,[11] (ii) copolymerizing polyfluorene with other fluorescent units.[12] A number of polyfluorenes with different homo- and heteroaromatic comonomers, such as anthracene,[13] carbazole,[14] oxadiazole,[15] triphenyl-amine,[16] thiophene[17] have been prepared. Interestingly, we could not find any isoindole-containing polyfluorenes in the literature. This is peculiar considering that a number of aryl substituted isoindoles were characterized to show strong fluorescence and electroluminescence in *N*,*N*-dimethylformamide solution more than 40 years ago by Zweig et al.[18]

Substituted isoindoles, especially *N*-substituted ones, are of more interest because they are more stable than the non-substituted ones.[19] Preparation of phenyl substituted polyisoindoles is reported from dibenzoylbenzenes with anilines, which are highly fluorescent polymers with good thermal stability.[20] Condensation methods offer a simple way to obtain substituted isoindole derivatives. We recently reported the preparation of phenylene-containing polyisoindoles via the catalyst free polycondensation between *ortho*-phthalaldehyde (OPA) and aminothiophenols.[21]

Zhang et al. recently published a three-component reaction yielding 1-carboxamido-isoindoles via the reaction of OPA, amines, and isocyanides.[22] It is noteworthy that there was no example for the use of an aromatic isocyanide component among the described three-component reactions. It is also important to note that the application of aromatic amine and isocyanide partners in the three-component reaction allows us to combine the 1-carboxamido-isoindole group with other fluorescent aromatic (e.g., phenylene, fluorene) or heteroaromatic (e.g., thiophene, pyridine) groups. Thus, employing bromo-substituted amine and isocyanide partners in the three-component reaction we can obtain a series of new fluorescent polymerizable monomers.

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Here, we describe the synthesis of three new fluorene-1-carboxamido-isoindole-containing monomers. We also report the polymerization reactions of the obtained monomers by Yamamoto coupling.[23] Finally, the optical properties of the monomers are compared with those of the obtained oligomers.

2. Results and discussion

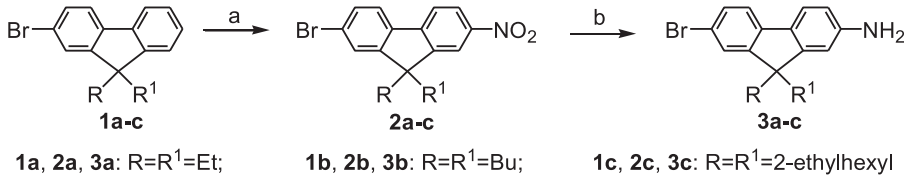
2.1. Synthesis of the monomers 7a–c and oligomers 8a–c

The preparation of the targeted polymerizable fluorene-1-carboxamido-isoindole-containing monomers **7a**–**c** was planned by the aforementioned three-component reaction.[22] First, the bromo-substituted amine (**3a**–**c**) and isocyanide (**5a**–**c**) components were synthesized.

The synthesis of the amines **3a**,[24] **3b**,[25] and **3c**[26] was accomplished by using the same strategy as shown in Scheme 1. The known 2-bromo-9,9-dialkylfluorenes **1a**,[27] **1b**,[28] and **1c**[29] were prepared started from the commercially available 2-bromo-fluorene as reported in the literature.[30] Compounds **1a**–**c** were nitrated using HNO_3 in the presence of a supported catalyst of SiO_2/H_2SO_4[31] to afford the desired 2-bromo-9,9-dialkyl-7-nitrofluorenes **2a**, **2b**,[32] and **2c** with good regioselectivity. Reduction of nitrofluorenes (**2a**–**c**) by Fe/ammonium chloride[33] gave 7-bromo-9,9-dialkylfluorenyl-2-amines (**3a**–**c**) in good yields.

reacted for overnight at room temperature. After 12 h under these conditions, we did not observe any noticeable formation of the desired product **7a**. Prolonging the reaction time still failed to produce any desired product. Addition of acetonitrile in order to increase the solubility of the isocyanide **5a** proved to be also insufficient to obtain **7a**. Next we decided to increase the temperature, and after several attempts at different temperatures we found that the best conversion could be achieved in 4 h at 100 °C, and due to the low solubility of the isocyanide **5a** in the mixture of DMSO/H_2O (1:1), the addition of 1 part of acetonitrile was also needed. Thus, we obtained the targeted compound **7a**, by employing the optimized conditions, in 65% isolated yield (Scheme 3).

The above established optimized conditions were used for the preparation of isoindoles **7b** and **7c** starting from the amines **3b**, **3c** and isocyanides **5b**, **5c**, respectively, as depicted in Scheme 3. In this case, the moderate to low isolated yields obtained for compounds **7b** and **7c** were the consequence of partial decomposition of the isoindole derivatives **7b** and **7c** during the work-up and purification procedures owing to their low stability in solution, in the presence of air and light (especially in the case of **7c**). We tried to overcome the undesirable decomposition by using neutral aluminum oxide in the purification step instead of silica gel chromatography, but even in these conditions the products (**7b** and **7c**) partially decomposed. It is noteworthy, however that below 0 °C, in the dark and under inert atmosphere, crystalline **7a** and **7b** or **7c** in the form of solid

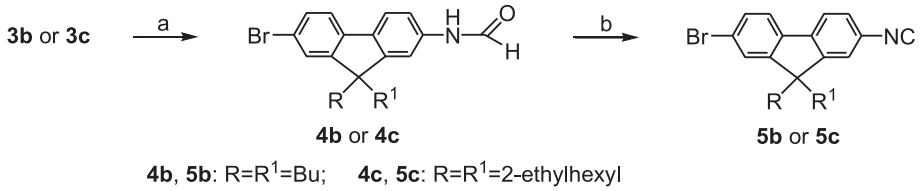


Scheme 1. Synthesis of the amines **3a**–**c**. Reagents and conditions: (a) SiO_2/H_2SO_4, HNO_3, CH_2Cl_2, rt, 10 min, 67% for **2a**, 63% for **2b**, 62% for **2c**; (b) Fe (powder), NH_4Cl, EtOH/H_2O (18:5), 85 °C, 2 h, 78% for **3a**, 76% for **3b**, 80% for **3c**.

In order to obtain the aromatic isocyanide partners for the 1-carboxamido-isoindole reactions amines **3b** and **3c** were converted into the isocyanide derivatives **5b** and **5c** by a two-step procedure (Scheme 2). N-Formylation of the amines **3b** and **3c** was carried out by applying the procedure established by Dawane et al.[34] Thus, compounds **3b** and **3c** were treated with 6 equiv of formic acid for 3 h at 70 °C affording the corresponding formamides **4b** and **4c** in excellent yields, respectively. Dehydration of the formamides **4b** and **4c** using phosphoryl chloride and diisopropylamine[35] resulted in the desired isocyanides **5b** and **5c** in high yields.

spume can be stored for several months. Under these conditions we have not observed noticeable decomposition during our investigations.

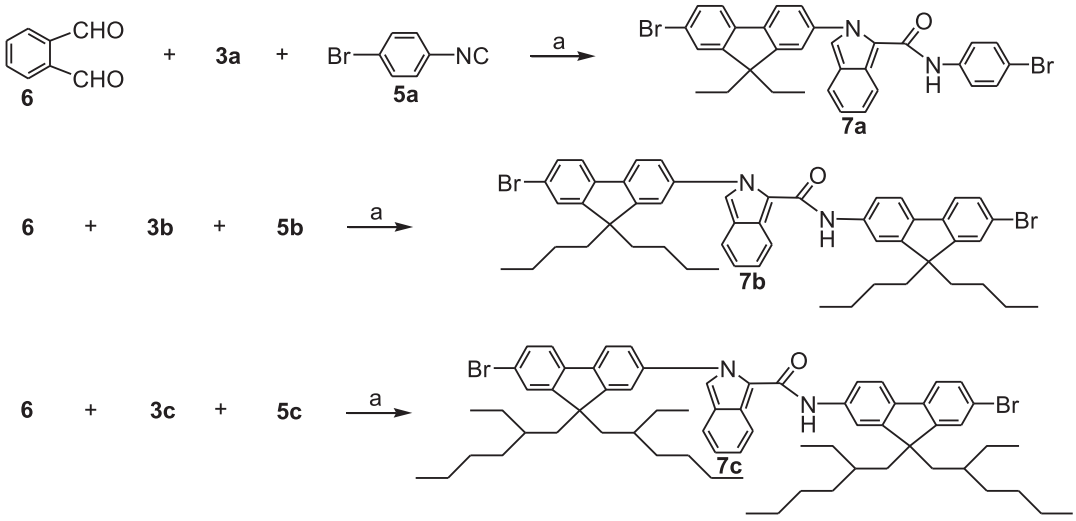
Thereafter, we explored the possibility to polymerize the obtained monomers (**7a**–**7c**) via Ni(0) mediated Yamamoto coupling reaction.[23] First, the monomer **7a** dissolved in dry toluene was reacted with a pretreated mixture of $Ni(cod)_2$, 2,2′-bipyridine, 1,5-cyclooctadiene, and dry DMF at 85 °C for 3 days under argon atmosphere, in the dark. Purification of the crude product gave a mixture of oligomers **8a** in 60% yield (Scheme 4). According to MALDI-TOF MS spectra the obtained mixture contained a series of



