Symmetrical Electron-Deficient Materials Incorporating Azaheterocycles

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Abstract: To investigate the potential of di- and tri-azaheterocycles as building blocks for π-conjugated materials with high electron affinity, linear oligomers incorporating pyrazine and a C_3-symmetric discotic molecule based on triazine were synthesized. The tridodecyloxyphenyl end-capped ethynylene pyrazinylene oligomers showed remarkable solvatochroism in absorption and emission in solution. The oligomers containing one and two pyrazine rings displayed liquid crystallinity in the solid state. The largest ethynylene pyrazinylene oligomer containing three pyrazine rings had the lowest first reduction potential at −1.08 V. The triazine-derived discotic molecule exhibited UV/Vis and fluorescence behavior comparable to that of the linear oligomers and featured a first reduction potential at −1.49 V, somewhat lower than expected.

Keywords: conjugation · electron-deficient compounds · liquid crystals · nitrogen heterocycles · oligomers

Introduction

The application of π-conjugated materials in electronic devices such as field-effect transistors[1] and light-emitting diodes[2] has gained much attention over the last two decades. Their ease of modification and good processability potentially help to reduce costs of the devices while on the other hand the flexibility and, therefore, the applicability of the devices might be enhanced. Most organic semiconductors reported so far exhibit *p*-type characteristics. However, for the fabrication of real ′plastic electronics′, for example, bipolar transistors, *p*-*n* junction diodes or complementary circuits, both *p*-type (electron-rich) and *n*-type (electron-deficient) materials are needed. For use as the *n*-type semiconductors in these devices, materials like C_{60},[3] and naphthalene-1,4,5,8-tetracarboxylic dianhydride[4] have been proposed, but these structures cannot be used in air and are also sparingly soluble. In fact, it is the environmental sensitivity, low field mobility and difficult synthesis of the *n*-type materials which has hampered major progress in this field.[5] Recently, however, the groups of Bao,[6] Katz,[7] and Friend[8] described organic *n*-type semiconductors which were air stable, showed field mobilities of around 10^{-2} cm^2 V^{-1} s^{-1} and could be applied in thin film transistors by means of vapor deposition. In all these cases fluorine atoms were used to increase the electron deficiency of the π-conjugated system.[9] Even sexithiophene, normally used as a *p*-type material, was transformed into an *n*-type material in this manner.[10]

In principle, azaheterocycles can be used as the electron-deficient units in π-conjugated materials. However, to obtain materials which are stable under ambient conditions, azaheterocyclic structures must be synthesized with first reduction potentials of around −0.5 V.[11] Although the suitability of azaheterocycles as the basic building blocks for *n*-type materials was shown by Yamamoto and co-workers,[12] the use of azaheterocycles such as pyridine,[13] triazine[14] and quinoline[15] has only been of limited value in polymer light emitting diodes. Pyrazine especially has hardly been implemented in electronic devices,[16] which might be the direct result of difficulties encountered in the synthesis of functionalized pyrazine monomers and polymers. This is illustrated by the fact that, to our knowledge, only one polypyrazine has been described up to now,[17] while reports of pyrazine-containing copolymers are also scarce.[16,18] The electron-deficient nature of *s*-triazine has led to the successful use of this compound as a central acceptor group in the field of nonlinear optics.[19,20] Recently, we started a program to explore the potential of azaheterocycles as the electron-deficient building block for *n*-type materials.[21] We now report on the synthesis and characterization of well-defined oligomers containing pyrazine or triazine as azaheterocycles.

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Results and Discussion

Synthesis: For the synthesis of the pyrazine oligomers, the ethynylene moiety was introduced as a coupling unit between the pyrazine rings and end-capped by tridodecyloxyphenyl moieties. This should induce liquid crystallinity in the oligomers and, therefore, can help to organize the molecules in the solid phase. Instead of using the C_2-symmetric pyrazine unit as the electron-deficient building block, *s*-triazine should also be capable of fulfilling that role. Its C_3-symmetry leads to the formation of discotic molecules. The latter generally feature liquid-crystalline mesophases over broader temperature ranges than their linear analogues of similar size. However, due to the *meta*-substitution of the triazine unit, the effective conjugation length will be limited to just one branch of the discotic molecule.

As a first building block the synthesis of a monosubstituted pyrazine derivative was programmed. The reaction of equimolar amounts of 2,5-dibromopyrazine and 3,4,5-tridodecyloxyphenylacetylene (**5**),[22] using $[Pd(PPh_3)_4]$ as the catalyst,[23] however, led mainly to the formation of a disubstituted pyrazine **1** (Scheme 1).

To allow the synthesis of longer oligomers, monosubstitution of the pyrazine unit is a prerequisite. An elegant solution to this problem would be the preparation of a pyrazine building block containing two different halogens, since the latter would also imply a difference in reactivity of the two substituents. Therefore, 5-bromo-2-iodopyrazine (**6**) was synthesized by a diazotation reaction starting from 5-bromopyrazine-2-amine (Scheme 1). Although initial yields were low, asymmetric pyrazine **6** could be prepared in 41 % yield after some adaptations of the reaction procedure. Using asymmetric pyrazine **6** as the starting material and Sonogashira reaction conditions,[24] monosubstituted pyrazine **7** could, indeed, be synthesized in high yield and selectivity. After pyrazine **7** had been allowed to react with trimethylsilylacetylene, the trimethylsilyl group of the obtained pyrazine derivative **8** was removed with tetrabutylammonium fluoride. Even though the deprotection step should be quantitative, compound **9** was obtained in only 47 % yield, presumably due to degradation of the product during the chromatographic purification. To further elongate the π-conjugated system and finalize the synthetic route towards oligomer **2**, pyrazine derivative **9** was subsequently coupled to 5-bromo-2-iodopyrazine, followed by a reaction with 3,4,5-tridodecyloxyphenylacetylene to end-cap the oligomer.

To prepare the next oligomer in this series, disubstituted pyrazine **11** was first synthesized starting from 2,5-dibromopyrazine and trimethylsilylacetylene (Scheme 1). After removal of the trimethylsilyl protecting groups by treatment with tetrabutylammonium fluoride, 2,5-diethynylpyrazine (**12**) was obtained, again only in a moderate yield after purification by column chromatography. The desired ethynylene pyrazinylene oligomer could then be synthesized by coupling **12** with two equivalents of bromopyrazine **7**, affording **3** in 47 % yield.

The discotic molecule **4** was obtained after nucleophilic substitution of the triazine ring by reaction of cyanuric fluoride with three equivalents of the appropriate acetylide (Scheme 1).[19] The latter was prepared in modest yield at low temperature by the addition of *n*-butyllithium to a solution of a 3,4,5-tridodecyloxyphenylacetylene in THF.

