RSC Advances

PAPER

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Cite this: RSC Adv., 2015, 5, 89731

Liquid crystalline dihydroazulene photoswitches†

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Received 11th September 2015
Accepted 13th October 2015

DOI: 10.1039/c5ra18649h

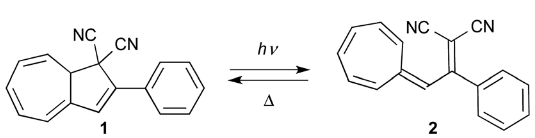
www.rsc.org/advances

A large selection of photochromic dihydroazulene (DHA) molecules incorporating various substituents at position 2 of the DHA core was prepared and investigated for their ability to form liquid crystalline phases. Incorporation of an octyloxy-substituted biphenyl substituent resulted in nematic phase behavior and it was possible to convert one such compound partly into its vinylheptafulvene (VHF) isomer upon irradiation with light when in the liquid crystalline phase. This conversion resulted in an increase in the molecular alignment of the phase. In time, the meta-stable VHF returns to the DHA where the alignment is maintained. The systematic structural variation has revealed that a biaryl spacer between the DHA and the alkyl chain is needed for liquid crystallinity and that the one aromatic ring in the spacer cannot be substituted by a triazole. This work presents an important step towards employing the dihydroazulene-vinylheptafulvene photo/thermoswitch in photoactive liquid crystalline materials.

1. Introduction

In the field of liquid crystals, it has been a goal to control the phases and order with an external stimulus. Some of the stimuli which have been applied include temperature, magnetic field, electric field and light.[1] Light is an interesting stimulus, since this gives the possibility for remote control. Indeed, it has found use in image storing devices.[2,3] Specifically, this has been shown with azobenzene polymer matrix, where an image was stored for 8 months without significant decay.[2] Other photochromic molecules such as dithienylethenes, spiropyrans and fulgides have also shown suitable properties for this kind of application.[4–6] Here we present a study on liquid crystalline systems based upon the dihydroazulene (DHA) photoswitch (Scheme 1). When irradiated with light, DHA **1** undergoes a ring-opening to the vinylheptafulvene (VHF) **2**, which can then close back to the initial DHA *via* a thermal electrocyclization reaction.[7]

The main advantage of the DHA–VHF photoswitch system is that only the DHA to VHF conversion is light-induced, which means that a broad spectrum of light can be used without triggering the VHF to DHA back-reaction. The DHA ring-opening is associated with significant changes in the physical properties of the corresponding VHF. Thus, ring-opening is associated with an increase in dipole moment and a change in color from yellow (DHA) to intense red (VHF).[8,9] We became interested to elucidate if this difference in properties could give rise to reversible, photochemically induced phase transitions.



Scheme 1 DHA **1**/VHF **2** system.

Molecules with liquid crystalline properties can have differing constructions, but for the purpose of this work, attention was given to rod-like structures. Typically, rod-like, liquid crystalline structures have two aliphatic chains extending from a rigid 'core' unit such as biphenyl or one alkyl chain with an additional terminal substituent such as a nitrile.[10] It was decided to incorporate either a cyanophenyl-substituted alkyl in the one end of DHA or an octyl chain. In the literature there are many examples of the cyanobiphenyl being used as the terminal substituent,[11] but as this unit has absorption properties which conflict with the wavelength needed for the ring-opening event of DHA, the cyanophenyl substituent was used predominantly in this study, as in structures **3a–e** and **4a–e** (Fig. 1). Structures **3f–i** and **4j** instead have an octyl end-group. Both cyanophenyl and octyl groups have been used previously to achieve liquid crystallinity.[12]

2. Results and discussion

2.1 Synthesis

The most convenient method for the construction of 2-substituted DHAs originates from derivatized acetophenones. Several strategies were undertaken in the pursuit of obtaining the starting acetophenones (Scheme 2). From the simple precursors **5a–e**, **6**, **7a–e**, **8**, acetophenones **9a–e** were prepared

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† Electronic supplementary information (ESI) available. See DOI: 10.1039/c5ra18649h

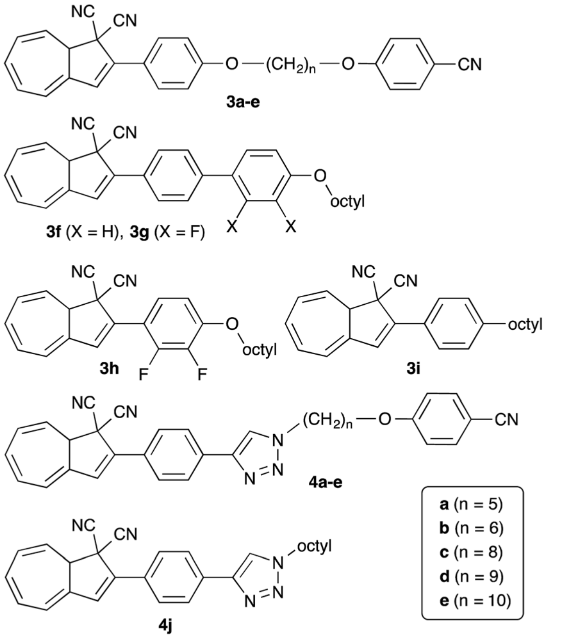
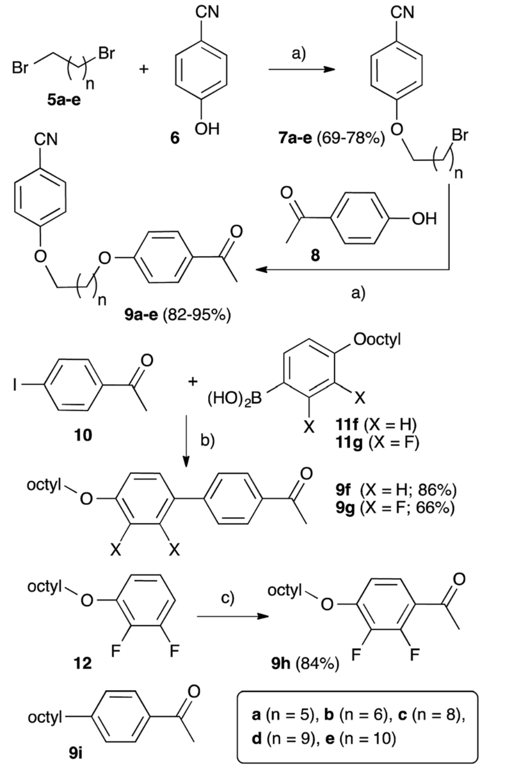


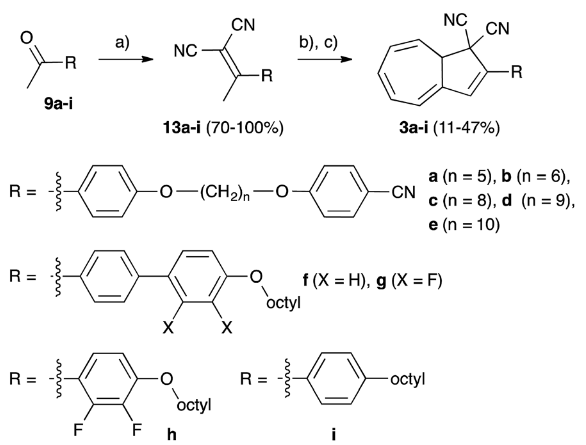
Fig. 1 DHAs employed in this study.

in two successive reactions. Thus, dibromoalkanes **5a–e** of various chain lengths were treated with phenols **6** and **8**. Conversely, acetophenones containing biaryl units, **9f** and **9g**, were obtained in good yields from a palladium-catalyzed Suzuki cross-coupling reaction from 4-iodoacetophenone **10** with boronic acids **11f** and **11g**, respectively, using conditions that proved fruitful in the synthesis of the benzaldehyde analogues.[13] Finally, **9h** could be formed in high yield by a Friedel–Crafts reaction of **12** with acetyl chloride using a literature procedure.[14] Compound **9i** was purchased.

Acetophenones **9a–i** could be transformed successfully into the corresponding DHAs **3a–i** (Scheme 3) by firstly converting the carbonyl moiety into a crotononitrile unit in a Knoevenagel condensation furnishing intermediates **13a–i**, generally in good yields. Intermediates **13a–i** were then treated with tropylium tetrafluoroborate in the presence of triethylamine to affix the cycloheptatriene unit to the malonitriles which could be further converted into **3a–i** by subsequent oxidation using tritylium tetrafluoroborate followed by treatment with triethylamine. Alternatively, biaryl DHAs **3f** and **3g** could be obtained directly from DHA **15** in a Suzuki reaction with boronic acids **11f** and **11g**, using the catalytic system of palladium acetate and RuPhos (Scheme 4). A separate strategy involving the introduction of the extended chains could also be effected using the copper-catalyzed azide–alkyne cycloaddition (CuAAC)[15] to form triazole compounds. Triazoles have previously been incorporated successfully into liquid crystalline compounds[16] and, synthetically, DHA has been found to withstand the conditions.[17] Alkyl bromides **7a–e** were converted into their corresponding azides **14a–e** (Scheme 5) and when subjected to treatment with 10 mol% cuprous iodide in the presence of **16** and Hünig's base, triazoles **4a–e** were achieved. DHA **4j** could be made from a CuAAC of octyl azide with **16** in the same manner.

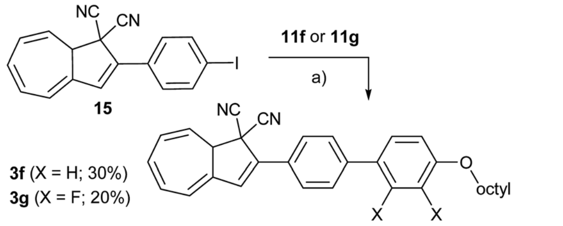


Scheme 2 Synthesis of acetophenone starting materials. Conditions: (a) K_2CO_3, acetone, reflux; (b) 5% $Pd(PPh_3)_4$, K_3PO_4, toluene/H_2O, rt to 80 °C; (c) $FeCl_3$, AcCl, CH_2Cl_2, 0 °C to rt.