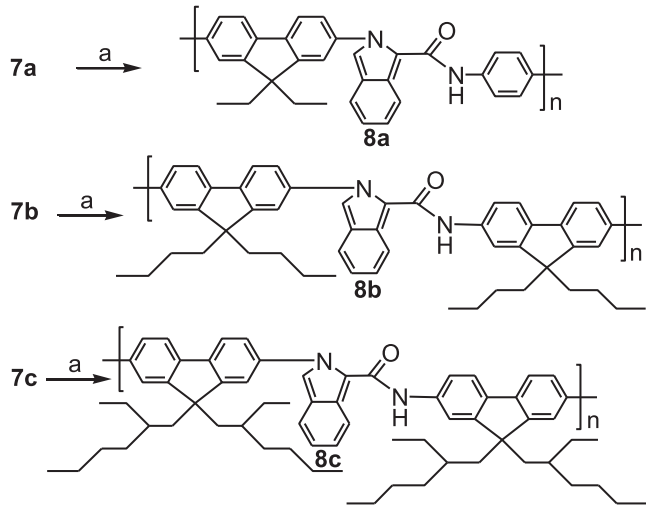
Scheme 2. Synthesis of the isocyanides **5b** and **5c**. Reagents and conditions: (a) HCOOH, 70 °C, 3 h, 91% for **4b**, 97% for **4c**; (b) $POCl_3$, DIPA, CH_2Cl_2, 0 °C, 1 h, 93% for **5b**, 91% for **5c**.

Next, we attempted to synthesize the target 1-carboxamido-isoindole-containing monomer **7a** using the general procedure described by Zhang et al.[22] Accordingly, a mixture of commercially available OPA (**6**), 1 equiv of amine **3a**, 2 equiv of 4-bromo-phenyl isocyanide (**5a**)[36] and 2 equiv of $NaHSO_3$ in DMSO/H_2O (1:1) was

monobrominated and bromine-free linear and cyclic oligomers from two up to twelve repeat units (see Figs. 1S–3S in the Supplementary data). The almost exclusive presence of monobrominated and bromine-free oligomers revealed the occurrence of Ni-mediated hydrolysis of the bromines[37] during the



Scheme 3. Synthesis of the monomers **7a**–**c**. Reagents and conditions: (a) $NaHSO_3$, $DMSO/H_2O/CH_3CN$ (5:5:6), 100 °C, 4 h, 65% for **7a**, 46% for **7b**, 10% for **7c**.



Scheme 4. Polymerization of the monomers **7a**–**c** via Yamamoto coupling. Reagents and conditions: (a) $Ni(cod)_2$, 2,2′-bipyridine, 1,5-cyclooctadiene, dry DMF/dry toluene (3:5), 85 °C, 72 h for **8a**, 1 week for **8b** and **8c**, 60% for **8a**, 30% for **8b**, 28% for **8c**.

polymerization reaction, causing the early termination of the propagation of the polymer chain.

Polymerization reactions of monomers **7b** and **7c** after 3 days, under the same reaction conditions, showed approximately 30% formation of the desired oligomers (**8b** and **8c**). By increasing the reaction time up to 1 week the conversions could be enhanced to about 50%. Thus, **8b** and **8c** were isolated in 30% and 28% yields, respectively. Our attempts to improve the yields of the desired **8b** and **8c** by applying higher temperature, increasing the amount of the reagents, and prolonging the reaction time were unsuccessful. Like in the case of **8a**, hydrolysis of the bromines in these reactions could also be observed. In fact, APPI-TOF MS and ESI-HRMS measurements of the crude products of **8b** and **8c** demonstrated that partial and complete hydrolysis of the bromines occurred at both monomer and oligomer levels (see ESI-HRMS data of monobrominated and bromine-free derivatives of **7b** and **7c** in the subsections 4.19 and 4.20, respectively, and the APPI-TOF MS spectra of **8b** and **8c** in the Supplementary data, Fig. 4S and 5S, respectively, show the presence of monobrominated and bromine-free oligomers). Presumably, both the low conversion and the slow transformation of the monomers **7b** and **7c** into oligomers **8b** and **8c**, respectively, could be a result of the high susceptibility of **7b** and **7c** and their oligomer derivatives against the undesired side reaction of the Ni-mediated hydrolysis of the bromines. Since bromine hydrolysis occurred even at monomer level, the gradually diminishing concentration of the monomer present in the reaction mixture slowed down the product formation increasingly. The molecular weights of the obtained oligomers (**8a**–**c**) were characterized by gel permeation chromatography (GPC) and are summarized in Table 1.

Table 1
Characterization of the oligomers **8a**–**c**

Oligomer	M_n[a] (g/mol)	M_w[a] (g/mol)	PDI[a]
8a	2350	4610	2.0
8b	3760	5020	1.3
8c	2700	2930	1.1

[a] The number average molecular weight (M_n), the weight average molecular weight (M_w), and polydispersity index (PDI) were estimated by GPC in THF against polystyrene standards.

2.2. Optical properties of the monomers 7a–c and oligomers 8a–c

The UV–vis and excitation spectra of the monomers **7a**–**c** and oligomers **8a**–**c** were recorded in CH_2Cl_2 and are presented in Fig. 1a. (The absorbance spectra match the excitation spectra.) All monomers (**7a**–**c**) exhibit similar absorption spectra containing wide absorption bands ranging from 250 to 400 nm and three peaks located at 285, 315, and 365 nm, with an absorption maximum at 285 nm. The absorption spectra of the oligomers **8a**–**c** are also similar to each other containing a large peak at 355 nm as absorption maximum and a significant or moderate shoulder at 285 nm, the intensity of the shoulders decrease in the order of **8a**, **8c**, and **8b**, respectively. Comparing the absorption spectra of the monomers (**7a**–**c**) with those of the oligomers (**8a**–**c**) we can observe a substantial bathochromic shift (from 285 to 355 nm) of the absorption maximum and significant changes in the structure of the absorption bands due to the extended π-conjugation system along the whole oligomer molecules (**8a**–**c**) via the amide bridges[38] (Fig. 1a).

The characteristics of the fluorescence emission spectra of the monomers **7a**–**c** and oligomers **8a**–**c** are compiled in Table 2 (including the excitation wavelengths at which the emission spectra were recorded) and the emission spectra obtained in CH_2Cl_2 are

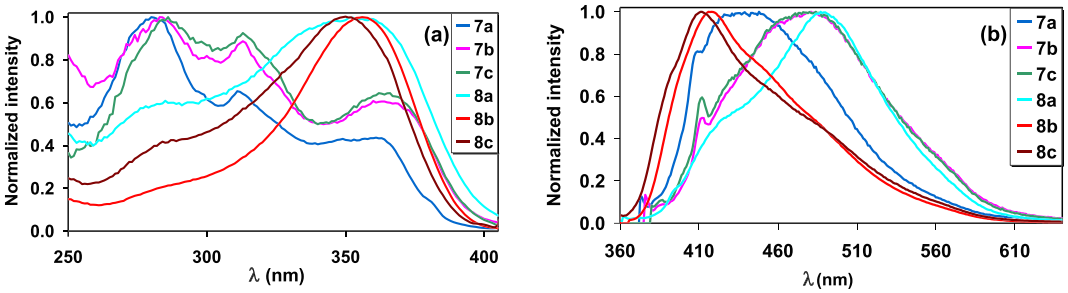


Fig. 1. Normalized excitation (a) and emission (b) spectra of monomers **7a**–**c** and oligomers **8a**–**c** obtained in CH_2Cl_2.