The final products were fully characterized by ^{1}H and ^{13}C NMR, UV/Vis, and IR spectroscopy, MALDI-TOF mass spectrometry, and elemental analysis. ^{1}H NMR spectra of the obtained oligomers **1, 2** and **3** featured signals of the pyrazine protons around $\delta = 8.8$ ppm. The signals at highest field could be assigned to the protons closest to the electron-releasing tridodecyloxyphenyl group. Extension of the oligomers from one to three pyrazine rings, led to a downfield shift of the protons closest to the center of the molecule due to the electron-withdrawing nature of the pyrazine rings.

Thermotropic properties: To investigate the assumed liquid crystalline behavior of the oligomers, their melting behavior was examined by differential scanning calorimetry (DSC) measurements and polarization microscopy. The smallest oligomer **1** showed a liquid crystalline mesophase from 13.5 °C ($\Delta H = 24$ kJ mol^{-1}) to 40.1 °C ($\Delta H = 13$ kJ mol^{-1}) during the second heating run (Figure 1), while the cooling run was reversible and revealed transitions at 33.9 °C ($\Delta H = -10$ kJ mol^{-1}) and 4.9 °C ($\Delta H = -16$ kJ mol^{-1}). Oligomer **2** exhibited two mesophases; the melting peak of the dodecyloxy tails was observed at 36.3 °C ($\Delta H = 4.9$ kJ mol^{-1}), while a transition from one mesophase to another was found at 58.3 °C ($\Delta H = 1.0$ kJ mol^{-1}). Both DSC measurements as well as polarization microscopy revealed a clearing temperature of 70.2 °C ($\Delta H = 0.9$ kJ mol^{-1}). The cooling run featured the same transitions, but the crystallization peak at 14.5 °C ($\Delta H = -2.5$ kJ mol^{-1}) was smaller than its corresponding melting peak. The latter might mean that **2** cannot crystallize in its preferred orientation, which in turn might explain the recrystallization peak observed in the heating run. The mesomorphic behavior exhibited by oligomer **2** is not unusual; molecules with rigid rod-like cores and half-disc shaped mesogenic endgroups have been shown previously to display nematic, smectic, cubic and columnar hexagonal mesophases.[25] Therefore, it was even more surprising that oligomer **3** revealed no liquid crystalline behavior at all; it featured

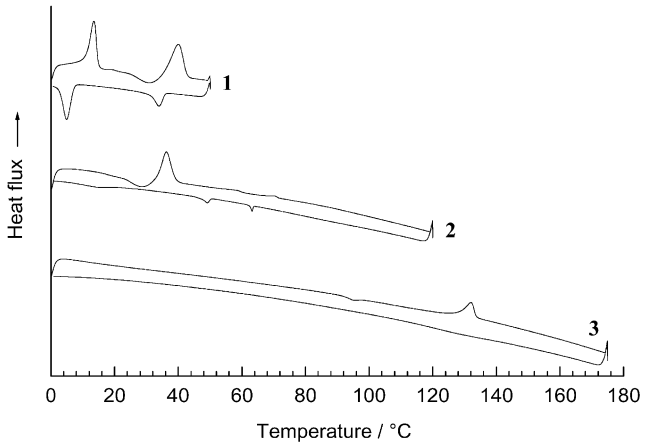
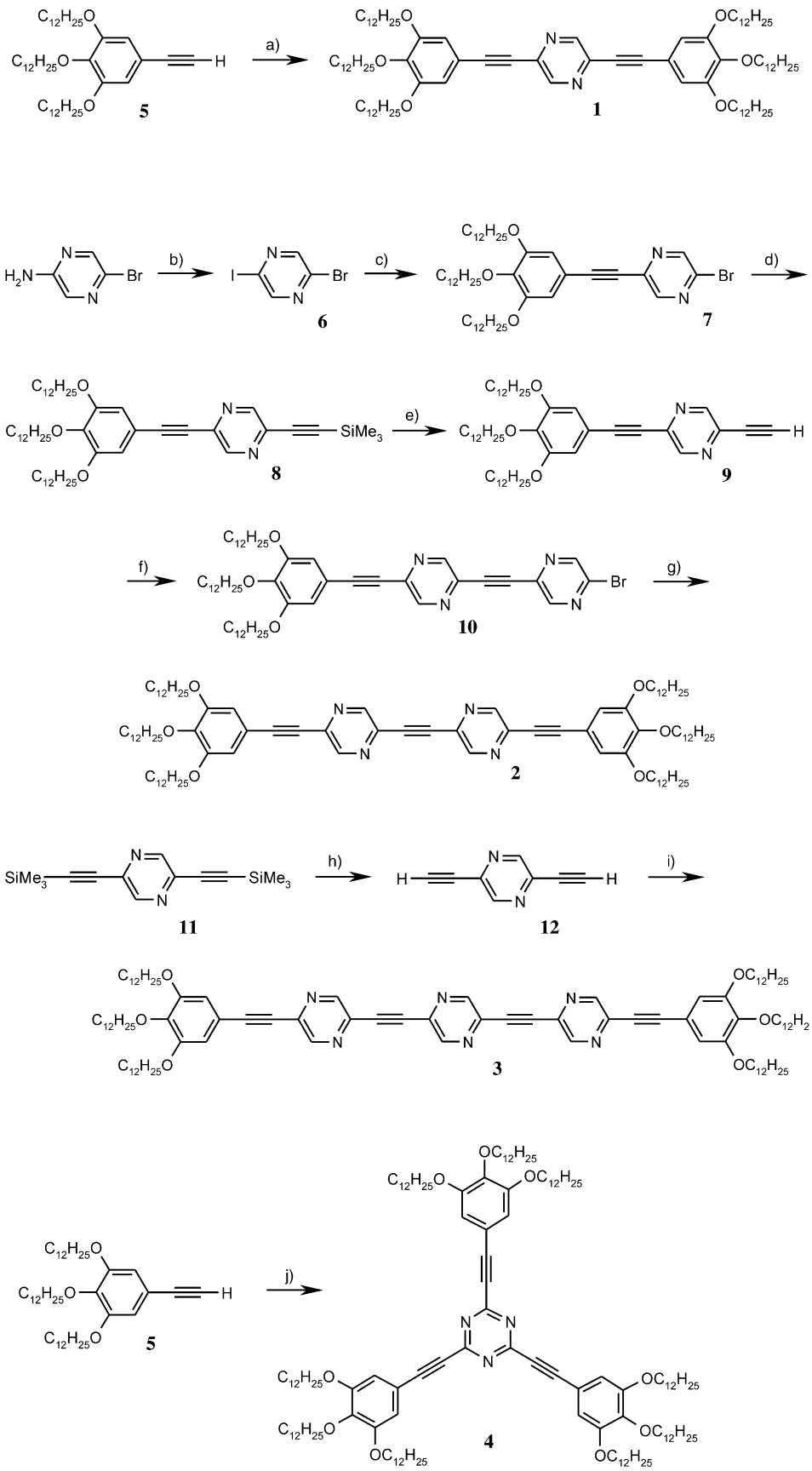


Figure 1. DSC thermograms of oligomers **1, 2**, and **3**.