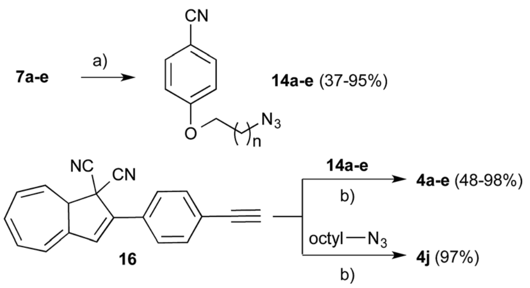


Scheme 3 Synthesis of DHAs. Conditions: (a) $CH_2(CN)_2$, NH_4OAc, toluene, AcOH, Δ. (b) $[C_7H_7]BF_4$, NEt_3, CH_2Cl_2, −78 °C. (c) $[Ph_3C]BF_4$, CH_2ClCH_2Cl, Δ, then toluene, NEt_3, 0 °C.

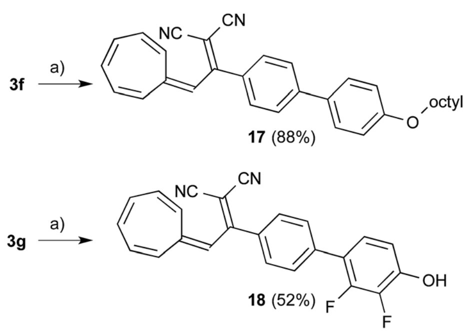
We also decided to prepare the corresponding VHFs of two of the DHAs (to study their liquid crystalline properties of relevance for the switching studies, *vide infra*). It has been shown that DHA can be ring-opened by treatment with $AlCl_3$ to afford the corresponding VHF[18] and this method could be used to convert **3f** into **17** in good yield (Scheme 6). When the method was used on **3g**, not only did the DHA undergo ring-opening to



Scheme 4 Functionalization of DHA *via* Suzuki cross-coupling. Conditions: (a) $Pd(OAc)_2$, RuPhos, K_3PO_4, toluene/H_2O. RuPhos = 2-dicyclohexylphosphino-2′,6′-diisopropoxybiphenyl.



Scheme 5 Functionalization of DHA *via* CuAAC. Conditions: (a) NaN_3, DMSO, 50 °C; (b) CuI, Hünig's base, toluene.



Scheme 6 Synthesis of VHFs. Conditions (a) $AlCl_3$, CH_2Cl_2, 0 °C/rt, then H_2O, 0 °C.

the VHF, but these reaction conditions also resulted in the cleavage of the octyl chain to form phenol **18**.

2.2 Photochemical properties

All DHAs made in this study show photoactive properties akin to that of unfunctionalized DHA **1**. All DHAs exhibited an absorption maximum at around 360 nm and when irradiated with light of this wavelength, they undergo an electrocyclic ring-opening reaction. Thereby a peak at 475 nm emerges, corresponding to the formation of the VHF (Table 1). The rate of VHF to DHA thermal ring-closure has been found to be influenced greatly by the introduction of electron-donating/accepting functional groups.[9,19] The VHFs of DHAs **3a–e** all exhibit a rate constant corresponding to that of the *p*-methoxy substituted derivative of DHA **1**. The rate of ring-closure for the VHFs of the triazole derivatives **4a–e** and **4j** show a small deviation from

Table 1 Characteristic absorption maxima and kinetics data for VHF to DHA conversions in acetonitrile at 25 °C

	DHA, λ_{max} (nm)	VHF, λ_{max} (nm)	VHF → DHA, k (10^{-5} s^{-1})	VHF → DHA, $t_{1/2}$ (min)
3a	365	469	5.04	229
3b	366	470	5.00	231
3c	367	471	4.97	232
3d	366	470	4.97	232
3e	365	470	4.97	232
3f	374	474	6.78	170
3g	366	475	7.30	158
3h	359	480	5.00	231
3i	358	471	4.98	232
4a	370	475	6.65	174
4b	370	476	6.72	172
4c	370	475	6.72	172
4d	368	475	6.68	173
4e	370	475	6.66	174
4j	369	475	6.63	174

a formerly reported triazole functionalized DHA,[17] which had a rate constant for the VHF ring-closure of 7.45 × 10^{-5} s^{-1}. The VHFs of **3h** and **3i** have comparable ring-closure rate constants as those of the VHFs of **3a–e** and of formerly reported DHA with a *p*-methyl substituent. Inclusion of fluorine seems to have no effect for the VHF of **3h**, or its effect is cancelled by the electron-donating octyloxy substituent. For the biphenyls **3f** and **3g** the rate of VHF to DHA conversion is higher and more similar to that of **4a–e**. Here the effect of the fluorine is clear; the rate increases to 7.30 × 10^{-5} s^{-1} compared to the non-fluorinated compound with a rate of 6.78 × 10^{-5} s^{-1}.

2.3 Physical properties

The synthesized molecules were examined by polarized optical microscopy (POM), but all starting materials en route to and including DHAs **3a–e** from the first two approaches did not show any liquid-crystalline properties. The same could also be said for DHAs **4a–e** and **4j**. Instead, biaryl containing acetophenones **9f** and **9g** and the corresponding DHAs **3f** and **3g** exhibited a liquid-crystalline phase and were examined by both POM and differential scanning calorimetry (DSC). Compound **9f** was found to exhibit a mesophase. Indeed, **9f** (Fig. 2) has been previously reported with two different transitions, where in one, it exhibited a smectic E phase,[20] and in the other, a melt was reported at 115–118 °C.[21] We found that under the microscope **9f** did exhibit a smectic phase (see Fig. 2), in agreement with the former report although definitive phase assignment was not possible due to the short range of supercooling. Hence, we denote it smectic X. Fig. 3 shows the DSC thermogram.

DSC showed a transition for a mesophase, where the size of the associated enthalpy to the phase transition is indicative of the formation of a smectic mesophase. The partially fluorinated analogue **9g** gave a lower melt and did not exhibit a liquid-crystalline phase during the heating process. Upon cooling, a peak corresponding to a liquid-crystalline phase could only be observed in the DSC at 53.8 °C. It was only possible to observe

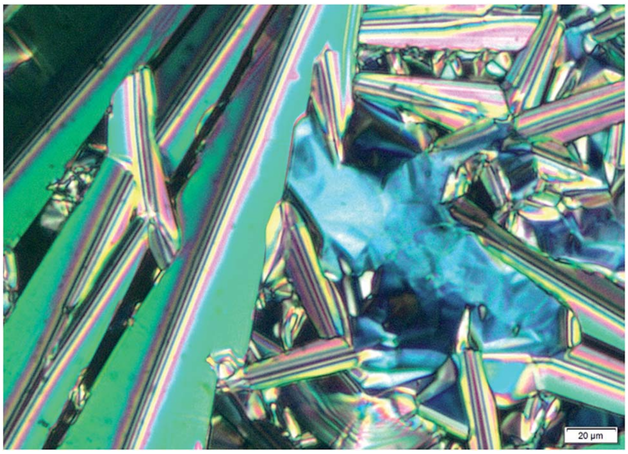


Fig. 2 Photomicrographs of the smectic X phase of **9f** at 118 °C.

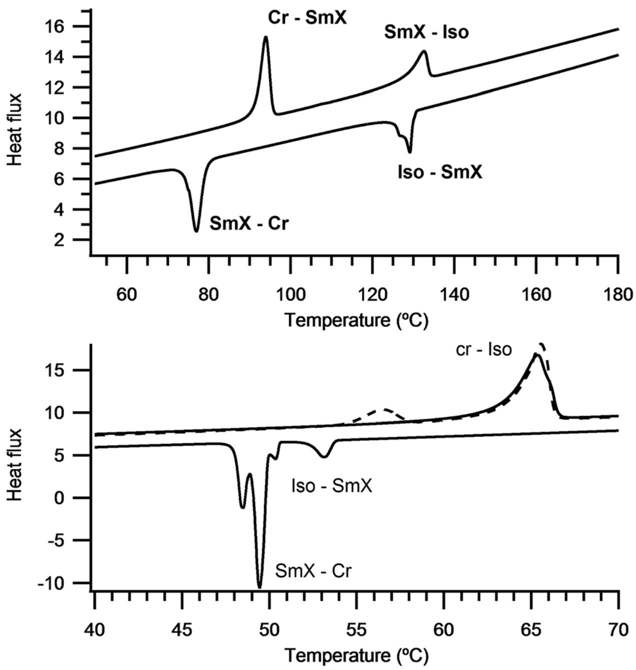
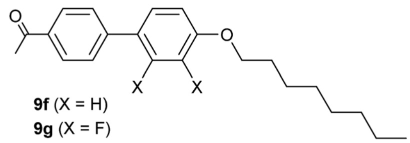


Fig. 3 (Top) DSC thermograms at a heating–cooling rate of 10 °C min^{-1} for compound **9f**. (Bottom) DSC thermograms at a heating–cooling rate of 5 °C min^{-1} for compound **9g**, where the dashed line is the first heating.

this phase when the sample had been heated to 100 °C prior to cooling. When compound **9g** was heated to a lesser extent, such as 67 or 80 °C, the sample underwent crystallization during the cooling phase prior to the temperature where this initial phase transition was observed. When examined by POM, the crystallization occurred prior to the liquid crystal phase transition temperature. Table 2 lists transition temperatures for **9f** and **9g** and Table 3 the enthalpies and entropies associated with the transitions.