Table 2
The wavelengths of excitation (λ_{ex}), fluorescence emission maxima ($\lambda_{em,max}$), Stokes shifts and the quantum yield (Φ_F) of monomers **7a**–**c** and oligomers **8a**–**c** in CH_2Cl_2. The Stokes shift is defined as $\Delta\bar{\nu}=\bar{\nu}_{abs.max}-\bar{\nu}_{em.max}$, where $\bar{\nu}_{abs.max}$ and $\bar{\nu}_{em.max}$ are the wavenumbers of absorption (excitation) and emission maxima, respectively. The error in the measurements of Φ_F values were within ±10%

Compound	Solvent	λ_{ex} (nm)	$\lambda_{em,max}$ (nm)	ε (dm^3/mol cm)[a]	Stokes shift ($\Delta\bar{\nu}$, cm^{-1})	Φ_F
7a	CH_2Cl_2	363	439	1.7×10^4	4769	0.01
8a	CH_2Cl_2	352	489	1.4×10^5	7959	0.03
7b	CH_2Cl_2	365	481	2.7×10^4	6607	0.01
8b	CH_2Cl_2	356	418	1.4×10^5	4167	0.17
7c	CH_2Cl_2	366	480	2.7×10^4	6489	0.01
8c	CH_2Cl_2	350	411	3.8×10^4	4240	0.15

[a] Molar extinction coefficient values (ε) were determined at the corresponding λ_{ex} values.

shown in Fig. 1b. As seen from the data of Fig. 1b and Table 2 emission spectra of the monomers, **7a**–**c** show low fluorescence emission with wavelengths ranging from λ=390 nm up to λ=570 nm. Monomers **7b** and **7c** show almost identical emission spectra with emission maxima at 481 and 480 nm, respectively, near to the green region. However, the monomer **7a** with an emission maximum at 439 nm presents emission predominantly in the blue region of the visible light.

The fluorescence emission spectra of the oligomers **8a** exhibit a red shift of the emission maximum (from 439 to 489 nm) in comparison with that of the monomer **7a**. The shape of the emission spectra is also changed containing a large peak at 489 nm as emission maximum and a moderate shoulder at 423 nm. Surprisingly, the similar fluorescence emission spectra of the oligomers **8b** and **8c** show a hypsochromic shift (blue shift) of the emission maxima (from 481 to 418 nm and from 480 to 413 nm, respectively) in comparison with those of the monomers **7b** and **7c**. The blue shift of the emission maxima in the case of the oligomers **8b** and **8c** can be explained by the different type of conjugation present in monomers and oligomers. The fluorene units are separated by the 1-carboxamide-isoindolene moiety in the case of the monomers **7b** and **7c**, while oligomers **8b** and **8c** contain alternating difluorene and isoindolene units. Thus, the characteristic emission bands of simple polyfluorenes (oligofluorenes from trimer up to heptamer with $\lambda_{em,max}$ in the range of 394–434 nm assigned to the 0-0 and 0-1 intrachain singlet transitions)[26] are more pronounced in the case of oligomers **8b** and **8c**, probably due to the direct π-conjugation system between the aromatic fluorene rings.

It is worth mentioning that the shape and the wavelength at the maximum emission intensity are independent of the excitation wavelength, i.e., similar emission spectra were obtained using shorter excitation wavelengths (in the range of 280–315 nm), indicating that electronic transition occurs from each excited state to the same lowest ground state.

The optical properties of the monomers **7a**–**c** and oligomers **8a**–**c** are summarized in Table 2. It can be surmised from Table 2 that relatively high quantum yields were obtained for both difluorene-containing oligomers (Φ_F=0.17 for **8b** and Φ_F=0.15 for **8c**) in comparison with the fluorescence quantum yield values obtained for the starting monomers (Φ_F=0.01 for **7b** and Φ_F=0.01 for **7c**), respectively. (Quantum yields were calculated by using quinine sulfate reference with absolute quantum efficiency (Φ_F=55%). However, in the case of oligomer **8a** low quantum yield was obtained (Φ_F=0.03), which is three times higher than that of the obtained for the monomer **7a** (Φ_F=0.01). The fluorescence properties of the monomers **7a**–**c** and oligomers **8a**–**c** demonstrated in Fig. 2 are in good agreement with the data of Fig. 1b and Table 2.

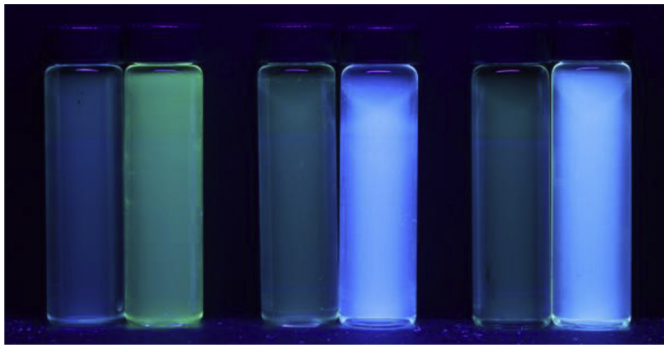


Fig. 2. Demonstration of the fluorescence properties of monomers **7a**–**c** and oligomers **8a**–**c** in CH_2Cl_2 illuminated by light of λ=365 nm. Compounds from left to the right are: **7a** (pale blue), **8a** (light green), **7b** (pale green), **8b** (sky blue), **7c** (pale green), **8c** (sky blue).

3. Conclusion

Three new fluorene–isoindole-containing light-emitting mono- and oligomers were prepared. The synthesis of the monomers **7a**–**c** was accomplished by the three-component reaction of *ortho*-phthalaldehyde with the amines **3a**–**c** and isocyanides **5a**–**c**, respectively. The polymerization of the obtained monomers proceeds via Ni(0) mediated Yamamoto coupling reaction. GPC, MALDI-TOF MS, and APPI-TOF MS investigation showed the formation of a series of oligomers (**8a**–**c**) from two up to twelve repeat units. The degree of polymerization was limited by the undesirable side reaction of partial or complete hydrolysis of the bromines. Optical study of the oligomers showed green light emission when in solution in dichloromethane for the phenylene-containing oligomer (**8a**), while blue light emission could be observed for both difluorene-containing oligomers (**8b** and **8c**), under the same conditions, with relatively good quantum efficiency. Unlike the monomers, the oligomers proved to be stable even in solution for several days. The reported procedure for **7a**–**c** and **8a**–**c** can serve as a model for the synthesis of a series of novel fluorescent

isoindole-containing light-emitting oligomers/polymers by combining the 1-carboxamido-isoindole moiety with bromo-substituted fluorescent aromatic or heteroaromatic groups.