Scheme 1. a) $[Pd(PPh_3)_4]$, KOAc, DMF/toluene, reflux, 2 h; 37 %; b) 5-bromopyrazinamine, I_2, HI, $NaNO_2$, 0 °C, 3 h; 41 %; c) **5**, $[Pd(PPh_3)_2Cl_2]$, CuI, Et_3N, 20 °C, 2 h; 94 %; d) trimethylsilylacetylene, $[Pd(PPh_3)_2Cl_2]$, CuI, Et_3N, 60 °C, 45 min; 63 %; e) Bu_4NF, THF, 20 °C, 10 min; 47 %; f) **6**, $[Pd(PPh_3)_2Cl_2]$, CuI, Et_3N, 70 °C, 20 min; 56 %; g) **5**, $[Pd(PPh_3)_2Cl_2]$, CuI, Et_3N, reflux, 1 h; 14 %; h) Bu_4NF, THF, 20 °C, 1 min; 50 %; i) **7**, $[Pd(PPh_3)_2Cl_2]$, CuI, Et_3N, reflux, 2 h; 47 %; j) *n*BuLi, THF, −78 °C, cyanuric fluoride, 20 °C, 2 h; 23 %.

only a crystalline to isotropic transition at 132.0 °C ($\Delta H =$ 15 kJ mol^{-1}) in the heating run. The latter was confirmed by polarization microscopy of the isotropic melt, which clearly showed the growth of crystalline needles upon cooling. Similar to **2**, oligomer **3** only revealed a broad crystallization peak on the cooling runs and a recrystallization peak around 90 °C in the heating runs. The melting behavior of discotic compound **4** was also investigated by DSC and polarization microscopy (Figure 2) and showed a liquid crystalline mesophase from 22.9 °C ($\Delta H = 32$ kJ mol^{-1}) to 60.3 °C ($\Delta H = 5.5$ kJ mol^{-1}) on the heating run. The cooling run was reversible and featured transitions at 56.6 °C ($\Delta H = -5.4$ kJ mol^{-1}) and 16.2 °C ($\Delta H = -29$ kJ mol^{-1}). The temperature range of the liquid crystalline state was similar to the one observed for oligomer **2**, despite the C_3 symmetry of **4**. The latter might be a direct result of the shape of the core, which has only a small π–π overlap with neighboring discs.

Although a hexagonal columnar arrangement of the molecules in the mesophase seems logical, the texture observed by polarization microscopy displayed a pattern unlike those seen for other discotic molecules. Therefore, a more in-depth investigation of the liquid crystalline behavior of discotic molecule **4** was initiated by measuring X-ray diffraction patterns at different temperatures (Figure 3). The experiments clearly revealed a change in intensity and in width of the peaks around 55 °C, which was rationalized by the transition from the liquid crystalline phase to the isotropic melt. The effect of the melting of the alkoxy tails on the X-ray diffraction patterns was less pronounced and could be observed around 15 °C by the disappearance of the peak at 10.5°. At low temperatures the X-ray diffraction patterns revealed low intensity signals between 2 and 6° (Figure 3, inset), which could be assigned to higher order reflections. Unfortunately, these reflections also disappeared around 15 °C and, hence, exact determination of the liquid crystalline phase was not possible. The thermal stability of **4** was determined by thermal gravimetric analysis (TGA), which revealed no degradation below 300 °C.

Optical properties: To determine the optical properties of the oligomers in solution, UV/Vis, excitation and fluorescence spectra were measured (Table 1). As expected, the λ_{max} values increased with increasing length of the oligomers, due to the extension of the π-conjugated system. Bathochromic shifts were observed for all λ_{max} values when the spectra measured in the polar solvents were compared to those in hexane, the red shift, however, being larger for the chloroform solutions. The λ_{max} values of the excitation spectra

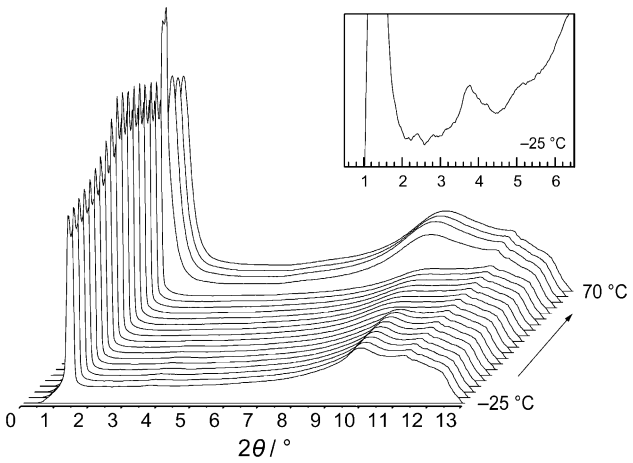


Figure 3. Circularly integrated X-ray diffraction patterns of neat **4** at different temperatures.

Table 1. Spectroscopic data of **1**–**4**.

Compd	Solvent	UV/Vis λ_{max} [nm^{-1}] (ε [L^{-1} mol^{-1} cm^{-1}])	Excitation λ_{max} [nm^{-1}]	Fluorescence λ_{max} [nm^{-1}]
1	hexane	369 (4.9×10^4)	384	409
	chloroform	383 (4.7×10^4)	389	484
	tetrahydrofuran	376 (4.8×10^4)	386	472
2	hexane	380 (6.6×10^4)	390	438
	chloroform	396 (6.0×10^4)	396	535
	tetrahydrofuran	393 (6.4×10^4)	392	536
3	hexane	395 (8.8×10^4)	391	451
	chloroform	404 (8.2×10^4)	400	579
	tetrahydrofuran	397 (8.9×10^4)	396	579
4	hexane	358 (8.3×10^4)	358	399
	chloroform	370 (6.8×10^4)	373	514

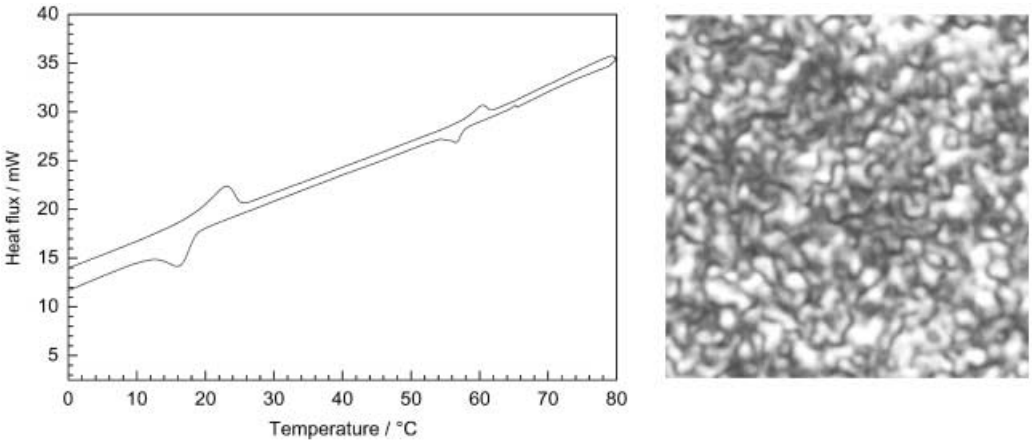


Figure 2. DSC thermogram of star-shaped **4** (left) and the texture of the liquid crystalline mesophase as observed by polarization microscopy at 32 °C (right).

showed less solvent dependency than those of the UV/Vis spectra, but the trends displayed by both were comparable.