The two DHAs **3f** and **3g** showed liquid crystalline properties, whilst **3h** and **3i** did not exhibit any mesophases. This suggests that the additional aryl ring is important for the modified DHAs

Table 2 Transition temperatures (°C) for compounds **9f** and **9g**



9f (X = H)
9g (X = F)

	Transition temperatures (°C)	
9f	Cr 91.0 SmX 128 Iso	Iso 130.2 SmX 79.5 Cr
9g	Cr 63.2 Iso	Iso 53.8 SmX 48.8 Cr

Table 3 Enthalpies (kJ mol^{-1}) and dimensionless entropies associated with transitions for compounds **9f** and **9g**

		Cr-Iso	Cr-SmX	SmX-Iso	Iso-SmX	SmX-Cr
9f	ΔH	—	23.48	13.377	12.54	24.10
	$\Delta S/R$	—	7.755	4.0106	3.739	8.819
9g	ΔH	25.91	—	—	2.713	22.95
	$\Delta S/R$	9.265	—	—	0.9980	8.574

to demonstrate liquid crystalline properties. Neither **3f** nor **3g** exhibited a mesophase in the first heating cycle, but upon cooling, a nematic phase appeared (Fig. 4). Further cooling did not result in crystallization, instead a glass transition occurred and when reheating the glass, the nematic phase reappeared and the transition from nematic to isotropic liquid could also

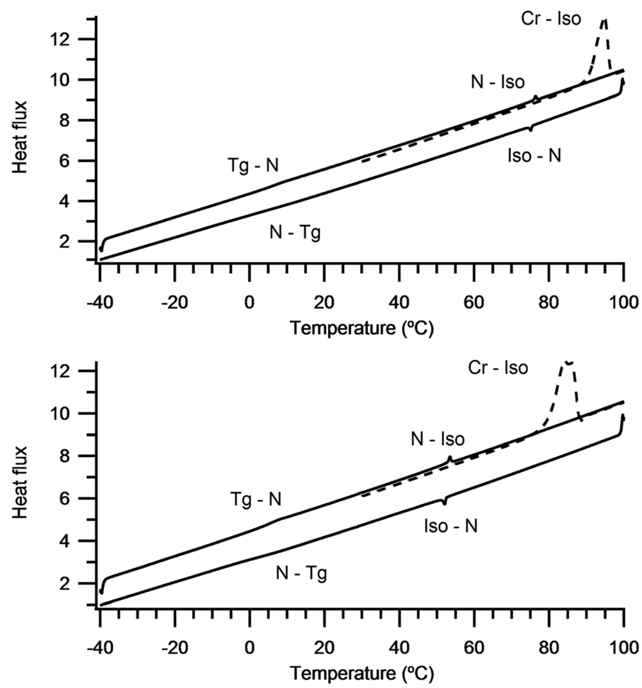
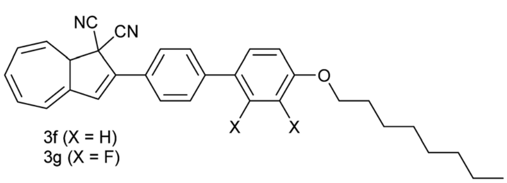


Fig. 4 DSC thermograms at a heating-cooling rate of 5 °C min^{-1} for compound **3f** (Top) and compound **3g** (Bottom). The dashed line corresponds to the first heating.

be observed. DHA **3f** gave a melt at 90.6 °C and the nematic phase appeared upon cooling at 75.7 °C, see Fig. 4. On heating, the clearing point was found to be at 75.6 °C. The phase transitions showed small enthalpy changes, which agrees with the changes from nematic to liquid phase and *vice versa*. For the fluorinated **3g** analogue, the melt occurred at a temperature about 10 °C lower than for **3f**. The clearing point for the nematic phase of **3g** is 52.6 °C, while it is 75.7 °C for **3f**. Table 4 lists transition temperatures for **3f** and **3g** and Table 5 the enthalpies and entropies associated with the transitions.

When **3f** is irradiated (at 365 nm) in the nematic phase, a color change from yellow-orange to red can be observed by the naked eye, but this did not correspond to a change in the phases. When solid VHF **17** was heated to 40 °C for 24 h, neither a change in color nor a phase change was observed, while heating the same material to 80 °C resulted in a simultaneous melt and color change to yellow ascribed to conversion to the DHA state. When **3g** was irradiated with light in the nematic phase at 40 °C for 60 min, conversion to the corresponding VHF occurred in a ratio of 3 : 7 (VHF/DHA) as determined by NMR spectroscopy. After one hour of irradiation, using POM one could see an increase in the alignment of the nematic phase, such that the defects disappear (Fig. 5c). Irradiation for a prolonged period (16 hours) afforded no further changes in neither the POM picture nor in the isomer ratio determined by NMR spectroscopy. When left in the dark to reclose to form the DHA, the alignment is maintained. If the top glass slide is sheared horizontally to disrupt the alignment, the nematic texture appears for the DHA, (Fig. 5d). If the same disruption is done with the VHF present, the alignment reforms over several minutes. In addition to the VHF structure being planar, it also has a larger dipole moment, which could in essence lead to this larger degree of alignment of the total system relative to the corresponding neat nematic DHA. There are several examples in the literature[22] with photoalignment; the difference is that our experiment was performed in between untreated glass slides, which gives a texture. This texture then disappears upon irradiation. On the other hand, when heating pure VHF **17**, no mesophases were observed for VHF **17**, instead a rapid ring-closure to **3f** occurred.

Table 4 Transition temperatures (°C) for compounds **3f** and **3g**



	Transition temperatures (°C)
3f	Cr 90.6 (T_g 29.8 N 75.7) Iso
3g	Cr 79.9 (T_g 30.8 N 52.6) Iso

Table 5 The enthalpies (kJ mol^{-1}) and dimensionless entropies associated with transition for compound **3f** and **3g**

		N-Iso	Cr-Iso	Iso-N
3f	ΔH	0.4612	30.53	0.4044
	$\Delta S/R$	0.1590	10.09	0.1394
3g	ΔH	0.4526	31.70	0.4057
	$\Delta S/R$	0.1671	10.80	0.1498

3. Conclusions

In order to ascertain the requirements of substitution needed to make the DHA photoswitch liquid crystalline, we have prepared a large selection of compounds with various substituents at position 2 of the DHA core. Of these compounds, two exhibited a nematic liquid crystal phase, both of which had an octyloxy-biaryl attached to C2 of DHA. Irradiation of the one compound, with fluorine substitution of the biaryl, in its nematic phase partly formed the VHF. This DHA/VHF mixture exhibited a higher degree of alignment. In time, the DHA was regenerated and the order maintained. Nevertheless, full conversion to the VHF from the DHA in the nematic phase was not possible. This work presents an important step in using the DHA–VHF system in photoactive liquid crystalline materials. Future work will be aiming at exploring the influence of having two substituent groups on the DHA core.

4. Experimental

4.1 General methods

Chemicals were used as purchased from commercial sources. Purification of products was carried out by flash chromatography on silica gel (40–63 μm, 60 Å). Thin-layer chromatography (TLC) was carried out using aluminum sheets precoated with silica gel. ^{1}H NMR (500 MHz) and ^{13}C NMR (125 MHz) spectra were recorded on an instrument with a noninverse cryoprobe using the residual solvent as the internal standard ($CDCl_3$, ^{1}H 7.26 ppm and ^{13}C 77.16 ppm). All chemical shifts are quoted on the δ scale (ppm), and all coupling constants (J) are expressed in Hz. In APT spectra, CH and CH_3 correspond to negative signals and C and CH_2 correspond to positive signals. High resolution mass spectra (HRMS) were acquired either using an electrospray method of ionization (ESP) or using MALDI. Melting points are uncorrected. Compounds **15** (ref. 23) and **16** (ref. 24) were made by their respective literature methods.

General procedure for 7a–e. A mixture consisting of 4-cyanophenol **6**, the dibromide **5** (either **a–e**; 2–2.5 molar equivalents) and K_2CO_3 (1.5–2 molar equivalents) in acetone (200 mL) was heated to reflux point for 16 h. The contents of the vessel were allowed to cool to rt and filtered. The solvent was removed from the filtrate and the crude residue was subjected to column chromatography (gradient elution of petroleum spirit to toluene) to afford **7** (either **a–e**) as a white solid.

4-((5-Bromopentyl)oxy)benzonitrile (7a). Mp = 54.0–55.9 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.57 (d, J = 8.8 Hz, 2H), 6.93 (d, J =

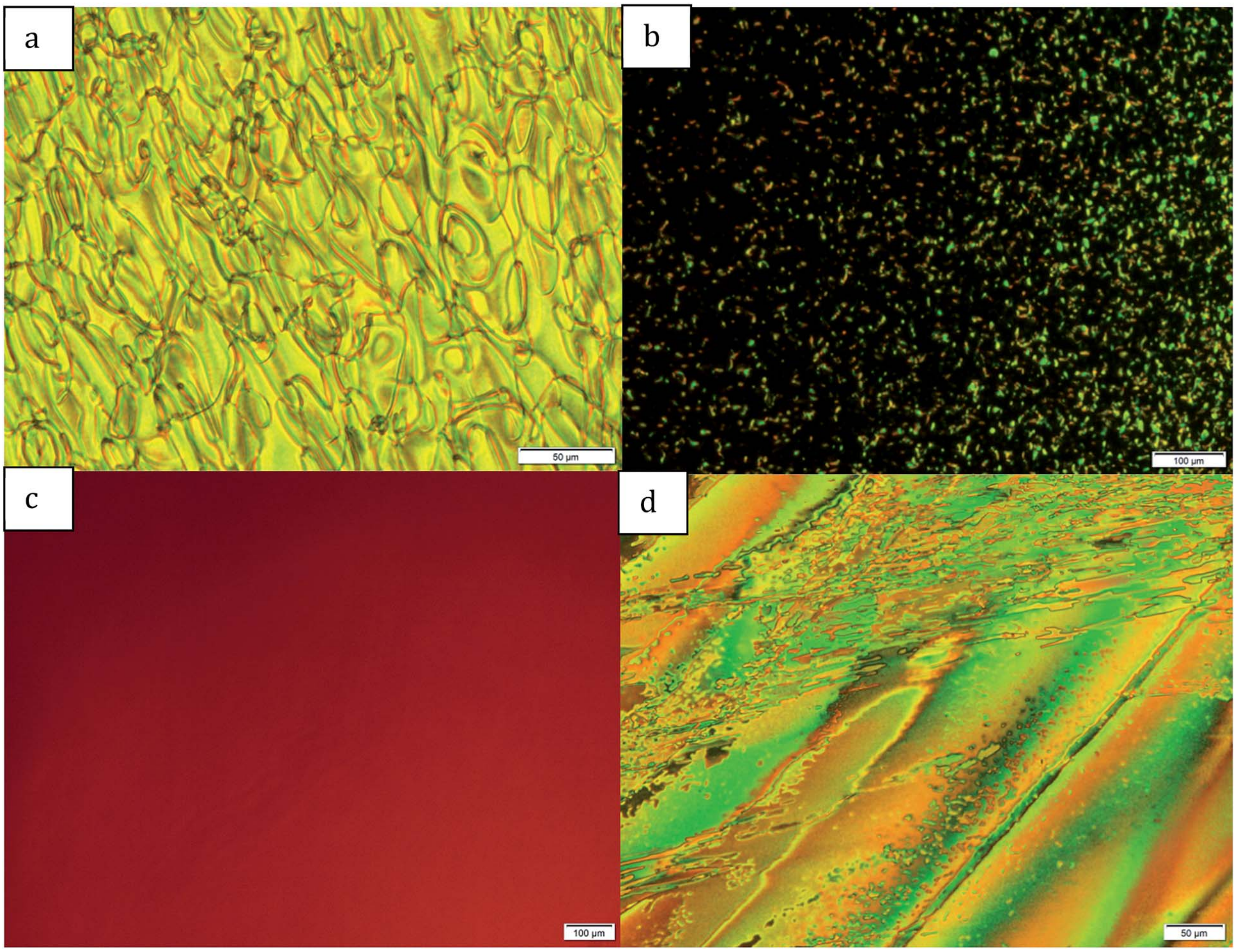


Fig. 5 (a) Photomicrographs of the nematic phase of **3f** at 60 °C. (b–d) Photomicrographs of the nematic phase of **3g** at 40 °C, (b) before light, (c) after 60 min of light, (d) after dark for 16 h.