4. Experimental

4.1. General information

Compound **5a** was prepared in our laboratory according to the literature procedure.[36] TLC was performed on Kieselgel 60 F_{254} (Merck) or aluminum oxide F_{254} neutral (type T, Merck) with detection by UV lamps (emission at 254 nm or 365 nm). Column chromatography was performed on Silica gel 60 (Merck 0.063–0.200 mm) or aluminum oxide acc. to Brockmann (II, neutral; Reanal, Hungary). The ^{1}H (360 MHz) and ^{13}C NMR (90.54 MHz) spectra were recorded with a Bruker DRX-360 spectrometer. Chemical shifts are referenced to Me_4Si (0.00 ppm for ^{1}H) or to the residual solvent signals ($CDCl_3$: 77.00 ppm). IR spectra were recorded on a Perkin–Elmer 16 PC FTIR spectrometer. The MALDI MS measurements were performed with a Bruker BIFLEX III™ mass spectrometer equipped with a time-of-flight (TOF) mass analyzer. In all cases 19 kV acceleration voltage was used with pulsed ion extraction (PIE™). The positive ions were detected in the reflectron mode (20 kV). A nitrogen laser (337 nm, 3 ns pulse width, 106–107 W/cm^2) operating at 4 Hz was used to produce laser desorption and 500 shots were summed. Samples were prepared with a dithranol matrix (20 mg/cm^3), analyte solution of 10 mg/cm^3 and sodium trifluoroacetate was added (5 mg/cm^3) as the cationization agent in tetrahydrofuran. ESI-HRMS analyses of the compounds were carried out in Electrospray Quadrupole Time-of-Flight MS/MS (ESI-QqTOF). MS measurements were performed with a MicroTOF-Q type QqTOF MS instrument equipped with an ESI source from Bruker (Bruker Daltoniks, Bremen, Germany). The sample solutions were introduced directly into the ESI source with a syringe pump (Cole–Parmer Ins. Co.) at a flow rate of 3 μL/min. The temperature of the drying gas (N_2) was maintained at 180 °C. The voltages applied on the ESI source were 4 kV. Each spectrum was calibrated externally with the salt clusters produced from the electrosprayed solution of sodium trifluoroacetate. In the case of compounds **5b** and **5c**: Ion source for Atmospheric Pressure Chemical Ionization (APCI) source was from Bruker (Bruker Daltoniks, Bremen, Germany). The solutions were delivered directly into the APCI source with a syringe pump (Cole–Parmer Ins. Co., Vernon Hills, IL, USA) at a flow rate of 15 μL/min together with a carrier flow of methanol at a flow rate of 0.2 mL/min by means of a T-piece. The temperature of the drying gas (N_2) was maintained at 390 °C. The APCI mass spectra were calibrated by APCI/APPI calibrant solution from Agilent, USA. Atmospheric pressure photoionization (APPI) measurements were performed in negative ion modes with a MicroTOF-Q type Qq-TOF MS instrument (Bruker Daltonik, Bremen, Germany) equipped with an atmospheric pressure photoionization source (PhotoMate, Kr discharge lamp, VUV photons of 10.0, and 10.6 eV in intensity ratio of 4:1, respectively) from Syagen Ltd. (Syagen Technology, Inc., Tustin, CA). The samples were dissolved in toluene (dopant) at a concentration of 1 mg/mL. The solutions were delivered directly into the APPI source with a syringe pump (Cole–Parmer Ins. Co., Vernon Hills, IL, USA) at a flow rate of 25 μL/min together with a carrier flow of CCl_4 at a flow rate of 200 μL/min by means of a T-piece. The heater of the APPI source was kept at 450 °C. The end-plate offset and capillary voltage were set to 500 V and 2500 V, respectively. The accuracy of mass determination was within 5 ppm. The mass spectra recorded were evaluated by the Data Analysis 3.4 software from Bruker. The measured monoisotopic mass and isotopic distributions are in good agreement with those calculated based on the composition proposed. The UV–vis spectra were recorded on a HP 8453 diode array spectrophotometer in a quartz cuvette of 1 cm optical length. A 3.00 cm^3 solution was prepared from the sample. Fluorescence measurements were carried out using a Jasco FP-8200 fluorescence spectrophotometer equipped with a Xe lamp light source. The excitation and emission spectra were recorded at room temperature, using 2.5 nm excitation, 5.0 nm emission bandwidth, and 100 nm/min scanning speed. Fluorescence quantum yields were calculated by using quinine-sulfate in 0.1 mol/L sulfuric acid as the reference absolute quantum efficiency (Φ_n=55%). For UV–vis and fluorescence measurements of monomers **7a**–**c** and oligomers **8a**–**c** were dissolved in CH_2Cl_2 at concentration of 0.2 mg/mL and was diluted to 4.00 mg/L and 0.800 mg/L. Gel Permeation Chromatograms were recorded in THF at a 144 flow rate of 0.5 cm^3/min at 35 °C with a Waters chromatograph equipped with four gel columns (4.6×300 mm, 4.6 μm Styragel columns: HR 0.5, 1, 2 and 4), a Waters Alliance e2695 HPLC pump, and with Waters 2414 refractive index detector.

4.2. General method A for the synthesis of 2-bromo-9,9-dialkyl-7-nitrofluorene derivatives (2a–c)

2-Bromo-9,9-dialkylfluorene (10.0 mmol, **1a**, **1b** or **1c**) was dissolved in CH_2Cl_2 (60 mL), in the presence of a supported catalyst of SiO_2/H_2SO_4 (4.60 g) prepared according to the literature procedure.[31] HNO_3 (417 μL, 10.0 mmol) was added, and the heterogeneous mixture was stirred at room temperature for 10 min. The solution was then filtered, and the filtrate was washed with aqueous saturated $NaHCO_3$ solution (10 mL) and water (10 mL). The organic layer was dried over anhydrous $MgSO_4$ and the solvent was evaporated under reduced pressure.

4.3. General method B for the preparation of 7-bromo-9,9-dialkylfluorenyl-2-amine derivatives (3a–c)

A mixture of nitrofluorene (10.0 mmol, **2a**, **2b** or **2c**), iron powder (1.68 g, 30.0 mmol), and NH_4Cl (1.07 g, 20.0 mmol) was refluxed in aqueous ethanol (144 mL of alcohol and 40 mL of water) at 85 °C for 2 h under inert atmosphere. The reaction mixture was treated with 50 mL of aqueous saturated $NaHCO_3$ solution and filtered off through a pad of Celite. The obtained solution was concentrated in vacuum in order to remove ethanol. The formed residue was extracted with CH_2Cl_2 (2×50 mL), and the organic phase was dried over anhydrous $MgSO_4$ and evaporated under reduced pressure.

4.4. General method C for the preparation of formamide derivatives (4b, 4c)

Formic acid (2.26 mL, 60.0 mmol) was added to the amine (10.0 mmol, **3b** or **3c**) and the resulting mixture was stirred for 3 h at 70 °C. Then, the reaction mixture was cooled and diluted with EtOAc (50 mL). The obtained solution was washed carefully with aqueous saturated $NaHCO_3$ solution (10 mL), and water (10 mL). The organic layer was dried over anhydrous $MgSO_4$ and evaporated under diminished pressure.

4.5. General method D for the preparation of isocyanide derivatives (5b, 5c)

To a solution of the formamide (10.0 mmol, **4b** or **4c**) in CH_2Cl_2 (10 mL) and diisopropylamine (3.78 mL, 27.0 mmol), phosphoryl chloride (1.03 mL, 11.0 mmol) was added dropwise with stirring at 0 °C. Stirring was continued for 1 h at 0 °C. A solution of Na_2CO_3 (2 g) in water (20 mL) was added at a sufficiently slow rate in order to maintain 25–30 °C. After stirring for 1 h at rt, more water (10 mL) and CH_2Cl_2 (5 mL) were added and the organic layer was washed

with water (3×5 mL). The organic phase was dried over anhydrous $MgSO_4$ and evaporated under reduced pressure.

4.6. General method E for the preparation of 1-carboxamido-isoindole derivatives (7a–c)

A mixture of 268 mg *ortho*-phthalaldehyde (2.00 mmol), 431 mg $NaHSO_3$ (4.14 mmol), and DMSO/H_2O (5 mL/5 mL) was stirred at room temperature in a reaction flask protected from light under argon atmosphere. After 0.5 h amine (2.00 mmol, dissolved in 3 mL of CH_3CN, **3a**, **3b** or **3c**) and isocyanide (4.00 mmol, dissolved in 3 mL of CH_3CN, **5a**, **5b** or **5c**) were added. The reaction mixture was then heated to 100 °C, and stirred for 4 h at this temperature. The reaction mixture was diluted with 150 mL of EtOAc and extracted with saturated NH_4Cl (3×50 mL). The organic layer was dried over anhydrous $MgSO_4$ and evaporated under diminished pressure.

4.7. General method F for the Yamamoto coupling (8a–c)

A solution of $Ni(cod)_2$ (300 mg, 1.09 mmol), 2,2′-bipyridine (75 mg, 1.09 mmol), and 1,5-cyclooctadiene (134 μL, 1.09 mmol) in dry DMF (6 mL) was heated at 75 °C for 30 min in a flask protected from light under argon atmosphere. A solution of the monomer (1.00 mmol, **7a**, **7b** or **7c**) in dry toluene (10 mL) was added under argon to the DMF solution, and the polymerization was maintained at 85 °C for 72 h for **7a** or 1 week for **7b** and **7c** in the dark. The reaction mixture was then poured into a methanol/$HCl_{(cc)}$ (2:1) mixture (150 mL). In the case of monomers **7a** and **7b** the precipitated crude products were collected by filtration and washed with a MeOH/H_2O 2:1 mixture (2×) and then with H_2O (5×). The obtained crude products were dried at 40 °C under diminished pressure. In the case of monomer **7c** the crude product was collected by extraction using CH_2Cl_2 (3×50 mL). The organic layer was washed successively with water (50 mL), aqueous saturated $NaHCO_3$ solution (50 mL), and water (50 mL). The organic phase was dried over anhydrous $MgSO_4$ and evaporated under reduced pressure.