In contrast to the excitation spectra, the fluorescence spectra of the oligomers revealed a strong solvent dependency of the λ_{max} values (Table 1). The Stokes shift of the longest oligomer **3** tripled, going from the hexane to the THF solution (Figure 4). The intensity of the emission bands was also directly related to the polarity of the solvent and showed a decrease with increasing polarity. Again, the strongest effects were observed for oligomer **3** (Table 1). The strong solvent dependency of the Stokes shift as well as the fluorescence intensity could point to the occurrence of a twisted intramolecular charge transfer (TICT) state. The latter has been observed previously for other donor–acceptor substituted ethynylene derivatives[26] and is due to the interconversion from a locally excited to a charge transfer state, facilitated by rotation about a bond. The charge transfer state, which is stabilized by polar solvents, could in our case lead to energy dissipation by nonradiative pathways and thus explain the difference in fluorescence intensity between solutions of the oligomers in polar and apolar solvents.

UV/Vis spectra of discotic molecule **4** in hexane and chloroform solutions featured λ_{max} values of 358 nm and 370 nm (Table 1, Figure 5), respectively, and were similar to those found for smallest linear oligomer **1**. The latter is in agreement with the limited π-conjugation in discotic compound **4** as a consequence of the *meta*-substitution of the triazine unit.

Fluorescence spectroscopy revealed the same solvent dependent emission behavior as observed for the linear oligomers, showing an increase of the Stokes shift and a decrease in emission intensity with increasing solvent polarity (Figure 5). Moreover, in contrast to the linear oligomers, the λ_{max} values of the excitation spectra of **4** also exhibited strong solvent dependency.

Electrochemistry: To test the electron-withdrawing properties, the first reduction potentials of the synthesized oligo−mers were determined by cyclic voltammetry (Figure 6). Oligomers **1, 2** and **3** showed quasi-reversible first reduction potentials (E_{pc}) at −1.68, −1.38 and −1.08 V, respectively. In addition, oligomer **3** could be quasi-reversibly reduced a second time at −1.31 V, while all oligomers could be reduced once more below −2.3 V, but these reductions were not reversible.

Since discotic compound **4** has limited π-conjugation, a first reduction potential similar to the one obtained for oligomer **1** (−1.68 V) was expected; however, a first reduction potential of −1.49 V was measured by CV. The latter is obviously due to the higher electron affinity of the triazine unit compared to pyrazine. Although multiple CV scans of **4** showed no change in signal intensity, the cyclic voltammogram of the latter showed no oxidation wave and was thus deemed irreversible. A second reduction, which was found at −2.08 V, revealed the same electrochemical behavior.

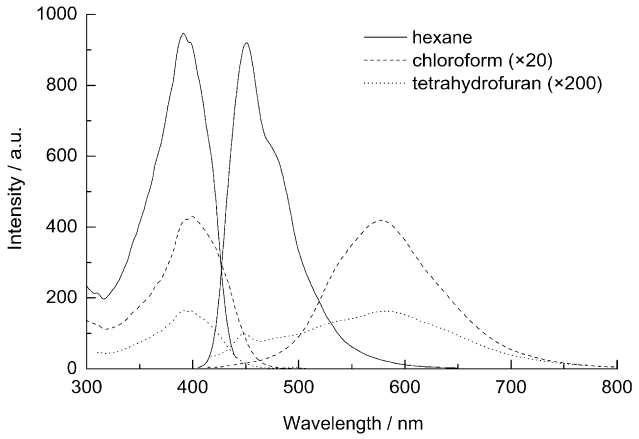


Figure 4. Excitation and fluorescence spectra of oligomer **3** in various solvents.

Conclusion

A discotic molecule incorporating triazine and oligomeric structures incorporating pyrazine were synthesized. Since direct coupling of the pyrazine rings proved to be difficult, ethynylene groups were introduced as coupling units. The latter did not diminish the stability or negatively influence

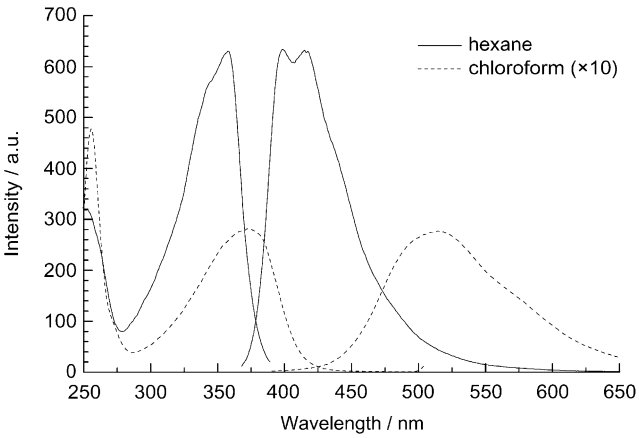


Figure 5. Excitation and fluorescence spectra of **4** in hexane and chloroform.

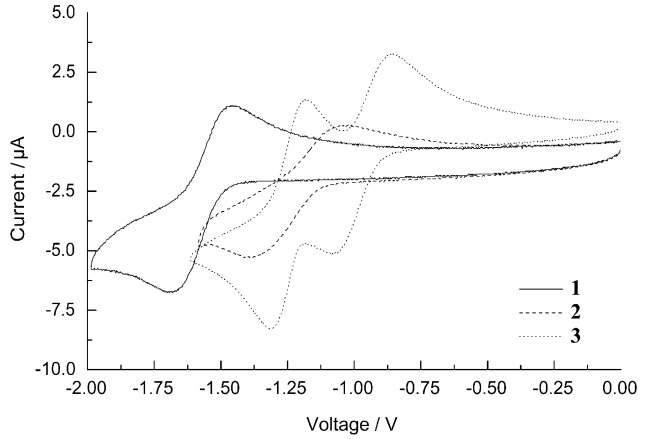


Figure 6. Cyclic voltammograms of ethynylene pyrazinylene oligomers **1, 2** and **3** (conditions: tetrahydrofuran, 0.1 M Bu_4NPF_6, SCE, 100 mV s^{-1}).

the electronic properties of the oligomers. Although none of the obtained structures showed a first reduction potential as low as −0.5 V, they demonstrate the value of azaheterocycles in the design and synthesis of electron-deficient materials. The evolution of the first reduction potentials of the ethynylene pyrazinylene series from −1.68 to −1.08 V ($n = 1 \rightarrow 3$), suggests that with $n \approx 6$ the target value can be approached. The liquid crystalline or crystalline behavior exhibited by the tridodecyloxyphenyl substituted compounds might be used as a tool to organize the molecules on a nanoscopic level and, thus, enhance their properties in organic-based electronic devices.