8.8 Hz, 2H), 4.01 (t, $J = 6.3$ Hz, 2H), 3.44 (t, $J = 6.7$ Hz, 2H), 1.97–1.91 (m, 2H), 1.87–1.81 (m, 2H), 1.67–1.60 (m, 2H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): $\delta = 162.4$, 134.1, 119.4, 115.3, 104.0, 68.1, 33.6, 32.5, 28.3, 24.8 ppm. MS (ESP +ve): $m/z = 290$ [(M + Na)$^+$]. Analysis calcd (%) for $C_{12}H_{14}BrNO$ (268.15): C 53.75, H 5.26, N 5.22; found: C 53.75, H 4.90, N 5.13.

*4-((6-Bromohexyl)oxy)benzonitrile (**7b**).* Mp = 44.0–46.5 °C. ^{1}H NMR (500 MHz, $CDCl_3$): $\delta = 7.57$ (d, $J = 8.9$ Hz, 2H), 6.93 (d, $J = 8.9$ Hz, 2H), 4.00 (t, $J = 6.4$ Hz, 2H), 3.43 (t, $J = 6.6$ Hz, 2H), 1.90 (p, $J = 6.6$ Hz, 2H), 1.82 (p, $J = 6.6$ Hz, 2H), 1.53–1.50 (m, 4H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): $\delta = 162.5$, 134.1, 119.4, 115.3, 103.9, 68.3, 33.8, 32.7, 29.0, 28.0, 25.3 ppm. MS (ESP +ve): $m/z =$ 282 [(M + H)$^+$]. Analysis calcd (%) for $C_{13}H_{16}BrNO$ (282.18): C 55.33, H 5.72, N 4.96; found: C 55.66, H 5.72, N 4.98.

*4-((8-Bromooctyl)oxy)benzonitrile (**7c**).* $R_f = 0.50$ (toluene). Mp = 68.5–69.8 °C. ^{1}H NMR (500 MHz, $CDCl_3$): $\delta = 7.57$ (d, $J = 8.8$ Hz, 2H), 6.93 (d, $J = 8.8$ Hz, 2H), 3.99 (t, $J = 6.5$ Hz, 2H), 3.41 (t, $J = 6.8$ Hz, 2H), 1.89–1.84 (m, 2H), 1.82–1.77 (m, 2H), 1.49–1.42 (m, 4H), 1.39–1.33 (m, 4H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): $\delta =$ 162.5, 134.1, 119.4, 115.3, 103.8, 68.5, 34.1, 32.9, 29.2, 29.1, 28.8, 28.2, 26.0 ppm. MS (ESP +ve): $m/z = 310$ [(M + H)$^+$]. Analysis calcd (%) for $C_{15}H_{20}BrNO$ (310.24): C 58.07, H 6.50, N 4.51; found: C 58.26, H 6.53, N 4.51.

*4-((9-Bromononyl)oxy)benzonitrile (**7d**).* $R_f = 0.50$ (toluene). Mp = 64.1–65.7 °C. ^{1}H NMR (500 MHz, $CDCl_3$): $\delta = 7.55$ (d, $J = 8.9$ Hz, 2H), 6.91 (d, $J = 8.9$ Hz, 2H), 3.98 (t, $J = 6.5$ Hz, 2H), 3.39 (t, $J = 6.5$ Hz, 2H), 1.86–1.75 (m, 4H), 1.46–1.39 (m, 4H), 1.36–1.29 (m, 6H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): $\delta = 162.5$, 134.0, 119.4, 115.2, 103.7, 68.4, 34.1, 32.8, 29.3, 29.2, 29.0, 28.7, 28.2, 25.9 ppm. MS (ESP +ve): $m/z = 324$ [(M + H)$^+$]. Analysis calcd (%) for $C_{16}H_{22}BrNO$ (324.26): C 59.27, H 6.84, N 4.32; found: C 59.52, H 6.93, N 4.32.

*4-((10-Bromodecyl)oxy)benzonitrile (**7e**).* $R_f = 0.50$ (toluene). Mp = 73.2–74.7 °C. ^{1}H NMR (500 MHz, $CDCl_3$): $\delta = 7.57$ (d, $J =$ 8.9 Hz, 2H), 6.93 (d, $J = 8.9$ Hz, 2H), 3.99 (t, $J = 6.5$ Hz, 2H), 3.41 (t, $J = 6.8$ Hz, 2H), 1.88–1.77 (m, 4H), 1.48–1.40 (m, 4H), 1.36–1.28 (m, 8H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): $\delta = 162.6$, 134.1, 119.5, 115.3, 103.8, 68.5, 34.2, 32.9, 29.5, 29.5, 29.4, 29.1, 28.9, 28.3, 26.1 ppm. MS (ESP +ve): $m/z = 360$ [(M + Na)$^+$]. Analysis calcd (%) for $C_{17}H_{24}BrNO$ (338.29): C 60.36, H 7.15, N 4.14; found: C 60.53, H 7.19, N 4.15.

General procedure for 9a–e. A mixture consisting of 4-hydroxyacetophenone **8**, bromide **7** (either **a–e**; 0.8–0.85 molar equivalents) and K_2CO_3 (1–2 molar equivalents) in acetone (100 mL) was heated to reflux point for 24 h. The contents of the vessel were allowed to cool to rt, diluted with CH_2Cl_2 (200 mL) and filtered. The solvent was removed from the filtrate and the crude residue was passed through a short SiO_2 column (CH_2Cl_2) to afford **9** (either **a–e**) as a white solid.

*4-((5-(4-Acetylphenoxy)pentyl)oxy)benzonitrile (**9a**).* R_f = 0.39. Mp = 100.8–102.8 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.96 (d, J = 8.9 Hz, 2H), 7.60 (d, J = 8.9 Hz, 2H), 6.93 (d, J = 8.9 Hz, 2H), 6.92 (d, J = 8.9 Hz, 2H), 4.06 (t, J = 6.2 Hz, 2H), 4.04 (t, J = 6.3 Hz, 2H), 2.55 (s, 3H), 1.92–1.87 (m, 4H), 1.70–1.64 (m, 2H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 196.9, 163.0, 162.4, 134.1, 130.7, 130.4, 119.4, 115.3, 114.2, 104.0, 68.2, 68.0, 29.0, 28.9, 26.5, 22.8 ppm. HRMS (MALDI +ve) calcd for $C_{20}H_{22}NO_3$ ([M + H]$^+$): m/z = 324.1594; exp 324.1595. Analysis calcd (%) for $C_{20}H_{21}NO_3$ (323.39): C 74.28, H 6.55, N 4.33; found: C 74.09, H 6.28, N 4.27.

*4-((6-(4-Acetylphenoxy)hexyl)oxy)benzonitrile (**9b**).* R_f = 0.33. Mp = 99.5–101.3 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.92 (d, J = 8.9 Hz, 2H), 7.57 (d, J = 8.9 Hz, 2H), 6.93 (d, J = 8.9 Hz, 2H), 6.91 (d, J = 8.9 Hz, 2H), 4.04 (t, J = 6.4 Hz, 2H), 4.02 (t, J = 6.4 Hz, 2H), 2.55 (s, 3H), 1.87–1.82 (m, 4H), 1.57–1.55 (m, 4H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 196.9, 163.1, 162.5, 134.1, 130.7, 130.4, 119.4, 115.3, 114.2, 103.9, 68.3, 68.1, 29.2, 29.1, 26.5, 25.9, 25.9 ppm. HRMS (MALDI +ve) calcd for $C_{21}H_{24}NO_3$ ([M + H]$^+$): m/z = 338.1751; exp 338.1751. Analysis calcd (%) for $C_{21}H_{23}NO_3$ (337.42): C 74.75, H 6.87, N 4.15; found: C 74.60, H 6.73, N 3.99.

*4-((8-(4-Acetylphenoxy)octyl)oxy)benzonitrile (**9c**).* R_f = 0.35. Mp = 91.1–92.3 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.92 (d, J = 8.9 Hz, 2H), 7.56 (d, J = 8.8 Hz, 2H), 6.92 (d, J = 8.9 Hz, 2H), 6.91 (d, J = 8.8 Hz, 2H), 4.02 (t, J = 6.5 Hz, 2H), 3.99 (d, J = 6.5 Hz, 2H), 2.55 (s, 3H), 1.84–1.78 (m, 4H), 1.50–1.45 (m, 4H), 1.41–1.38 (m, 4H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 196.9, 163.2, 162.5, 134.1, 130.7, 130.3, 119.4, 115.3, 114.2, 103.8, 68.5, 68.3, 29.4, 29.4, 29.2, 29.1, 26.5, 26.1, 26.0 ppm. HRMS (MALDI +ve) calcd for $C_{23}H_{28}NO_3Na$ ([M + Na]$^+$): m/z = 388.1883; exp 388.1884. Analysis calcd (%) for $C_{23}H_{27}NO_3$ (365.47): C 75.59, H 7.45, N 3.83; found: C 75.51, H 7.28, N 3.78.