4.8. 2-Bromo-9,9-diethyl-7-nitrofluorene (2a)

2-Bromo-9,9-diethylfluorene[27] (**1a**, 2.26 g, 7.50 mmol), SiO_2/H_2SO_4 (3.45 g), and HNO_3 (312 μL, 7.50 mmol) were reacted in CH_2Cl_2 (45 mL) according to general method A. The crude product was purified by silica gel chromatography in 7:3 *n*-hexane/CH_2Cl_2, to give **2a** (1.73 g, 67%) as yellow crystals; mp 142–144 °C; R_f 0.45 (7:3 *n*-hexane/CH_2Cl_2); IR ν_{max} (KBr): 3435, 2962, 2918, 2875, 2849, 1599, 1523, 1455, 1348, 1254, 1136, 1062, 823, 768, 739, 419 cm^{-1}; ^1H NMR (360 MHz, $CDCl_3$, Me_4Si): δ (ppm) 8.28 (dd, 1H, J=2.0 Hz, J=8.4 Hz, arom), 8.21 (d, 1H, J=2.0 Hz, arom), 7.80 (d, 1H, J=8.4 Hz, arom), 7.68 (d, 1H, J=8.8 Hz, arom), 7.56–7.53 (m, 2H, arom), 2.18–2.01 (m, 4H, 2× CH_2), 0.32 (t, 6H, J=7.4 Hz, 2× CH_3); ^{13}C NMR (90 MHz, $CDCl_3$): δ (ppm) 153.4, 150.7, 147.3, 146.7, 138.0, 130.6, 126.5, 123.6, 123.4, 122.4, 119.8, 118.2 (12C, arom), 56.9 (Cq), 32.3 (2× CH_2), 8.3 (2× CH_3). ESI-HRMS: m/z calcd for $C_{17}H_{16}BrNO_2Na^+$ $[M+Na]^+$ 368.026. Found: 368.023.

4.9. 2-Bromo-9,9-dibuthyl-7-nitrofluorene (2b)[32]

2-Bromo-9,9-dibutylfluorene[28] (**1b**, 8.00 g, 22.4 mmol), SiO_2/H_2SO_4 (10.3 g), and HNO_3 (933 μL, 22.4 mmol) were reacted in CH_2Cl_2 (135 mL) according to general method A. The crude product was purified by silica gel chromatography in 7:3 *n*-hexane/CH_2Cl_2 and recrystallized from EtOH to give **2b** (5.70 g, 63%) as yellow crystals. Mp 127 °C; R_f 0.50 (7:3 *n*-hexane/CH_2Cl_2); ^1H NMR (360 MHz, $CDCl_3$, Me_4Si): δ (ppm) 8.27 (dd, 1H, J=2.0 Hz, J=8.3 Hz, arom), 8.20 (d, 1H, J=1.8 Hz, arom), 7.78 (d, 1H, J=8.4 Hz, arom), 7.66 (d, 1H, J=8.7 Hz, arom), 7.55–7.52 (m, 2H, arom), 2.10–1.95 (m, 4H, 2× CH_2Cq), 1.15–1.04 (m, 4H, 2× CH_2), 0.70–0.49 (m, 10H, 2× CH_2, 2× CH_3); ^{13}C NMR (90 MHz, $CDCl_3$): δ (ppm) 154.3, 151.5, 147.4, 146.4, 137.7, 130.7, 126.5, 123.6, 123.4, 122.4, 119.9, 118.2 (12C, arom), 55.9 (Cq), 39.7 (2× CH_2Cq), 25.8 (2× CH_2), 22.8 (2× CH_2), 13.7 (2× CH_3).

4.10. 2-Bromo-9,9-bis(2-ethylhexyl)-7-nitrofluorene (2c)

2-Bromo-9,9-bis-(ethylhexyl)-fluorene[29] (**1c**, 26.1 g, 55.6 mmol), SiO_2/H_2SO_4 (13.0 g), and HNO_3 (2.32 mL, 55.6 mmol) were reacted in CH_2Cl_2 (250 mL) according to general method A. The crude product was purified by silica gel chromatography in 9:1 *n*-hexane/CH_2Cl_2 and recrystallized from EtOH to give **2c** (17.8 g, 62%) as yellow crystals. Mp 69–71 °C; R_f 0.36 (isomeric mixture, 9:1 *n*-hexane/CH_2Cl_2); IR ν_{max} (KBr): 3444, 2959, 2925, 2870, 2857, 1598, 1517, 1456, 1335, 1081, 1062, 901, 822, 739, 431 cm^{-1}; ^1H NMR (360 MHz, $CDCl_3$, Me_4Si): δ (ppm) 8.28–8.26 (m, 2H, arom), 7.78 (d, 1H, J=8.6 Hz, arom), 7.66 (d, 1H, J=8.1 Hz, arom), 7.62–7.58 (m, 1H, arom), 7.54 (dd, 1H, J=1.4 Hz, J=8.1 Hz, arom), 2.10–1.98 (m, 4H, 2× CH_2Cq), 0.90–0.41 (m, 30H, 8× CH_2, 2× CH, 4× CH_3); ^{13}C NMR (90 MHz, $CDCl_3$): δ (ppm) 154.2, 151.6, 151.5, 151.4, 146.8, 146.5, 137.7, 130.6, 127.8, 127.7, 127.7, 123.3, 123.3, 123.1, 122.3, 119.9, 119.4, 119.3, 119.3 (12C, arom), 55.7 (Cq), 44.2 (2× CH_2Cq), 34.8 (2× CH), 33.7, 33.5 (2× CH_2), 28.0 (2× CH_2), 27.1, 26.9 (2× CH_2), 22.6, 22.6 (2× CH_2), 14.0, 13.8 (2× CH_3), 10.3, 10.2 (2× CH_3). ESI-HRMS: m/z calcd for $C_{29}H_{40}BrNO_2Na^+$ $[M+Na]^+$ 536.213. Found: 536.213.

4.11. 2-Amino-7-bromo-9,9-diethylfluorene (3a)[24]

Compound **2a** (1.40 g, 4.04 mmol), iron powder (676 mg, 12.1 mmol), and NH_4Cl (432 mg, 8.08 mmol) were reacted in aqueous ethanol (55 mL of alcohol and 15 mL of water) according to general method B. The crude product was purified by silica gel chromatography in 1:1 *n*-hexane/CH_2Cl_2, to give **3a** (1.00 g, 78%) as a yellow syrup; R_f 0.22 (1:1 *n*-hexane/CH_2Cl_2); ^1H NMR (360 MHz, $CDCl_3$, Me_4Si): δ (ppm) 7.41–7.37 (m, 4H, arom), 6.61–6.57 (m, 2H, arom), 3.73 (br s, 2H, NH_2), 1.96–1.81 (m, 4H, 2× CH_2), 0.31 (t, 6H, J=7.4 Hz, 2× CH_3); ^{13}C NMR (90 MHz, $CDCl_3$): δ (ppm) 151.3, 151.1, 146.3, 140.9, 131.3, 129.6, 125.7, 120.4, 119.5, 118.8, 113.9, 109.4 (12C, arom), 56.0 (Cq), 32.7 (2× CH_2), 8.3 (2× CH_3).

4.12. 2-Amino-7-bromo-9,9-dibutylfluorene (3b)[25]

Compound **2b** (4.00 g, 9.94 mmol), iron powder (1.66 g, 29.8 mmol), and NH_4Cl (1.06 g, 19.9 mmol) were reacted in aqueous ethanol (145 mL of alcohol and 40 mL of water) according to general method B. The crude product was purified by silica gel chromatography in 1:1 *n*-hexane/CH_2Cl_2, to give **3b** (2.81 g, 76%) as white crystals; mp 131 °C, (mp 131 °C; lit.[25]); R_f 0.20 (7:3 *n*-hexane/CH_2Cl_2); ^1H NMR (360 MHz, $CDCl_3$, Me_4Si): δ (ppm) 7.43 (dd, 1H, J=1.2 Hz, J=7.3 Hz, arom), 7.38–7.36 (m, 3H, arom), 6.66–6.63 (m, 2H, arom), 3.76 (br s, 2H, NH_2), 1.93–1.80 (m, 4H, 2× CH_2Cq), 1.13–1.03 (m, 4H, 2× CH_2), 0.70–0.53 (m, 10H, 2× CH_2, 2× CH_3); ^{13}C NMR (90 MHz, $CDCl_3$): δ (ppm) 152.3, 152.0, 146.3, 140.6, 131.3, 129.6, 125.8, 120.6, 119.6, 119.0, 114.0, 109.6 (12C, arom), 55.0 (Cq), 40.4 (2× CH_2Cq), 25.8 (2× CH_2), 23.0 (2× CH_2), 13.8 (2× CH_3).