Experimental Section

General: All solvents used were p.a. quality. Tetrahydrofuran (THF) was distilled over Na/K/benzophenone, while triethylamine was dried over KOH. For column chromatography Merck silica gel 60 was used or Merck alumina 90 (activity II-III), while for preparative size exclusion chromatography Bio-Rad S-X1 Beads were used. ^{1}H and ^{13}C NMR spectra were recorded on a Varian Gemini spectrometer with frequencies of 300.1 and 75.0 MHz, respectively, an AM-400 Bruker spectrometer with frequencies of 400.1 and 100.6 MHz, respectively, or a Varian Mercury spectrometer with frequencies of 400.1 and 100.6 MHz, respectively. Chemical shifts are given in ppm (δ) downfield from tetramethylsilane (TMS). UV/Vis spectra were recorded on a Perkin Elmer Lambda 3B spectrophotometer, a Perkin Elmer Lambda 40P spectrophotometer or a Perkin Elmer Lambda 900 UV/Vis/NIR spectrophotometer. Fluorescence spectra were recorded on a Perkin Elmer LS50B luminescence spectrometer and infrared spectra on a Perkin-Elmer Spectrum One using an attenuated total reflection (ATR) sample accessory. The optical properties and melting points were determined using a Jenaval polarization microscope equipped with a Linkam THMS 600 heating device. DSC data was collected on a Perkin Elmer Pyris 1 under a nitrogen atmosphere, while TGA data was collected on a Perkin Elmer TGA 7. Mass spectra were recorded on a Perseptive DE Voyager MALDI-TOF spectrometer utilizing α-cyano-4-hydroxycinnamic acid as the matrix. Elemental analysis was performed on a Perkin Elmer 2400 series analyzer. Cyclic voltammograms were obtained in THF with 0.1 M tetrabutylammonium hexafluorophosphate as supporting electrolyte using a Potentioscan Wenking POS73 potentiostat. A platinum disk (diameter 5 mm) was used as working electrode, the counter electrode was a platinum plate (5×5 mm^2) and a saturated calomel electrode (SCE) was used as reference electrode.

2,5-Bis(3,4,5-tridodecyloxyphenylethynyl)pyrazine (1): 2,5-Dibromopyrazine[27] (0.367 g, 1.50 mmol) and 3,4,5-tridodecyloxyphenylacetylene[22] (0.993 g, 1.50 mmol) were dissolved in a mixture of DMF (4 mL) and toluene (4 mL). To this mixture KOAc (0.234 g, 2.25 mmol) and $[Pd(PPh_3)_4]$ (70 mg, 0.060 mmol, 4 mol%) were added under an argon atmosphere and subsequently the heterogeneous mixture was heated under reflux for 2 h. Toluene was removed in vacuo and the DMF suspension was poured into a mixture of diethyl ether (50 mL), and aqueous 0.25 M HCl (25 mL). After separation, the organic layer was washed with another portion of aqueous 0.25 M HCl (25 mL) and evaporated to dryness. The residue was purified by column chromatography (SiO_2, dichloromethane (30%) in heptane), yielding **1** as an off-white solid (0.380 g, 0.274 mmol, 37%). ^{1}H NMR ($CDCl_3$): $\delta = 8.70$ (s, 2H; H-3,6), 6.83 (s, 4H; H_{Ph}-2,6), 3.99 (m, 12H; OCH_2), 1.83–1.69 (m, 12H; OCH_2CH_2), 1.47 (m, 12H; $OCH_2CH_2CH_2$), 1.26 (m, 96H; $(CH_2)_8$), 0.88 ppm (t, $J = 6.8$ Hz, 18H; CH_3); ^{13}C NMR ($CDCl_3$): $\delta = 153.3$ (C_{Ph}-3,5), 147.2 (C-3,6), 140.5 (C_{Ph}-4), 137.9 (C-2,5), 115.8 (C_{Ph}-1), 110.9 (C_{Ph}-2,6), 96.1 (C_{Pz}–C≡C-C_{Ph}), 85.3 (C_{Pz}–C≡C-C_{Ph}), 73.8 (C_{Ph}-4-OCH_2), 69.4 (C_{Ph}-3,5-OCH_2), 32.2, 30.6, 30.0, 29.9, 29.9, 29.9, 29.8, 29.6, 29.5, 26.3, 22.9 ($(CH_2)_{10}$), 14.3 ppm (CH_3); IR (ATR): $\tilde{\nu} = 2917$, 2849, 2213, 1573, 1505, 1467, 1422, 1385, 1360, 1300, 1267, 1233, 1121, 1028, 1011, 991, 970, 910, 826, 721 cm^{-1}; MALDI-TOF MS [M+H$^+$]: calcd 1387.2 Da; found 1387.0 Da; elemental analysis calcd (%) for $C_{92}H_{156}N_2O_6$ (1386.26): C 79.71, H 11.34, N 2.02; found: C 79.80, H 11.24, N 2.01.

5-Bromo-2-iodopyrazine (6): In a 100 mL three-necked flask equipped with a mechanical stirrer, 5-bromopyrazinamine[28] (2.0 g, 11.5 mmol) was suspended in hydroiodic acid (57% in water, 7.4 mL), which was cooled using an ice-salt bath. I_2 (2.0 g, 7.8 mmol) was slowly added, keeping the temperature of the mixture below 2 °C, followed by the addition of $NaNO_2$ (3.31 g, 48.0 mmol) over a period of 3 h. The mixture was made alkaline by first adding a $Na_2S_2O_5$ solution (10% in water, 50 mL) and then a saturated Na_2CO_3 solution (30 mL). The obtained mixture was extracted with diethyl ether (3×80 mL) and the organic layer was subsequently washed with a $Na_2S_2O_5$ solution (10% in water, 100 mL), dried over $MgSO_4$, filtered and evaporated to dryness. Purification of the residue by column chromatography (SiO_2, diethyl ether (25%) in hexane, $R_f = 0.7$) afforded pure **6** as a white solid (1.34 g, 4.70 mmol, 41%). ^{1}H NMR ($CDCl_3$): $\delta = 8.61$ (d, $J = 1.4$ Hz, 1H; H-3), 8.50 ppm (d, $J = 1.4$ Hz, 1H; H-6); ^{13}C NMR ($CDCl_3$): $\delta = 152.8$ (C-3), 148.6 (C-6), 140.5 (C-5), 115.0 ppm (C-2).