*4-((9-(4-Acetylphenoxy)nonyl)oxy)benzonitrile (**9d**).* R_f = 0.35. Mp = 86.4–87.2 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.92 (d, J = 8.6 Hz, 2H), 7.57 (d, J = 8.6 Hz, 2H), 6.93 (d, J = 8.6 Hz, 2H), 6.91 (d, J = 8.6 Hz, 2H), 4.02 (t, J = 6.5 Hz, 2H), 3.99 (t, J = 6.5 Hz, 2H), 2.55 (s, 3H), 1.83–1.77 (m, 4H), 1.49–1.43 (m, 4H), 1.39–1.35 (m, 6H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 196.9, 163.2, 162.6, 134.1, 130.7, 130.3, 119.5, 115.3, 114.3, 103.8, 68.5, 68.3, 29.6, 29.4, 29.4, 29.2, 29.1, 26.5, 26.1, 26.1 ppm. HRMS (MALDI +ve) calcd for $C_{24}H_{30}N_3O_2$ ([M + H]$^+$): m/z = 380.2220; exp 380.2221. Analysis calcd (%) for $C_{24}H_{29}NO_3$ (379.50): C 75.96, H 7.70, N 3.69; found: C 75.82, H 7.68, N 3.55.

*4-((10-(4-Acetylphenoxy)decyl)oxy)benzonitrile (**9e**).* R_f = 0.40. Mp = 71.5–73.5 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.92 (d, J = 8.8 Hz, 2H), 7.56 (d, J = 8.8 Hz, 2H), 6.92 (d, J = 8.8 Hz, 2H), 6.91 (d, J = 8.8 Hz, 2H), 4.01 (t, J = 6.5 Hz, 2H), 3.99 (d, J = 6.5 Hz, 2H), 2.55 (s, 3H), 1.83–1.76 (m, 4H), 1.48–1.42 (m, 4H), 1.37–1.32 (m, 8H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 196.9, 163.2, 162.6, 134.1, 130.7, 130.3, 119.4, 115.3, 114.2, 103.8, 68.5, 68.4, 29.6, 29.4, 29.4, 29.2, 29.1, 26.5, 26.1, 26.1 ppm, 1C masked. HRMS (MALDI +ve) calcd for $C_{25}H_{32}NO_3$ ([M + H]$^+$): m/z = 394.2377; exp 394.2377. Analysis calcd (%) for $C_{25}H_{31}NO_3$ (393.53): C 76.30, H 7.94, N 3.56; found: C 76.29, H 7.90, N 3.52.

*1-(4′-(Octyloxy)-[1,1′-biphenyl]-4-yl)ethan-1-one (**9f**).*[20,21] To a degassed biphasic mixture of 4-iodoacetophenone **10** (5.03 g, 20.4 mmol), K_3PO_4 (11.94 g, 56.71 mmol) and **11f** (6.43 g, 25.7 mmol) in toluene (120 mL) and water (20 mL) was added $Pd(PPh_3)_4$ (1.00 g, 0.86 mmol) and the biphasic mixture was stirred 20 h at rt and heated to 80 °C for 10 h. The reaction mixture was cooled to rt and was diluted with water (80 mL) and the phases were separated. The aqueous phase was extracted with CH_2Cl_2 (2 × 50 mL) and the combined organic extracts dried over $MgSO_4$, filtered and the solvent removed *in vacuo*. The solid was triturated with CH_2Cl_2 and heptane to give **9f** (5.73 g, 86%) as an off white solid. R_f = 0.41 (toluene). Mp = Cr 91.0 SmX 128 Iso; Iso 130.2 SmX 79.5 Cr °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.00 (d, J = 8.4 Hz, 2H), 7.64 (d, J = 8.4 Hz, 2H), 7.57 (d, J = 8.6 Hz, 2H), 6.99 (d, J = 8.6 Hz, 2H), 4.01 (t, J = 6.5 Hz, 2H), 2.63 (s, 3H), 1.84–1.78 (m, 2H), 1.50–1.45 (m, 2H), 1.42–1.20 (m, 8H), 0.89 (t, J = 6.8 Hz, 3H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 197.9, 159.7, 145.6, 135.4, 132.1, 129.1, 128.5, 126.7, 115.1, 68.3, 32.0, 29.5, 29.4, 26.8, 26.2, 22.8, 14.3 ppm, 1C masked. HRMS (MALDI +ve) calcd for $C_{22}H_{28}O_2Na$ [(M + Na)$^+$]: m/z = 347.1982; exp 347.1991. Analysis calcd (%) for $C_{22}H_{28}O_2$ (324.46): C 81.44, H 8.70; found: C 80.99, H 8.42.

*1-(2′,3′-Difluoro-4′-(octyloxy)-[1,1′-biphenyl]-4-yl)ethan-1-one (**9g**).* To a degassed biphase of 4-iodoacetophenone **10** (5.20 g, 21.1 mmol) in toluene (120 mL) and water (20 mL) were added $Pd(PPh_3)_4$ (1.00 g, 0.86 mmol), K_3PO_4 (14.90 g, 70.2 mmol) and **11g** (9.08 g, 31.7 mmol) and the biphasic mixture was stirred 20 h at rt, followed by heating at 80 °C for 7 h. The reaction was allowed to cool to rt and the vessel was diluted with water (80 mL) and the phases were separated. The aqueous phase was extracted with CH_2Cl_2 (2 × 50 mL) and the combined organic phases dried over $MgSO_4$, filtered and the solvent removed *in vacuo*. The residue was subjected to flash column chromatography (gradient elution of 50–80% CH_2Cl_2/heptane) and triturated from CH_2Cl_2 and heptane to give **9g** (5.01 g, 66%) as a white solid. R_f = 0.51 (toluene). Mp = Cr 63.2 Iso; Iso 53.8 SmX 48.8 Cr °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.02 (d, J = 7.9 Hz, 2H), 7.61 (d, J = 7.9 Hz, 2H), 7.13 (td, J = 8.4, 2.2 Hz, 1H), 6.82 (td, J = 8.4, 1.6 Hz, 1H), 4.09 (t, J = 6.5 Hz, 2H), 2.64 (s, 3H), 1.87–1.82 (m, 2H), 1.51–1.45 (m, 2H), 1.43–1.22 (m, 8H), 0.89 (t, J = 6.9 Hz, 3H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 197.8, 149.1 (dd, J = 249.8, 11.22 Hz), 148.8 (dd, J = 8.3, 3.1 Hz), 141.9 (dd, J = 248.2, 14.9 Hz), 139.8 (dd, J = 2.8, 1.9 Hz), 136.2, 129.0 (d, J = 3.1 Hz), 128.7, 123.8 (t, J = 4.1 Hz), 121.8 (d, J = 10.7 Hz), 109.8 (dd, J = 3.2, 0.9 Hz), 70.1, 32.0, 29.4, 29.4, 29.3, 26.8, 26.0, 22.8, 14.2 ppm. HRMS (MALDI +ve) calcd for $C_{22}H_{26}F_2O_2Na$ [(M + Na)$^+$]: m/z = 383.1793; exp 383.1805. Analysis calcd (%) for $C_{22}H_{26}F_2O_2$ (360.44): C 73.31, H 7.27; found: C 73.25, H 7.34.

*2,3-Difluoro-4-(octyloxy)acetophenone (**9h**).*[14] To a degassed solution of **12** (6.22 g, 25.7 mmol) and $FeCl_3$ (5.32 g, 32.8 mmol) in CH_2Cl_2 (150 mL), under argon and in an ice bath, was added a solution of acetyl chloride (2.1 mL in 50 mL CH_2Cl_2, 29.4 mmol) dropwise over a period of 80 min. The resulting mixture was stirred for 22 h during which time the vessel was allowed to reach rt. The reaction was quenched with water (500 mL) and the phases separated. The aqueous phase was extracted with CH_2Cl_2 (100 mL) and the combined organic extracts were washed with saturated aqueous saturated $NaHCO_3$ (200 mL), dried over $MgSO_4$, filtered and concentrated *in vacuo*. The residue was purified by flash column chromatography (gradient elution of heptane to toluene) to give **9h** (6.14 g, 84%) as a pale yellow oil. $R_f = 0.55$ (toluene). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.65 (ddd, J = 9.0, 6.7, 2.3 Hz, 1H), 6.78 (ddd, J = 9.0, 7.0, 1.8 Hz, 1H), 4.10 (t, J = 6.6 Hz, 2H), 2.61 (d, J = 5.0 Hz, 3H), 1.96–1.78 (m, 2H), 1.52–1.41 (m, 2H), 1.37–1.25 (m, 8H), 0.88 (t, J = 6.8 Hz, 3H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 193.9 (dd, J = 3.8, 2.4 Hz), 152.8 (dd, J = 8.1, 3.8 Hz), 152.0 (dd, J = 255.7, 11.3 Hz), 141.1 (dd, J = 248.4, 15.6 Hz), 125.0 (dd, J = 4.1, 3.4 Hz), 119.5 (dd, J = 10.5, 2.1), 108.9 (dd, J = 2.7, 1.0 Hz), 70.1, 31.9, 31.3 (d, J = 7.2 Hz), 29.4, 29.3, 29.1, 25.9, 22.8, 14.2 ppm. HRMS (ESP +ve) calcd for $C_{16}H_{22}F_2O_2Na$ [(M + Na)$^+$]: m/z = 307.1480; exp 307.1483. Analysis calcd (%) for $C_{16}H_{22}F_2O_2$ (284.35): C 67.59, H 7.80; found: C 67.69, H 7.71.