4.13. 2-Amine-7-bromo-9,9-bis(2-ethylhexyl)fluorene (3c)[26]

Compound **2c** (20.0 g, 38.9 mmol), iron powder (6.53 g, 117 mmol), and NH_4Cl (4.16 g, 77.8 mmol) were reacted in aqueous ethanol (540 mL of alcohol and 150 mL of water) according to general method B. The crude product was purified by silica gel chromatography in 65:35 *n*-hexane/CH_2Cl_2, to give **3c** (15.1 g, 80%) as a yellow syrup; R_f 0.24, 0.29 and 0.35 (isomeric mixture, 7:3 *n*-

hexane/CH_2Cl_2); ^{1}H NMR (360 MHz, $CDCl_3$, Me_4Si): δ (ppm) 7.42–7.35 (m, 4H, arom), 6.64–6.59 (m, 2H, arom), 3.66 (br s, 2H, NH_2), 1.95–1.81 (m, 4H, 2× CH_2Cq), 0.94–0.70 (m, 22H), 0.60–0.52 (m, 8H); ^{13}C NMR (90 MHz, $CDCl_3$): δ (ppm) 152.0, 151.9, 151.8, 145.9, 145.9, 145.8, 140.7, 131.4, 131.3, 131.3, 129.5, 127.0, 126.9, 126.8, 120.5, 119.5, 118.4, 118.4, 118.3, 114.0, 110.6 (12C, arom), 54.7 (Cq), 44.6, 44.6 (2× CH_2Cq), 34.5 (2× CH), 33.5, 33.4 (2× CH_2), 28.1, 27.9 (2× CH_2), 27.0, 26.8 (2× CH_2), 22.7 (2× CH_2), 14.0 (2× CH_3), 10.3, 10.1 (2× CH_3).

4.14. 7-Bromo-9,9-dibutylfluorenyl-2-formamide (4b)

Compound **3b** (1.55 g, 4.16 mmol) and formic acid (943 μL, 25.0 mmol) were reacted according to general method C. The crude product was purified by silica gel chromatography in 97:3 CH_2Cl_2/acetone, to give **4b** (1.51 g, 91%) as white crystals; mp 150–152 °C; R_f 0.48 (95:5 CH_2Cl_2-acetone); IR ν_{max} (KBr): 3444, 2955, 2928, 2858, 2370, 2351, 2320, 1680, 1615, 1543, 1456, 1303, 1219, 1131, 1062, 813, 772 cm^{-1}; ^{1}H NMR (360 MHz, $CDCl_3$, Me_4Si, tautomeric mixture): δ (ppm) 8.77 (d, 0.44H, J=11.4 Hz), 8.50 (d, 0.44H, J=11.3 Hz), 8.42 (d, 0.44H, J=1.8 Hz), 7.64–7.42 (m, 5.24H), 7.08 (dd, 0.44H, J=2.0 Hz, J=8.1 Hz), 7.04 (d, 0.44H, J=1.8 Hz), 1.96–1.91 (m, 4H, 2× CH_2Cq), 1.79 (s, 0.56H, OH), 1.14–1.02 (m, 4H, 2× CH_2), 0.70–0.48 (m, 10H, 2× CH_2, 2× CH_3); ^{13}C NMR (90 MHz, $CDCl_3$): δ (ppm) 162.6, 158.8 (O=C–N, O–C=N), 152.8, 152.6, 152.4, 151.6, 139.5, 139.2, 137.5, 136.7, 136.5, 136.1, 130.1, 129.9, 126.1, 121.0, 120.9, 120.8, 120.7, 120.2, 118.7, 117.9, 114.5, 113.4 (12C, arom), 55.5 (Cq), 40.0 (2× CH_2Cq), 25.8 (2× CH_2), 22.9 (2× CH_2), 13.8 (2× CH_3). ESI-HRMS: m/z calcd for $C_{22}H_{26}BrNONa^+$ $[M+Na]^+$ 422.109. Found: 422.107.

4.15. 7-Bromo-9,9-bis(2-ethylhexyl)fluorenyl-2-formamide (4c)

Compound **3c** (3.00 g, 6.19 mmol) and formic acid (1.40 mL, 37.1 mmol) were reacted according to general method C. The crude product was purified by silica gel chromatography in 85:15 n-hexane/EtOAc, to give **4c** (3.09 g, 97%) as a colorless syrup; R_f 0.26, 0.32 and 0.37 (isomeric mixture, 8:2 n-hexane/EtOAc); IR ν_{max} (KBr): 3423, 2957, 2925, 2871, 2856, 1692, 1615, 1598, 1546, 1457, 1403, 1305, 1063, 812, 502 cm^{-1}; ^{1}H NMR (360 MHz, $CDCl_3$, Me_4Si): δ (ppm) 9.03 (d, 0.51H, J=11.3 Hz), 8.78–8.74 (m, 0.52H), 8.43 (d, 0.38H, J=1.6 Hz), 7.84–7.72 (m, 0.81H), 7.64–7.58 (m, 0.96H), 7.51–7.41 (m, 3.30H), 7.14–7.08 (m, 1.09H), 2.03–1.91 (m, 4H), 0.91–0.69 (m, 22H), 0.57–0.45 (m, 8H); ^{13}C NMR (90 MHz, $CDCl_3$): δ (ppm) 162.8, 158.9, 158.8, 158.8 (O=C–N, O–C=N), 152.6, 152.4, 152.2, 152.2, 152.1, 151.5, 151.4, 151.3, 139.6, 139.3, 137.7, 136.8, 136.2, 136.1, 135.6, 130.0, 129.8, 127.3, 120.8, 120.7, 120.6, 120.4, 120.1, 120.1, 120.0, 118.6, 118.5, 118.4, 118.1, 118.1, 118.0, 115.7, 114.5 (12C, arom), 55.3 (Cq), 44.4, 44.3 (2× CH_2Cq), 34.6 (2× CH), 33.5 (2× CH_2), 28.0, 27.9 (2× CH_2), 27.0, 26.9 (2× CH_2), 22.6 (2× CH_2), 14.0, 13.9 (2× CH_3), 10.3, 10.2 (2× CH_3). ESI-HRMS: m/z calcd for $C_{30}H_{42}BrNONa^+$ $[M+Na]^+$ 534.234. Found: 534.233.

4.16. 7-Bromo-9,9-dibutylfluorenyl-2-isocyanide (5b)

Compound **4b** (1.45 g, 3.62 mmol), diisopropylamine (1.37 mL, 9.77 mmol), and phosphoryl chloride (371 μL, 3.98 mmol) were reacted in CH_2Cl_2 (4 mL) according to general method D. The crude product was purified by silica gel chromatography in CH_2Cl_2, to give **5b** (1.29 g, 93%) as greenish crystals; mp 97–98 °C; R_f 0.51 (98:2 n-hexane/acetone); IR ν_{max} (KBr): 3434, 2952, 2931, 2857, 2122, 1674, 1599, 1455, 1426, 1404, 1379, 1270, 1131, 1109, 1062, 1008, 886, 816, 741, 500, 446 cm^{-1}; ^{1}H NMR (360 MHz, $CDCl_3$, Me_4Si): δ (ppm) 7.65 (d, 1H, J=8.0 Hz, arom), 7.55 (d, 1H, J=8.6 Hz, arom), 7.50–7.48 (m, 2H, arom), 7.36 (dd, 1H, J=1.8 Hz, J=8.0 Hz, arom), 7.32 (d, 1H, J=1.3 Hz, arom), 1.94 (t, 4H, J=8.4 Hz, 2× CH_2Cq), 1.14–1.04 (m, 4H, 2× CH_2), 0.69 (t, 6H, J=7.3 Hz, 2× CH_3), 0.61–0.48 (m, 4H, 2× CH_2); ^{13}C NMR (90 MHz, $CDCl_3$): δ (ppm) 164.1 (CN), 153.2, 151.7, 141.2, 138.3, 130.4, 126.3, 125.6, 122.4, 121.6, 121.0, 120.4 (12C, arom), 55.7 (Cq), 39.9 (2× CH_2Cq), 25.8 (2× CH_2), 22.9 (2× CH_2), 13.7 (2× CH_3). ESI-HRMS: m/z calcd for $C_{22}H_{25}BrN^+$ $[M+H]^+$ 382.116. Found: 382.115.