2-Bromo-5-(3,4,5-tridodecyloxyphenylethynyl)pyrazine (7): 5-Bromo-2-iodopyrazine (**6**, 0.43 g, 1.51 mmol) and 3,4,5-tridodecyloxyphenylacetylene[22] (0.98 g, 1.50 mmol) were dissolved in triethylamine (10 mL) and the catalysts $[Pd(PPh_3)_2Cl_2]$ (0.0127 g, 0.0181 mmol, 1 mol%) and CuI (0.0088 g, 0.046 mmol, 3 mol%) were added. The mixture was stirred at room temperature for 2 h, evaporated to dryness, dissolved in toluene and again evaporated to dryness to remove any residual triethylamine. Purification by column chromatography (SiO_2, hexane (40%) in dichloromethane, $R_f = 0.3$) yielded **7** as a yellow-orange waxy solid (1.14 g, 1.40 mmol, 94%). ^{1}H NMR ($CDCl_3$): $\delta = 8.65$ (d, $J = 1.5$ Hz, 1H; H-6), 8.48 (d, $J = 1.5$ Hz, 1H; H-3), 6.81 (s, 2H; H_{Ph}-2,6), 3.97 (m, 6H; OCH_2), 1.84–1.72 (m, 6H; OCH_2CH_2), 1.46 (m, 6H; $OCH_2CH_2CH_2$), 1.26 (m, 48H; $(CH_2)_8$), 0.88 ppm (t, $J = 7.0$ Hz, 9H; CH_3); ^{13}C NMR ($CDCl_3$): $\delta = 153.3$ (C_{Ph}-3,5), 147.4, 147.3 (C-3,6), 140.6 (C_{Ph}-4), 138.9, 138.8 (C-2,5), 115.6 (C_{Ph}-1), 110.9 (C_{Ph}-2,6), 95.7 (C_{Pz}–C≡C-C_{Ph}), 84.0 (C_{Pz}–C≡C-C_{Ph}), 73.8 (C_{Ph}-4-OCH_2), 69.4 (C_{Ph}-3,5-OCH_2), 32.2, 30.5, 30.0, 29.9, 29.9, 29.8, 29.6, 29.5, 26.3, 22.9 ($(CH_2)_{10}$), 14.3 ppm (CH_3).

5-(3,4,5-Tridodecyloxyphenylethynyl)-2-trimethylsilylethynylpyrazine (8): 2-Bromo-5-(3,4,5-tridodecyloxyphenylacetylene)pyrazine (**7**, 0.5 g, 0.62 mmol) was dissolved in triethylamine (3.5 mL) and trimethylsilylacetylene (0.09 mL, 0.64 mmol) was added. After addition of $[Pd(PPh_3)_2Cl_2]$ (0.0448 g, 0.0064 mmol, 1 mol%) and CuI (0.0037 g, 0.0192 mmol, 3 mol%), the reaction mixture was heated at 60 °C for 45 min, allowed to cool and filtered. The filter was washed with triethylamine and the combined filtrates were evaporated to dryness. Purification of the crude material by column chromatography (SiO_2, heptane (40%) in dichloromethane) afforded **8** as a dark colored solid (0.32 g, 0.39 mmol, 63%). ^{1}H NMR ($CDCl_3$): $\delta = 8.66$ (d, $J = 1.5$ Hz, 1H; H-3), 8.64 (d, $J = 1.5$ Hz, 1H; H-6), 6.81 (s, 2H; H_{Ph}-2,6), 4.00–3.95 (m, 6H; OCH_2), 1.82–1.72 (m, 6H; OCH_2CH_2), 1.46 (m, 6H; $OCH_2CH_2CH_2$), 1.26 (m, 48H; $(CH_2)_8$), 0.88 (t, $J = 6.8$ Hz, 9H; CH_3), 0.29 ppm (s, 9H; $Si(CH_3)_3$); ^{13}C NMR ($CDCl_3$): $\delta = 153.3$ (C_{Ph}-3,5), 147.5, 147.0 (C-3,6), 140.6 (C_{Ph}-4), 138.5, 137.2 (C-2,5), 115.7 (C_{Ph}-1), 110.9 (C_{Ph}-2,6), 101.9 (C_{Pz}–C≡C-Si), 101.0 (C_{Pz}–C≡C-Si), 96.3 (C_{Pz}–C≡C-C_{Ph}), 85.2 (C_{Pz}–C≡C-C_{Ph}), 73.8 (C_{Ph}-4-OCH_2), 69.4 (C_{Ph}-3,5-OCH_2), 32.2, 31.8, 30.5, 29.9, 29.9, 29.9, 29.9, 29.8, 29.6, 29.5, 26.3, 22.9 ($(CH_2)_{10}$), 14.3 (CH_3), −0.2 ppm ($Si(CH_3)_3$).

5-Ethynyl-2-(3,4,5-tridodecyloxyphenylethynyl)pyrazine (9): Pyrazine derivative **8** (0.72 g, 0.87 mmol) was dissolved in THF (5 mL) and Bu_4NF (1 M in THF, 1.50 mL, 1.50 mmol) was added. The solution was stirred at room temperature for 10 min and then filtered over a short silica column using dichloromethane as the eluent. The filtrate was evaporated to dryness and the crude oil was purified by column chromatography (SiO_2, hexane (33%) in dichloromethane, $R_f = 0.46$), yielding pure **9** as a yellow solid (0.31 g, 0.41 mmol, 47%). ^{1}H NMR ($CDCl_3$): $\delta = 8.66$ (d, $J = 1.5$ Hz, 1H; H-6), 8.64 (d, $J = 1.5$ Hz, 1H; H-3), 6.81 (s, 2H; H_{Ph}-2,6), 3.98–3.94 (m, 6H; OCH_2), 3.43 (s, 1H; C≡C–H), 1.82–1.72 (m, 6H; OCH_2CH_2), 1.45 (m, 6H; $OCH_2CH_2CH_2$), 1.25 (m, 48H; $(CH_2)_8$), 0.86 ppm (t, $J = 6.8$ Hz, 9H; CH_3); ^{13}C NMR ($CDCl_3$): $\delta = 153.3$ (C_{Ph}-3,5), 147.6, 147.1 (C-3,6), 140.7 (C_{Ph}-4), 139.1 (C-2), 136.6 (C-5), 115.6 (C_{Ph}-1), 110.9 (C_{Ph}-2,6), 96.5 (C_{Pz}–C≡C–C_{Ph}), 85.1 (C_{Pz}–C≡C–C_{Ph}), 82.8 (C_{Pz}–C≡C–H), 80.3 (C_{Pz}–C≡C–H), 73.8 (C_{Ph}-4-OCH_2), 69.4 (C_{Ph}-3,5-OCH_2), 32.2, 30.5, 30.0, 29.9, 29.9, 29.8, 29.6, 29.5, 26.3, 22.9 ($(CH_2)_{10}$), 14.3 ppm (CH_3).