General procedure for 13a–i. A biphasic mixture of **9** (either **a–i**), malononitrile (3.5–9 molar equivalents), NH_4OAc (3–10 molar equivalents) in toluene (100–300 mL) and AcOH (4–23 mL) was heated using a Dean–Stark apparatus for 3–10 h. The vessel was cooled, diluted with toluene and decanted into a separatory funnel and water was added. The phases were separated and the organic phase washed with water and brine. The organic phase was dried over $MgSO_4$, filtered and the solvent removed *in vacuo*. For subsequent purification for obtaining **13** (either **a–i**), see ESI.†

*2-(1-(4-((5-(4-Cyanophenoxy)pentyl)oxy)phenyl)ethylidene)malononitrile (**13a**).* Yellowish solid. $R_f = 0.65$ (CH_2Cl_2). Mp = 83.2–84.9, 95.6–100.3 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.60 (d, J = 8.9 Hz, 2H), 7.57 (d, J = 8.9 Hz, 2H) 6.97 (d, J = 8.9 Hz, 2H), 6.94 (d, J = 8.9 Hz, 2H), 4.06 (t, J = 6.2 Hz, 2H), 4.04 (t, J = 6.2 Hz, 2H), 2.61 (s, 3H), 1.92–1.87 (m, 4H), 1.70–1.64 (m, 2H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 174.1, 162.7, 162.4, 134.1, 130.0, 127.9, 119.4, 115.3, 115.0, 113.8, 113.5, 104.0, 82.0, 68.2, 28.9, 28.8, 23.9, 22.8 ppm, 1C masked. HRMS (MALDI +ve) calcd for $C_{23}H_{22}N_3O_2$ ([M + H]$^+$): m/z = 372.1707; exp 372.1707. Analysis calcd (%) for $C_{23}H_{21}N_3O_2$ (371.44): C 74.37, H 5.70, N 11.31; found: C 73.41, H 5.76, N 10.80.

*2-(1-(4-((6-(4-Cyanophenoxy)hexyl)oxy)phenyl)ethylidene)malononitrile (**13b**).* White solid. $R_f = 0.61$ (CH_2Cl_2). Mp = 62.5–64.5 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.60 (d, J = 8.9 Hz, 2H), 7.57 (d, J = 8.9 Hz, 2H) 6.97 (d, J = 8.9 Hz, 2H), 6.93 (d, J = 8.9 Hz, 2H), 4.04 (t, J = 6.4 Hz, 2H), 4.02 (t, J = 6.3 Hz, 2H), 2.61 (s, 3H), 1.86–1.83 (m, 4H), 1.57–1.54 (m, 4H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 174.1, 162.8, 162.5, 134.1, 130.0, 127.9, 119.4, 115.3, 115.0, 113.8, 113.5, 103.9, 82.0, 68.3, 29.1, 29.1, 25.9, 25.9, 23.9 ppm, 1C masked. HRMS (MALDI +ve) calcd for $C_{24}H_{24}N_3O_2$ ([M + H]$^+$): m/z = 386.1858; exp 386.1864. Analysis calcd (%) for $C_{24}H_{23}N_3O_2$ (385.47): C 74.78, H 6.01, N 10.90; found: C 74.75, H 5.73, N 10.81.

*2-(1-(4-((8-(4-Cyanophenoxy)octyl)oxy)phenyl)ethylidene)malononitrile (**13c**).* White solid. $R_f = 0.62$ (CH_2Cl_2). Mp = 67.0–67.7 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.64 (d, J = 8.9 Hz, 2H), 7.60 (d, J = 8.9 Hz, 2H) 7.00 (d, J = 8.9 Hz, 2H), 6.96 (d, J = 8.9 Hz, 2H), 4.05 (t, J = 6.5 Hz, 2H), 4.02 (t, J = 6.4 Hz, 2H), 2.64 (s, 3H), 1.87–1.81 (m, 4H), 1.54–1.48 (m, 4H), 1.46–1.41 ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 174.2, 162.8, 162.5, 134.1, 130.0, 127.7, 119.5, 115.2, 114.9, 113.9, 113.6, 103.7, 81.8, 68.4, 29.4, 29.1, 29.1, 26.0, 26.0, 24.0 ppm. HRMS (MALDI +ve) calcd for $C_{26}H_{28}N_3O_2$ ([M + H]$^+$): m/z = 414.2176; exp 414.2177. Analysis calcd (%) for $C_{26}H_{27}N_3O_2$ (413.52): C 75.52, H 6.58, N 10.16; found: C 75.13, H 6.29, N 10.19.

*2-(1-(4-((9-(4-Cyanophenoxy)nonyl)oxy)phenyl)ethylidene)malononitrile (**13d**).* White solid. $R_f = 0.68$ (CH_2Cl_2). Mp = 87.1–88.1 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.60 (d, J = 8.9 Hz, 2H), 7.57 (d, J = 8.8 Hz, 2H), 6.97 (d, J = 8.9 Hz, 2H), 6.93 (d, J = 8.8 Hz, 2H), 4.01 (t, J = 6.5 Hz, 2H), 3.99 (t, J = 6.5 Hz, 2H), 2.61 (s, 3H), 1.83–1.77 (m, 4H), 1.49–1.43 (m, 4H), 1.39–1.35 (m, 6H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 174.2, 162.8, 162.5, 134.1, 130.0, 127.7, 119.5, 115.3, 115.0, 113.9, 113.6, 103.7, 81.8, 68.5, 68.5, 29.6, 29.4, 29.1, 29.1, 26.1, 26.0, 23.9 ppm, 1C masked. HRMS (MALDI +ve) calcd for $C_{27}H_{29}N_3O_2Na$ ([M + Na]$^+$): m/z = 450.2157; exp 450.2153. Analysis calcd (%) for $C_{27}H_{29}N_3O_2$ (427.55): C 75.85, H 6.84, N 9.83; found: C 75.50, H 6.81, N 9.80.

*2-(1-(4-((10-(4-Cyanophenoxy)decyl)oxy)phenyl)ethylidene)malononitrile (**13e**).* White solid. $R_f = 0.65$ (CH_2Cl_2). Mp = 62.6–63.8 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.60 (d, J = 8.9 Hz, 2H), 7.57 (d, J = 8.8 Hz, 2H), 6.97 (d, J = 8.9 Hz, 2H), 6.93 (d, J = 8.8 Hz, 2H), 4.01 (t, J = 6.5 Hz, 2H), 3.99 (t, J = 6.5 Hz, 2H), 2.61 (s, 3H), 1.83–1.77 (m, 4H), 1.47–1.43 (m, 4H), 1.37–1.31 (m, 8H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 174.2, 162.8, 162.5, 134.1, 130.0, 127.7, 199.5, 115.3, 115.0, 113.9, 113.6, 103.7, 81.8, 68.5, 68.5, 29.6, 29.4, 29.1, 29.1, 26.1, 26.0, 23.9 ppm, 2Cs masked. HRMS (MALDI +ve) calcd for $C_{28}H_{32}N_3O_2$ ([M + H]$^+$): m/z = 442.2489; exp 442.2491. Analysis calcd (%) for $C_{28}H_{31}N_3O_2$ (441.58): C, 76.16; H, 7.08; N, 9.52; found: C 76.30, H 7.07, N 9.50.

*2-(1-(4′-(Octyloxy)-[1,1′-biphenyl]-4-yl)ethylidene)malononitrile (**13f**).* White solid. $R_f = 0.56$ (toluene). Mp = 58.6–59.4 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.68 (d, J = 8.5 Hz, 2H), 7.64 (d, J = 8.5 Hz, 2H), 7.56 (d, J = 8.7 Hz, 2H), 6.99 (d, J = 8.7 Hz, 2H), 4.01 (t, J = 6.6 Hz, 2H), 2.67 (s, 3H), 1.84–1.78 (m, 2H), 1.51–1.45 (m, 2H), 1.40–1.26 (m, 8H), 0.90 (t, J = 6.9 Hz, 2H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 174.7, 159.9, 145.2, 133.8, 131.5, 128.4, 128.3, 127.1, 115.2, 113.2, 83.8, 68.3, 32.0, 29.5, 29.4, 29.4, 26.2, 24.1, 22.8, 14.3 ppm. HRMS (MALDI +ve) calcd for $C_{25}H_{28}N_2ONa$ [(M + Na)$^+$]: m/z = 395.2094; exp 395.2102. Analysis calcd (%) for $C_{25}H_{28}N_2O$ (372.51): C 80.61, H 7.58, N 7.52; found: C 80.67, H 7.67, N 7.38.

*2-(1-(2′,3′-Difluoro-4′-(octyloxy)-[1,1′-biphenyl]-4-yl)ethylidene)malononitrile (**13g**).* White solid. $R_f = 0.61$ (toluene). Mp = 59.5–60.4 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.65 (apparent s, 4H), 7.16–7.10 (ddd, J = 8.7, 8.2, 2.4, 1H), 6.83 (ddd, J = 9.1, 7.5, 1.8 Hz, 1H), 4.09 (t, J = 6.6 Hz, 2H), 2.68 (s, 3H), 1.92–1.81 (m, 2H), 1.54–1.44 (m, 2H), 1.42–1.22 (m, 8H), 0.89 (t, J = 6.8, 1H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 174.7, 149.1 (dd, J = 250, 11.4 Hz), 149.0 (dd, J = 8.1, 3.1 Hz), 141.9 (dd, J = 248.2, 14.8 Hz), 139.3, 134.9, 129.4, 129.4, 127.9, 123.8, 123.7, 123.7, 121.2, 121.1, 113.1, 112.9, 109.9, 84.7, 70.1, 31.9, 29.4, 29.4, 29.3, 26.0, 24.3, 22.8, 14.2 ppm. HRMS (MALDI +ve) calcd for $C_{25}H_{27}F_2N_2O$ [(M + H)$^+$]: m/z = 409.2086; exp 409.2095. Analysis calcd (%) for $C_{25}H_{26}F_2N_2O$ (408.49): C 73.51, H 6.42, N 6.86; found: C 73.33, H 6.30, N 6.78.