4.17. 7-Bromo-9,9-bis(2-ethylhexyl)fluorenyl-2-isocyanide (5c)

Compound **4c** (3.00 g, 5.85 mmol), diisopropylamine (2.21 mL, 15.8 mmol), and phosphoryl chloride (600 μL, 6.44 mmol) were reacted in CH_2Cl_2 (6.5 mL) according to general method D. The crude product was purified by silica gel chromatography in 96:4 n-hexane/EtOAc, to give **5c** (2.63 g, 91%) as greenish crystals; mp 57–61 °C; R_f 0.55 (isomeric mixture, 96:4 n-hexane/EtOAc); IR ν_{max} (KBr): 3430, 2958, 2925, 2871, 2857, 2365, 2310, 2121, 1680, 1614, 1523, 1457, 1340, 1306, 1064, 814, 418 cm^{-1}; ^{1}H NMR (360 MHz, $CDCl_3$, Me_4Si): δ (ppm) 7.65 (d, 1H, J=8.4 Hz, arom), 7.56–7.52 (m, 2H, arom), 7.48 (dd, 1H, J=1.6 Hz, J=8.1 Hz, arom), 7.38–7.35 (m, 2H, arom), 2.02–1.90 (m, 4H, 2× CH_2Cq), 0.90–0.70 (m, 22H), 0.55–0.51 (m, 6H), 0.48–0.40 (m, 2H); ^{13}C NMR (90 MHz, $CDCl_3$): δ (ppm) 164.0 (CN), 153.1, 153.0, 151.7, 151.6, 151.5, 141.3, 138.4, 130.3, 127.6, 127.5, 127.4, 125.6, 125.5, 124.8, 122.1, 122.0, 122.0, 121.8, 121.5, 120.3 (12C, arom), 55.4 (Cq), 44.3 (2× CH_2Cq), 34.7 (2× CH), 33.6, 33.4 (2× CH_2), 28.0, 27.9 (2× CH_2), 27.1, 26.9 (2× CH_2), 22.6 (2× CH_2), 14.0, 13.9 (2× CH_3), 10.3, 10.2 (2× CH_3). ESI-HRMS: m/z calcd for $C_{30}H_{41}BrN^+$ $[M+H]^+$ 494.242. Found: 494.237.

4.18. *N*-(4-Bromo-phenyl)-2-(7-bromo-9,9-diethylfluoren-2-yl)-isoindole-1-carboxamide (7a)

Amine **3a** (718 mg, 2.27 mmol), isocyanide (**5a**, 826 mg, 4.54 mmol), OPA (305 mg, 2.27 mmol), and $NaHSO_3$ (489 mg, 4.70 mmol) were reacted in a mixture of DMSO/H_2O/CH_3CN (5 mL/5 mL/6 mL) according to general method E. The crude product was purified by silica gel chromatography in 1:1 n-hexane/CH_2Cl_2, to give **7a** (900 mg, 65%) as beige crystals; mp 230–232 °C; R_f 0.56 (3:7 n-hexane/CH_2Cl_2); IR ν_{max} (KBr): 3436, 3410, 3328, 3116, 3055, 2958, 2927, 2873, 2852, 1670, 1585, 1508, 1488, 1459, 1416, 1404, 1352, 1305, 1239, 1210, 1132, 1100, 1071, 1006, 876, 821, 767, 737, 553, 502, 441 cm^{-1}; ^{1}H NMR (360 MHz, $CDCl_3$, Me_4Si): δ (ppm) 8.10 (dd, 1H, J=0.8 Hz, J=8.7 Hz, NH), 7.82 (d, 1H, J=8.0 Hz, arom), 7.67 (d, 1H, J=8.5 Hz, arom), 7.62 (d, 1H, J=8.0 Hz, arom), 7.53–7.48 (m, 4H, arom), 7.41 (d, 1H, J=2.0 Hz, arom), 7.33–7.23 (m, 6H, arom), 7.17–7.13 (m, 1H, arom), 2.02–1.96 (q, 4H, 2× CH_2), 0.32 (t, 6H, J=7.4 Hz, 2× CH_3); ^{13}C NMR (90 MHz, $CDCl_3$): δ (ppm) 158.8 (CO), 152.5, 151.2, 141.4, 139.0, 139.0, 137.2, 131.8, 130.5, 128.2, 126.4, 125.7, 125.0, 124.4, 122.8, 122.2, 121.6, 121.3, 120.8, 120.5, 120.4, 119.6, 116.2 (26C, arom), 56.8 (Cq), 32.5 (2× CH_2), 8.4 (2× CH_3). ESI-HRMS: m/z calcd for $C_{32}H_{26}Br_2N_2ONa^+$ $[M+Na]^+$ 635.030. Found: 635.031.

4.19. *N*-(7-Bromo-9,9-dibutylfluoren-2-yl)-2-(7-bromo-9,9-dibutylfluoren-2-yl)-isoindole-1-carboxamide (7b)

Amine **3b** (718 mg, 1.93 mmol), isocyanide (**5b**, 1.48 g, 3.86 mmol), OPA (259 mg, 1.93 mmol), and $NaHSO_3$ (416 mg, 4.00 mmol) were reacted in a mixture of DMSO/H_2O/CH_3CN (4 mL/4 mL/5 mL) according to general method E. The crude product was purified by aluminum oxide chromatography in 94:6 n-hexane/acetone, to give **7b** (778 mg, 46%) as yellow crystals; mp 223–224 °C; R_f 0.20 (94:6 n-hexane/acetone); IR ν_{max} (KBr): 3402, 2954, 2928, 2857, 2119, 1634, 1591, 1530, 1489, 1458, 1429, 1404, 1349, 1302, 1253, 1207, 1129, 1062, 1005, 886, 812, 771, 732, 533, 436 cm^{-1}; ^{1}H NMR (360 MHz, Py-d, Me_4Si): δ (ppm) 10.71 (s, 1H,

N*H*), 8.38 (d, 1H, *J*=8.7 Hz, arom), 8.25 (br s, 1H, arom), 8.21 (dd, 1H, *J*=1.5 Hz, *J*=8.3 Hz, arom), 7.95 (d, 1H, *J*=1.5 Hz, arom), 7.90–7.87 (m, 3H, arom), 7.82–7.80 (m, 2H, arom), 7.76–7.71 (m, 3H, arom), 7.68 (dd, 1H, *J*=1.6 Hz, *J*=8.1 Hz, arom), 7.63–7.59 (m, 2H, arom), 7.27–7.14 (m, 2H, arom), 2.13–1.97 (m, 8H, 4× CH_2Cq), 1.10–0.71 (m, 16H, 8× CH_2) 0.63 (t, 6H, *J*=7.2 Hz, 2× CH_3), 0.56 (t, 6H, *J*=7.2 Hz, 2× CH_3); ^{13}C NMR (90 MHz, Py-d): *δ* (ppm) 160.6 (*C*O), 154.5, 153.9, 152.4, 152.2, 141.2, 141.0, 140.8, 140.7, 140.2, 131.2, 130.9, 128.0, 127.2, 127.0, 125.8, 125.2, 125.2, 123.0, 122.6, 122.6, 121.9, 121.8, 121.3, 121.2, 121.1, 120.8, 120.3, 119.7, 118.8, 114.9 (32C, arom), 56.5, 56.3 (2× Cq), 40.7, 40.4 (4× *C*H_2Cq), 26.8 (4× *C*H_2), 23.6 (4× *C*H_2), 14.3, 14.3 (4× *C*H_3). ESI-HRMS: *m*/*z* calcd for $C_{51}H_{54}Br_2N_2ONa^+$ $[M+Na]^+$ 891.250. Found: 891.249.

Monobrominated derivative of **7b**: (*N*-(9,9-dibutylfluoren-2-yl)-2-(7-bromo-9,9-dibutylfluoren-2-yl)-isoindole-1-carboxamide or *N*-(7-bromo-9,9-dibutylfluoren-2-yl)-2-(9,9-dibutylfluoren-2-yl)-isoindole-1-carboxamide): ESI-HRMS: *m*/*z* calcd for $C_{51}H_{55}BrN_2ONa^+$ $[M+Na]^+$ 813.339. Found: 813.335.

Bromine-free derivative of **7b**: (*N*-(9,9-dibutylfluoren-2-yl)-2-(9,9-dibutylfluoren-2-yl)-isoindole-1-carboxamide): ESI-HRMS: *m*/*z* calcd for $C_{51}H_{56}N_2ONa^+$ $[M+Na]^+$ 735.428. Found: 735.425.