2-(5-Bromo-2-pyrazinylethynyl)-5-(3,4,5-tridodecyloxyphenylethynyl)pyrazine (10): Pyrazine derivative **9** (0.165 g, 0.22 mmol) and 5-bromo-2-iodopyrazine (**6**, 0.0693 g, 0.24 mmol) were dissolved in triethylamine (2

mL) and $[Pd(PPh_3)_2Cl_2]$ (0.0015 g, 0.0022 mmol, 1 mol %) and CuI (0.0013 g, 0.0066 mmol, 1 mol %) were added. The reaction mixture was heated at 70 °C for 20 min, allowed to cool and filtered. The filter was washed with triethylamine and the combined filtrates were then evaporated to dryness. Purification by column chromatography (SiO_2, dichloromethane) afforded **10** as a yellow solid (0.1126 g, 0.123 mmol, 56 %). ^{1}H NMR ($CDCl_3$): $\delta = 8.82$ (s, 1H; H-3), 8.75 (s, 1H; H-3′/6), 8.74 (s, 1H; H-3′/6), 8.62 (s, 1H; H-6′), 6.86 (s, 2H; H_{Ph}-2,6), 4.01–3.97 (m, 6H; OCH_2), 1.83–1.72 (m, 6H; OCH_2CH_2), 1.48 (m, 6H; $OCH_2CH_2CH_2$), 1.27 (m, 48H; $(CH_2)_8$), 0.88 ppm (t, $J = 6.8$ Hz, 9H; CH_3); ^{13}C NMR ($CDCl_3$): $\delta =$ 153.4 (C_{Ph}-3,5), 148.0, 147.8, 147.6, 147.4 (C-3,3′,6,6′), 140.9, 140.8 (C-2, C_{Ph}-4), 139.7, 137.3, 136.0 (C-2′,5,5′), 115.6 (C_{Ph}-1), 111.1 (C_{Ph}-2,6), 97.5 (C_{Pz}–C≡C–C_{Ph}), 90.3 (C_{Pz}–C≡C–$C_{Pz'}$), 89.3 (C_{Pz}–C≡C–$C_{Pz'}$), 85.4 (C_{Pz}–C≡ C–C_{Ph}), 73.9 (C_{Ph}-4-OCH_2), 69.5 (C_{Ph}-3,5-OCH_2), 32.3, 30.7, 30.0, 30.0, 29.9, 29.7, 29.6, 29.4, 26.4, 23.0 ($(CH_2)_{10}$), 14.4 ppm (CH_3).

1,2-Bis[2-{5-(3,4,5-tridodecyloxyphenylethynyl)pyrazinyl}]ethyne (2): Pyrazine derivative **10** (0.1102 g, 0.12 mmol) and 3,4,5-tridodecyloxyphenylacetylene (0.082 g, 0.12 mmol) were dissolved in triethylamine (3.3 mL) and $[Pd(PPh_3)_2Cl_2]$ (0.0008 g, 0.0012 mmol, 1 mol %) and CuI (0.0007 g, 0.0036 mmol, 1 mol %) were added. The reaction mixture was then heated under reflux for 1 h, allowed to cool and evaporated to dryness. The residue was dissolved in diethyl ether (10 mL), washed with water (2 × 10 mL), dried over $MgSO_4$ and again evaporated to dryness. Pure **2** was obtained as a yellow solid (0.0257 g, 0.017 mmol, 14 %), after two purifications by column chromatography (SiO_2, dichloromethane, $R_f = 0.44$). ^{1}H NMR ($CDCl_3$): $\delta = 8.82$ (d, $J = 1.5$ Hz, 2H; H-3), 8.75 (d, $J = 1.5$ Hz, 2H; H-6), 6.84 (s, 4H; H_{Ph}-2,6), 4.02–3.96 (m, 12H; OCH_2), 1.83–1.74 (m, 12H; OCH_2CH_2), 1.47 (m, 12H; $OCH_2CH_2CH_2$), 1.26 (m, 96H; $(CH_2)_8$), 0.88 ppm (t, $J = 6.8$ Hz, 18H; CH_3); ^{13}C NMR ($CDCl_3$): $\delta = 153.3$ (C_{Ph}-3,5), 147.9 (C-3), 147.4 (C-6), 140.8 (C_{Ph}-4), 139.5 (C-5), 136.1 (C-2), 115.6 (C_{Ph}-1), 111.0 (C_{Ph}-2,6), 97.3 (C_{Pz}–C≡C–C_{Ph}), 90.6 (C_{Pz}–C≡C–C_{Pz}), 85.3 (C_{Pz}–C≡C–C_{Ph}), 73.8 (C_{Ph}-4-OCH_2), 69.4 (C_{Ph}-3,5-OCH_2), 32.2, 30.5, 30.0, 29.9, 29.9, 29.9, 29.8, 29.6, 29.5, 26.3, 22.9 ($(CH_2)_{10}$), 14.3 ppm (CH_3); IR (ATR): $\tilde{\nu} = 2918$, 2850, 2207, 1572, 1500, 1467, 1420, 1360, 1298, 1261, 1234, 1149, 1113, 1029, 1011, 912, 801, 721 cm^{-1}. MALDI-TOF MS [M+H$^+$]: calcd 1489.4 Da; found 1490.4 Da.

2,5-Bis(trimethylsilylethynyl)pyrazine (11): 2,5-Dibromopyrazine[27] (1.55 g, 6.5 mmol) was dissolved in triethylamine (26 mL) and trimethylsilylacetylene (1.85 mL, 13 mmol) was added. Then, the catalysts $[Pd(PPh_3)_2Cl_2]$ (0.0844 g, 0.07 mmol 0.5 mol %) and CuI (0.0284 g, 0.15 mmol, 1 mol %) were added. The mixture was heated under reflux for 1 h, allowed to cool and filtered. The filter was then carefully washed with triethylamine and the combined filtrates were evaporated to dryness. Purification by column chromatography (SiO_2, dichloromethane (33 %) in heptane, $R_f = 0.25$) afforded **11** as a white solid (0.66 g, 2.4 mmol, 37 %). ^{1}H NMR ($CDCl_3$): $\delta = 8.60$ (s, 2H; H-3), 0.28 ppm (s, 18H; $Si(CH_3)_3$); ^{13}C NMR ($CDCl_3$): $\delta = 147.4$ (C-3,6), 137.8 (C-2,5), 102.2, 100.8 (C≡C), −0.2 ppm ($Si(CH_3)_3$).