*2-(1-(2,3-Difluoro-4-(octyloxy)phenyl)ethylidene)malononitrile (**13h**).* Off-white solid. $R_f = 0.62$ (toluene); Mp = 59.1–60.5 °C; ^{1}H NMR (500 MHz, $CDCl_3$): $\delta = 7.13$ (ddd, $J = 9.9, 7.6, 2.2$ Hz, 1H), 6.82 (ddd, $J = 9.9, 7.2, 1.8$ Hz, 1H), 4.09 (t, $J = 6.5$ Hz, 2H), 2.61 (d, $J = 1.6$ Hz, 3H), 1.92–1.74 (m, 2H), 1.50–1.39 (m, 2H), 1.41–1.19 (m, 8H), 0.94–0.76 (m, 3H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): $\delta = 170.3$ (dd, $J = 2.5, 1.5$ Hz), 151.9 (dd, $J = 8.1, 3.7$ Hz), 148.5 (dd, $J = 254.3, 12.1$ Hz), 141.6, (dd, $J = 251.7, 13.8$ Hz), 123.2 (dd, $J = 4.5, 3.2$ Hz), 117.4 (d, $J = 10.6$ Hz), 112.2, 112.1, 109.3 (dd, $J = 3.1, 1.3$ Hz), 87.3, 70.1, 31.8, 29.2, 29.2, 28.9, 25.8, 24.1 (d, $J = 4.6$ Hz), 22.7, 14.1 ppm; HRMS (MALDI +ve) calcd for $C_{19}H_{22}F_2N_2ONa$ [(M + Na)$^+$]: m/z: 355.1592, found m/z = 355.1600.

*2-(1-(4-Octylphenyl)ethylidene)malononitrile (**13i**).* White solid. $R_f = 0.65$ (toluene). Mp = 51.5–52.0 °C. ^{1}H NMR (500 MHz, $CDCl_3$): $\delta = 7.50$ (d, $J = 8.3$ Hz, 2H), 7.30 (d, $J = 8.3$ Hz, 2H), 2.66 (t, $J = 7.7$ Hz, 2H), 2.63 (s, 3H), 1.66–1.1.60 (m, 2H), 1.35–1.27 (m, 10H), 0.88 (t, $J = 7.1$ Hz, 3H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): $\delta = 175.3$, 148.5, 133.3, 129.3, 127.7, 113.3, 113.2, 83.7, 36.1, 32.0, 31.2, 29.5, 29.4, 29.3, 24.2, 22.8, 14.2 ppm. HRMS (MALDI +ve) calcd for $C_{19}H_{24}N_2Na$ ([M + Na]$^+$): $m/z = 303.1831$; exp 303.1838. Analysis calcd (%) for $C_{19}H_{24}N_2$ (280.42): C 81.38, H 8.63, N 9.99; found: C 81.60, H 8.62, N 10.05.

*2-(4-((5-(4-Cyanophenoxy)pentyl)oxy)phenyl)azulene-1,1(8aH)-dicarbonitrile (**3a**).* To a solution of **13a** (882 mg, 2.37 mmol) and $[C_7H_7]BF_4$ (483 mg, 2.71 mmol) in CH_2Cl_2 (100 mL) at −78 °C, under an argon atmosphere, was slowly added NEt_3 (0.70 mL, 5.0 mmol) and the resulting solution stirred for 30 min. The reaction was quenched by addition of aqueous 1 M HCl (100 mL) and the vessel allowed to reach ambient temperature. The phases were separated and the organic phase dried over $MgSO_4$, filtered and the solvent removed under reduced pressure. The residue was dissolved in CH_2ClCH_2Cl (50 mL) and to the vessel $[Ph_3C]BF_4$ (882 mg, 2.49 mmol) was added whereafter the mixture was heated to reflux point for 2 h. The cooled vessel was placed in an ice bath and NEt_3 (0.50 mL, 3.6 mmol) was added slowly to the flask. Toluene (50 mL) was added to the flask and the contents allowed to sit overnight at rt, after which time the solvent was removed *in vacuo* and the crude residue purified by flash column chromatography (2% EtOAc/toluene) to give **3a** (345 mg, 32%), as an orange solid. $R_f = 0.30$ (2% EtOAc/toluene). Mp = 141.0–145.2 °C. ^{1}H NMR (500 MHz, $CDCl_3$): $\delta = 7.70$ (d, $J = 8.9$ Hz, 2H), 7.61 (d, $J = 8.9$ Hz, 2H), 6.99 (d, $J = 8.9$ Hz, 2H); 6.97 (d, $J = 8.9$ Hz, 2H), 6.79 (s, 1H), 6.59 (dd, $J = 11.3, 6.4$ Hz, 1H), 6.47 (dd, $J = 11.3, 6.1$ Hz, 1H), 6.34–6.31 (m, 2H), 5.84 (dd, $J = 10.2, 3.9$ Hz, 1H), 4.08 (t, $J = 6.3$ Hz, 2H), 4.07 (t, $J = 6.3$ Hz, 2H), 3.80 (ddd, $J = 3.9, 1.9, 1.9$ Hz, 1H), 1.96–1.89 (m, 4H), 1.74–1.69 (m, 2H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): $\delta = 162.3$, 160.4, 139.9, 139.0, 134.0, 131.0, 130.4, 130.1, 127.8, 127.6, 123.0, 120.0, 119.4, 119.3, 115.3, 115.2, 115.1, 112.9, 103.7, 68.1, 67.8, 51.1, 45.2, 28.8, 28.8, 22.7 ppm. HRMS (MALDI +ve) calcd for $C_{30}H_{26}N_3O_2$ ([M + H]$^+$): m/z = 460.2020; exp 460.2021. Analysis calcd (%) for $C_{30}H_{25}N_3O_2$ (459.55): C 78.41, H 5.48, N 9.14; found: C 78.11, H 5.40, N 9.05.

*2-(4-((6-(4-Cyanophenoxy)hexyl)oxy)phenyl)azulene-1,1(8aH)-dicarbonitrile (**3b**).* To a solution of **13b** (1.05 g, 2.72 mmol) and $[C_7H_7]BF_4$ (527 mg, 2.96 mmol) in CH_2Cl_2 (100 mL) at −78 °C, under an argon atmosphere, was slowly added NEt_3 (1.0 mL, 7.2 mmol) and the resulting solution stirred for 30 min. The reaction was quenched by addition of aqueous 1 M HCl (100 mL) and the vessel allowed to reach ambient temperature. The phases were separated and the organic phase dried over $MgSO_4$, filtered and the solvent removed under reduced pressure. The residue was dissolved in CH_2ClCH_2Cl (50 mL) and to the vessel $[Ph_3C]BF_4$ (1.00 g, 3.03 mmol) was added whereafter the mixture was heated to reflux point for 2 h. The cooled vessel was placed in an ice bath and NEt_3 (0.70 mL, 5.0 mmol) was added slowly to the flask. Toluene (50 mL) was added to the flask and the contents allowed to sit overnight at rt, after which time the solvent was removed *in vacuo* and the crude residue purified by flash column chromatography (2% EtOAc/toluene) to give **3b** (603 mg, 47%), as a fluffy yellow solid. $R_f = 0.33$ (2% EtOAc/toluene). Mp = 122.1–124.0 °C. ^{1}H NMR (500 MHz, $CDCl_3$): $\delta = 7.67$ (d, $J = 8.9$ Hz, 2H), 7.57 (d, $J = 8.9$ Hz, 2H), 6.96 (d, $J = 8.9$ Hz, 2H), 6.93 (d, $J = 8.9$ Hz, 2H), 6.75 (s, 1H), 6.55 (dd, $J = 11.3, 6.4$ Hz, 1H), 6.44 (dd, $J = 11.3, 6.1$ Hz, 1H), 6.31–6.28 (m, 2H), 5.81 (dd, $J = 10.2, 3.9$ Hz, 1H), 4.03 (t, $J = 6.4$ Hz, 2H), 4.02 (t, $J = 6.4$ Hz, 2H), 3.77 (ddd, $J = 3.9, 2.0, 2.0$ Hz, 1H), 1.88–1.82 (m, 3H), 1.57–1.54 (m, 3H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 162.5, 160.6, 140.1, 139.2, 134.1, 131.1, 130.5, 130.2, 128.0, 127.8, 123.1, 120.1, 119.4, 119.4, 115.3, 115.3, 113.0, 68.3, 68.1, 51.3, 45.4, 29.2, 29.1, 25.9, 25.9 ppm, 1C masked. HRMS (MALDI +ve) calcd for $C_{31}H_{28}N_3O_2$ ([M + H]$^+$): m/z = 474.2176; exp 474.2176. Analysis calcd (%) for $C_{31}H_{27}N_3O_2$ (473.58): C 78.62, H 5.75, N 8.87; found: C 78.31, H 5.42, N 8.69.

*2-(4-((8-(4-Cyanophenoxy)octyl)oxy)phenyl)azulene-1,1(8aH)-dicarbonitrile (**3c**).* To a solution of **13c** (1.04 g, 2.52 mmol) and $[C_7H_7]BF_4$ (522 mg, 2.93 mmol) in CH_2Cl_2 (100 mL) at −78 °C, under an argon atmosphere, was slowly added NEt_3 (1.0 mL, 7.2 mmol) and the resulting solution stirred for 30 min. The reaction was quenched by addition of aqueous 1 M HCl (100 mL) and the vessel allowed to reach ambient temperature. The phases were separated and the organic phase dried over $MgSO_4$, filtered and the solvent removed under reduced pressure. The residue was dissolved in CH_2ClCH_2Cl (50 mL) and to the vessel $[Ph_3C]BF_4$ (929 mg, 2.81 mmol) was added whereafter the mixture was heated to reflux point for 2 h. The cooled vessel was placed in an ice bath and NEt_3 (0.70 mL, 5.0 mmol) was added slowly to the flask. Toluene (50 mL) was added to the flask and the contents allowed to sit overnight at rt, after which time the solvent was removed *in vacuo* and the crude residue purified by flash column chromatography (2% EtOAc/toluene) to give **3c** (200 mg, 16%) as an orange solid. R_f = 0.35 (2% EtOAc/toluene). Mp = 98.5–101.2 °C. ^{1}H NMR (500 MHz, $CDCl_3$): $\delta = 7.67$ (d, $J = 8.9$ Hz, 2H), 7.57 (d, $J = 8.9$ Hz, 2H), 6.96 (d, $J = 8.9$ Hz, 2H), 6.93 (d, $J = 8.9$ Hz, 2H), 6.75 (s, 1H), 6.55 (dd, $J = 11.2, 6.4$ Hz, 1H), 6.44 (dd, $J = 11.3, 6.1$ Hz, 1H), 6.31–6.28 (m, 2H), 5.81 (dd, $J = 10.2, 3.8$ Hz, 1H), 4.01 (t, $J = 6.5$ Hz, 1H), 4.00 (d, $J = 6.5$ Hz, 1H), 3.77 (ddd, $J = 3.9, 2.0, 2.0$ Hz, 1H), 1.84–1.78 (m, 4H), 1.51–1.45 (m, 4H), 1.42–1.39 (m, 4H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): $\delta = 162.6$, 160.7, 140.2, 139.2, 134.1, 131.1, 130.4, 130.2, 127.9, 127.8, 123.0, 120.0, 119.5, 119.4, 115.5, 115.3, 113.0, 103.8, 68.5, 68.3, 51.3, 45.4, 29.4, 29.2, 29.1, 26.1, 26.0 ppm, 2C masked. HRMS (MALDI +ve) calcd for $C_{33}H_{32}N_3O_2$ ([M + H]$^+$): $m/z = 502.2489$; exp 502.2490.