4.20. *N*-[7-Bromo-9,9-bis(2-ethylhexyl)-fluoren-2-yl]-2-[7-bromo-9,9-bis(2-ethylhexyl)-fluoren-2-yl]-isoindole-1-carboxamide (7c)

Amine **3c** (1.21 g, 2.50 mmol), isocyanide (**5c**, 2.47 g, 5.00 mmol), OPA (335 mg, 2.50 mmol), and $NaHSO_3$ (539 mg, 5.18 mmol) were reacted in a mixture of DMSO/H_2O/CH_3CN (6 mL/6 mL/8 mL) according to general method E. The crude product was purified by aluminum oxide chromatography in 85:15 *n*-hexane/CH_2Cl_2, to give **7c** (280 mg, 10%) as a brown solid spume; R_f 0.44 (8:2 *n*-hexane/CH_2Cl_2); IR ν_{max} (KBr): 3415, 2956, 2925, 2855, 1668, 1615, 1589, 1523, 1486, 1458, 1425, 1348, 1302, 1202, 1127, 1062, 1006, 881, 812, 765, 730, 535, 441 cm^{-1}; ^{1}H NMR (360 MHz, $CDCl_3$, Me_4Si): *δ* (ppm) 8.17–8.11 (m, 1H, N*H*), 7.78–7.11 (m, 17H, arom), 2.02–1.93 (m, 8H, 4× *C*H_2Cq), 0.92–0.52 (m, 60H, 4× *C*H, 16× *C*H_2, 8× *C*H_3); ^{13}C NMR (90 MHz, $CDCl_3$): *δ* (ppm) 158.4, 158.3 (*C*O), 153.1–151.3, 141.0–135.8, 130.3–114.6 (32C, arom), 55.5, 55.4, 55.2 (2× Cq), 44.6, 44.4, 44.2 (4× *C*H_2Cq), 34.8, 34.6, 34.5 (4× *C*H), 34.0, 33.7, 33.6, 33.5 (4× *C*H_2), 28.4, 28.0 (4× *C*H_2), 27.1, 27.0, 26.9 (4× *C*H_2), 22.8, 22.7 (4× *C*H_2), 14.3, 14.3 (4× *C*H_3), 10.4, 10.2, 10.1 (4× *C*H_3). ESI-HRMS: *m*/*z* calcd for $C_{67}H_{86}Br_2N_2ONa^+$ $[M+Na]^+$ 1115.500. Found: 1115.499.

Monobrominated derivative of **7c**: (*N*-[9,9-bis(2-ethylhexyl)-fluoren-2-yl]-2-[7-bromo-9,9-bis(2-ethylhexyl)-fluoren-2-yl]-isoindole-1-carboxamide or *N*-[7-bromo-9,9-bis(2-ethylhexyl)-fluoren-2-yl]-2-[9,9-bis(2-ethylhexyl)-fluoren-2-yl]-isoindole-1-carboxamide): ESI-HRMS: *m*/*z* calcd for $C_{67}H_{87}BrN_2ONa^+$ $[M+Na]^+$ 1037.589. Found: 1037.593.

Bromine-free derivative of **7c**: (*N*-[9,9-bis(2-ethylhexyl)-fluoren-2-yl]-2-[9,9-bis(2-ethylhexyl)-fluoren-2-yl]-isoindole-1-carboxamide): ESI-HRMS: *m*/*z* calcd for $C_{67}H_{88}N_2ONa^+$ $[M+Na]^+$ 959.679. Found: 959.680.

4.21. Oligo[*N*-(1,4-phenylene)-2-(9,9-diethylfluorenene-2,7-diyl)-isoindolene-1-carboxamide] (8a)

Monomer **7a** (270 mg, 0.440 mmol), Ni(cod)$_2$ (132 mg, 0.480 mmol), 2,2′-bipyridine (75 mg, 0.480 mmol), and 1,5-cyclooctadiene (59 μL, 0.480 mmol) were reacted in a mixture of dry DMF/dry toluene (6 mL/10 mL) according to general method F. The crude product was purified by recrystallization from 1:1 CH_2Cl_2/*n*-hexane, to give **8a** (120 mg, 60%) as a gray powder; IR ν_{max} (KBr): 3410, 3030, 2961, 2922, 2874, 2852, 1655, 1590, 1520, 1500, 1468, 1418, 1339, 1313, 1237, 1203, 1128, 1107, 1004, 883, 816, 762, 738, 522 cm^{-1}; ^{1}H NMR (360 MHz, $CDCl_3$, Me_4Si): *δ* (ppm) 8.32–6.84 (m, 16H, N*H*, arom), 2.36–1.49 (m, 4H, 2× CH_2), 0.62–0.28 (m, 6H, 2× CH_3); ^{13}C NMR (90 MHz, $CDCl_3$): *δ* (ppm) 158.8 (*C*O), 151.8–116.4 (26C, arom), 56.6, 56.5 (Cq), 32.5 (2× *C*H_2), 8.5 (2× *C*H_3).

4.22. Oligo[*N*-(9,9-dibutylfluorene-2,7-diyl)-2-(9,9-dibutylfluorene-2,7-diyl)-isoindolene-1-carboxamide] (8b)

Monomer **7b** (250 mg, 0.287 mmol), Ni(cod)$_2$ (86 mg, 0.313 mmol), 2,2′-bipyridine (49 mg, 0.313 mmol), and 1,5-cyclooctadiene (38 μL, 0.313 mmol) were reacted in a mixture of dry DMF/dry toluene (3 mL/3 mL) according to general method F. The crude product was purified by aluminum oxide chromatography, first in 8:2 *n*-hexane/acetone and then in 9:1 CH_2Cl_2/MeOH, to give **8b** (61 mg, 30%) as a brownish gray powder; IR ν_{max} (KBr): 3394, 2954, 2928, 2858, 1706, 1613, 1530, 1489, 1463, 1376, 1299, 1186, 1065, 1036, 991, 926, 887, 815, 755, 634 cm^{-1}; ^{1}H NMR (360 MHz, $CDCl_3$, Me_4Si): *δ* (ppm) 8.31–6.77 (m, 18H, N*H*, arom), 2.24–1.60 (m, 8H, 4× CH_2Cq), 1.26–0.61 (m, 28H, 8× CH_2, 4× CH_3); ^{13}C NMR (90 MHz, $CDCl_3$): *δ* (ppm) 158.7 (*C*O), 153.3–113.5 (32C, arom), 55.3, 55.2, 55.1, 55.0 (2× Cq), 40.0, 40.0, 39.9, 39.7 (4× *C*H_2Cq), 25.9, 25.8 (4× *C*H_2), 22.9, 22.8 (4× *C*H_2), 13.7, 13.6 (4× *C*H_3).

4.23. Oligo{*N*-[9,9-bis(2-ethylhexyl)fluorene-2,7-diyl]-2-[9,9-bis(2-ethylhexyl)fluorene-2,7-diyl]-isoindolene-1-carboxamide} (8c)

Monomer **7c** (250 mg, 0.228 mmol), Ni(cod)$_2$ (68 mg, 0.249 mmol), 2,2′-bipyridine (39 mg, 0.249 mmol), and 1,5-cyclooctadiene (31 μL, 0.249 mmol) were reacted in a mixture of dry DMF/dry toluene (2 mL/2 mL) according to general method F. The crude product was purified by aluminum oxide chromatography, first in 7:3 *n*-hexane/CH_2Cl_2 and then in 95:5 CH_2Cl_2/MeOH, to give **8c** (60 mg, 28%) as a brown syrup; IR ν_{max} (KBr): 3389, 2956, 2925, 2856, 1768, 1706, 1613, 1531, 1456, 1377, 1302, 1255, 1194, 1064, 1037, 887, 814, 756, 740, 695, 634, 500 cm^{-1}; ^{1}H NMR (360 MHz, $CDCl_3$, Me_4Si): *δ* (ppm) 8.24–6.96 (m, 18H, N*H*, arom), 2.04–1.92 (m, 8H, 4× CH_2Cq), 0.90–0.52 (m, 60H, 4× *C*H, 16× *C*H_2, 8× *C*H_3); ^{13}C NMR (90 MHz, $CDCl_3$): *δ* (ppm) 158.4 (*C*O), 153.0–151.3 (9 peaks), 142.2, 141.0–140.7 (5 peaks), 139.9, 138.8, 137.7, 137.6, 135.8, 135.8, 135.7, 130.3, 129.7, 128.6, 127.5–125.0 (11 peaks), 124.3, 122.6, 121.9, 121.8, 121.4, 120.3, 120.1, 119.9, 119.6, 119.5, 118.0, 117.9, 117.7, 117.1, 116.8, 116.7, 114.7 (32C, arom), 55.5, 55.4, 55.3, 55.2, 54.9 (2× Cq), 44.6, 44.5, 44.4 (4× *C*H_2Cq), 34.8, 34.6, 34.6 (4× *C*H), 34.0, 33.5 (4× *C*H_2), 28.4, 28.0 (4× *C*H_2), 27.1, 27.0, 26.8 (4× *C*H_2), 22.8, 22.7 (4× *C*H_2), 14.0 (4× *C*H_3), 10.3, 10.2, 10.1 (4× *C*H_3).

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Supplementary data

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