2,5-Diethynylpyrazine (12): 2,5-Bis(trimethylsilylethynyl)pyrazine (**11**, 1.06 g, 3.89 mmol) was dissolved in THF (20 mL) and Bu_4NF (1 M in THF, 8.0 mL, 8.0 mmol) was added. The reaction mixture was stirred for 1 min, poured into diethyl ether (50 mL) and washed with water (2 × 50 mL). The organic phase was then dried over $MgSO_4$, filtered and evaporated to dryness. Purification by column chromatography (SiO_2, diethyl ether (25 %) in pentane) afforded **12** as a yellow-white solid (0.25 g, 1.98 mmol, 50 %). ^{1}H NMR ($CDCl_3$): $\delta = 8.64$ (s, 2H; H-3,6), 3.44 ppm (s, 2H; C≡C–H); ^{13}C NMR ($CDCl_3$): $\delta = 147.6$ (C-3,6), 137.8 (C-2,5), 83.3 (C_{Pz}–C≡C–H), 80.1 ppm (C_{Pz}–C≡C–H).

Note: Since diethynylpyrazine **12** is rather volatile, evaporation of the solvents should be done at room temperature to prevent sublimation.

2,5-Bis[5-(3,4,5-tridodecyloxyphenylethynyl)-pyrazinylethynyl]pyrazine (3): 2,5-Diethynylpyrazine (**12**, 0.03 g, 0.24 mmol) and 2-bromo-5-(3,4,5-tridodecyloxyphenylethynyl)pyrazine (**7**, 0.3727 g, 0.46 mmol) were dissolved in triethylamine (2 mL) and spatula ends of $Pd(PPh_3)_2Cl_2$ and CuI were added. The reaction mixture was heated under reflux for 2 h, blanketed by argon, allowed to cool and filtered. The filter was washed with triethylamine and the combined filtrates were evaporated to dryness. Purification of the crude material by column chromatography (SiO_2, ethyl acetate (1 %) in dichloromethane) yielded pure **3** as a yellow waxy solid (0.1803 g, 0.114 mmol, 47 %). ^{1}H NMR ($CDCl_3$): $\delta = 8.87$ (s, 2H; H-3,6), 8.82 (d, $J = 1.1$ Hz, 2H; H-3′), 8.75 (d, $J = 1.1$ Hz, 2H; H-6′), 6.83 (s, 4H; H_{Ph}-2,6), 3.99–3.96 (m, 12H; OCH_2), 1.83–1.75 (m, 12H; OCH_2CH_2), 1.46 (m, 12H; $OCH_2CH_2CH_2$), 1.25 (m, 96H; $(CH_2)_8$), 0.87 ppm (t, $J =$ 7.0 Hz, 18H; CH_3); ^{13}C NMR ($CDCl_3$): $\delta = 153.3$ (C_{Ph}-3,5), 148.2 (C-3,6), 147.9 (C-3′), 147.5 (C-6′), 140.8 (C_{Ph}-4), 139.6 (C-5′), 137.7 (C-2,5), 135.9 (C-2′), 115.5 (C_{Ph}-1), 111.1 (C_{Ph}-2,6), 97.5 (C_{Pz}–C≡C-C_{Ph}), 91.4 (C_{Pz}–C≡ C–$C_{Pz'}$), 90.2 (C_{Pz}–C≡C–$C_{Pz'}$), 85.3 (C_{Pz}–C≡C–C_{Ph}), 73.8 (C_{Ph}-4–OCH_2), 69.4 (C_{Ph}-3,5-OCH_2), 32.2, 30.6, 29.9, 29.9, 29.6, 29.5, 26.3, 22.9 ($(CH_2)_{10}$), 14.3 ppm (CH_3); IR (ATR): $\tilde{\nu} = 2920$, 2851, 2206, 1572, 1499, 1467, 1420, 1358, 1298, 1262, 1233, 1188, 1151, 1114, 1030, 916, 833, 767, 721 cm^{-1}; MALDI-TOF MS [M+H$^+$]: calcd 1591.5 Da; found 1592.5 Da; elemental analysis calcd (%) for $C_{104}H_{160}N_6O_6$ (1590.45): C 78.54, H 10.14, N 5.28; found: C 78.25, H 10.06, N 4.94.

2,4,6-Tris(3,4,5-tridodecyloxyphenylethynyl)triazine (4): Blanketed by argon, nBuLi (1.6 M in hexane, 2.35 mL, 3.76 mmol) was added dropwise to a stirred solution of 3,4,5-tridodecyloxyphenylacetylene (2.47 g, 3.77 mmol) in THF (10 mL) at −78 °C.[19] The solution was stirred for 1 h, allowed to warm to room temperature and stirred for another 20 min. The solution was then cooled to −78 °C and a solution of cyanuric fluoride (0.146 g, 1. 08 mmol) in THF (1 mL) was added dropwise. The mixture was warmed to room temperature, stirred for 2 h, and water (10 mL) and dichloromethane (10 mL) were added. The layers were separated and the aqueous layer was extracted with dichloromethane (2 × 10 mL). The combined organic layers were then washed with brine, dried over Na_2SO_4, filtered and evaporated to dryness. The residue was purified by column chromatography (SiO_2, pentane (25 %) in dichloromethane) and preparative size exclusion chromatography (Biobeads, CH_2Cl_2), affording pure **4** as a yellow waxy solid (0.51 g, 0.25 mmol, 23 %). ^{1}H NMR ($CDCl_3$): $\delta =$ 6.92 (s, 6H; H_{Ph}-2,6), 4.03–3.94 (m, 18H; OCH_2), 1.85–1.70 (m, 18H; OCH_2CH_2), 1.48 (m, 18H; $OCH_2CH_2CH_2$), 1.27 (m, 144H; $(CH_2)_8$), 0.87 ppm (t, $J = 5.9$ Hz, 27H; CH_3); ^{13}C NMR ($CDCl_3$): $\delta = 160.7$ (C-2,4,6), 153.3 (C_{Ph}-3,5), 141.6 (C_{Ph}-4), 114.5 (C_{Ph}-1), 112.0 (C_{Ph}-2,6), 95.2 (C_{Tz}–C≡ C-C_{Ph}), 86.2 (C_{Tz}–C≡C–C_{Ph}), 73.9 (C_{Ph}-4-OCH_2), 69.4 (C_{Ph}-3,5-OCH_2), 32.2, 31.9, 30.6, 30.0, 29.9, 29.8, 29.7, 29.5, 26.3, 23.0 ($(CH_2)_{10}$), 14.3 ppm (CH_3); IR (ATR): $\tilde{\nu} = 2920$, 2852, 2218, 1575, 1492, 1468, 1421, 1377, 1306, 1236, 1168, 1115, 1052, 1002, 830, 819, 721 cm^{-1}; MALDI-TOF MS [M+H$^+$]: calcd 2041.8 Da; found 2042.1 Da; elemental analysis calcd (%) for $C_{135}H_{231}N_3O_9$ (2040.33): C 79.47, H 11.41, N 2.06; found: C 79.53, H 11.32, N 2.06.

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