*2-(4-((9-(4-Cyanophenoxy)nonyl)oxy)phenyl)azulene-1,1(8aH)-dicarbonitrile (**3d**).* To a solution of **13d** (1.02 g, 2.39 mmol) and $[C_7H_7]BF_4$ (500 mg, 2.81 mmol) in CH_2Cl_2 (100 mL) at −78 °C, under an argon atmosphere, was slowly added NEt_3 (1.0 mL, 7.2 mmol) and the resulting solution stirred for 30 min. The reaction was quenched by addition of aqueous 1 M HCl (100 mL) and the vessel allowed to reach ambient temperature. The phases were separated and the organic phase dried over $MgSO_4$, filtered and the solvent removed under reduced pressure. The residue was dissolved in CH_2ClCH_2Cl (50 mL) and to the vessel $[Ph_3C]BF_4$ (935 mg, 2.83 mmol) was added whereafter the mixture was heated to reflux point for 2 h. The cooled vessel was placed in an ice bath and NEt_3 (0.70 mL, 5.0 mmol) was added slowly to the flask. Toluene (50 mL) was added to the flask and the contents allowed to sit overnight at rt, after which time the solvent was removed *in vacuo* and the crude residue purified by flash column chromatography (2% EtOAc/toluene) to give **3d** (258 mg, 21%) as an orange solid. $R_f = 0.36$ (2% EtOAc/toluene). Mp = 98.9–103.8, 125.6–130.6 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.67 (d, J = 8.8 Hz, 2H), 7.57 (d, J = 8.8 Hz, 2H), 6.96 (d, J = 8.8 Hz, 2H), 6.93 (d, J = 8.8 Hz, 2H), 6.75 (s, 1H), 6.55 (dd, J = 11.2, 6.4 Hz, 1H), 6.44 (dd, J = 11.2, 6.1 Hz, 1H), 6.31–6.28 (m, 2H), 5.81 (dd, J = 10.2, 3.8 Hz, 1H), 4.01 (t, J = 6.8 Hz, 2H), 4.00 (t, J = 6.8 Hz, 2H), 3.77 (ddd, J = 3.8, 2.0, 2.0 Hz, 1H), 1.83–1.78 (m, 4H), 1.49–1.44 (m, 4H), 1.40–1.37 (m, 6H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 162.6, 160.7, 140.2, 139.2, 134.1, 131.1, 130.4, 130.2, 127.9, 127.8, 123.0, 120.0, 119.5, 119.4, 115.5, 115.3, 113.0, 103.8, 68.5, 68.3, 51.3, 45.4, 29.6, 29.4, 29.2, 29.1, 26.1, 26.1 ppm, 2Cs masked. HRMS (MALDI +ve) calcd for $C_{34}H_{34}N_3O_2$ ([M + H]$^+$): m/z = 516.2646; exp 516.2649. Analysis calcd (%) for $C_{34}H_{33}N_3O_2$ (515.66): C 79.19, H 6.45, N 8.15; found: C 78.68, H 6.18, N 8.11.

*2-(4-((10-(4-Cyanophenoxy)decyl)oxy)phenyl)azulene-1,1(8aH)-dicarbonitrile (**3e**).* To a solution of **13e** (1.12 g, 2.54 mmol) and $[C_7H_7]BF_4$ (503 mg, 2.83 mmol) in CH_2Cl_2 (100 mL) at −78 °C, under an argon atmosphere, was slowly added NEt_3 (1.0 mL, 7.2 mmol) and the resulting solution stirred for 30 min. The reaction was quenched by addition of aqueous 1 M HCl (100 mL) and the vessel allowed to reach ambient temperature. The phases were separated and the organic phase dried over $MgSO_4$, filtered and the solvent removed under reduced pressure. The residue was dissolved in CH_2ClCH_2Cl (50 mL) and to the vessel $[Ph_3C]BF_4$ (851 mg, 2.58 mmol) was added whereafter the mixture was heated to reflux point for 2 h. The cooled vessel was placed in an ice bath and NEt_3 (0.70 mL, 5.0 mmol) was added slowly to the flask. Toluene (50 mL) was added to the flask and the contents allowed to sit overnight at rt, after which time the solvent was removed *in vacuo* and the crude residue purified by flash column chromatography (2% EtOAc/toluene) to give **3e** (552 mg, 41%), as an orange solid. R_f = 0.38 (2% EtOAc/toluene). Mp = 102.2–121.8 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.67 (d, J = 8.9 Hz, 2H), 7.57 (d, J = 8.9 Hz, 2H), 6.97 (d, J = 8.9 Hz, 2H), 6.93 (d, J = 8.9 Hz, 2H), 6.75 (s, 1H), 6.55 (dd, J = 11.3, 6.3 Hz, 1H), 6.44 (dd, J = 11.3, 6.1 Hz, 1H), 6.31–6.28 (m, 2H), 5.81 (dd, J = 10.2, 3.8 Hz, 1H), 4.01 (d, J = 6.6 Hz, 2H), 3.99 (d, J = 6.6 Hz, 2H), 3.77 (ddd, J = 3.8, 1.9, 1.9 Hz, 1H), 1.83–1.77 (m, 4H), 1.49–1.43 (m, 4H), 1.39–1.32 (m, 6H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 162.6, 160.7, 140.2, 139.2, 134.1, 131.1, 130.4, 130.1, 127.9, 127.8, 123.0, 120.0, 119.5, 119.4, 115.5, 115.3, 115.3, 113.0, 103.8, 68.5, 68.3, 51.3, 45.4, 29.6, 29.6, 29.5, 29.5, 29.2, 29.1, 26.1, 26.1 ppm. HRMS (MALDI +ve) calcd for $C_{35}H_{36}N_3O_2$ ([M + H]$^+$): m/z = 530.2802; exp 530.2806.

*2-(4′-(Octyloxy)-[1,1′-biphenyl]-4-yl)azulene-1,1(8aH)-dicarbonitrile (**3f**). Method 1*: to a solution/suspension of the crude mixture from **13f** (3.54 g, 9.50 mmol) and $[C_7H_7]BF_4$ (1.71 g, 9.61 mmol) in CH_2Cl_2 (250 mL), at −78 °C under an argon atmosphere, was added NEt_3 (1.0 g, 1.4 mL, 10 mmol) over a 30 min period and the reaction mixture stirred at −78 °C for 2 h. Additional NEt_3 was added (0.5 mL, 3.58 mmol) and the reaction mixture was left to stir for 1 h and allowed to reach rt and subjected to ultrasonication. HCl (150 mL, 2 M) was added to the vessel and the phases separated. The aqueous phase was extracted with CH_2Cl_2 (100 mL) and the combined organic phases dried over $MgSO_4$, filtered, and the solvent was removed *in vacuo*. The residue was taken up in CH_2ClCH_2Cl (125 mL) and treated with $[Ph_3C]BF_4$ (3.85 g, 11.6 mmol) and subjected to reflux for 2 h under inert atmosphere. The reaction mixture was diluted with toluene (125 mL) and cooled to 0 °C and NEt_3 (1.2 g, 1.7 mL, 12 mmol) was added, where the mixture was stirred overnight and allowed to reach room temperature. The solvent was removed in vacuum, and the residue was subjected to flash chromatography (40–50% CH_2Cl_2/heptane) and crystallized from CH_2Cl_2/ethanol to furnish **3f** (502 mg, 11%) as a yellow solid. *Method 2*: To a degassed solution of **15** (1.54 g, 4.03 mmol) in toluene (60 mL) and water (15 mL) was added $Pd(OAc)_2$ (55 mg, 0.245 mmol), RuPhos (187 mg, 0.400 mmol), K_3PO_4 (1.31 g, 6.17 mmol) and **11f** (1.56 g, 6.24 mmol), and the biphasic mixture stirred for 18 h at 80 °C. TLC indicated an incomplete reaction and more $Pd(OAc)_2$ (60 mg, 0.267 mmol), RuPhos (195 mg, 0.419 mmol) and K_3PO_4 (2.32 g, 10.9 mmol) and **11f** (1.21 g, mmol) were added and the mixture heated to 80 °C for another 18 h. The contents of the vessel were diluted with water (100 mL) and the phases were separated. The aqueous phase was extracted with CH_2Cl_2 (100 mL) and the combined organic extracts were dried over $MgSO_4$, filtered and the solvent removed *in vacuo*. The crude residue was subjected to flash column chromatography (gradient elution of 55–70% toluene/heptane) and subsequently recrystallized from CH_2Cl_2/heptane to give pure **3f** (562 mg, 30%). R_f = 0.42 (50% CH_2Cl_2/heptane). Mp = Cr 90.6 (N 75.7) Iso; Iso 75.6 N 29.8 T_g °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.78 (d, J = 8.3 Hz, 2H), 7.66 (d, J = 8.3 Hz, 2H), 7.56 (d, J = 8.7 Hz, 2H), 6.99 (d, J = 8.7 Hz, 2H), 6.91 (s, 1H), 6.57 (dd, J = 11.2, 6.4 Hz, 1H), 6.47 (dd, J = 11.2, 6.1 Hz, 1H), 6.35 (d, J = 6.4 Hz, 1H), 6.31 (ddd, J = 10.1, 6.1, 2.1 Hz, 1H), 5.84 (dd, J = 10.1, 3.8 Hz, 1H), 4.01 (t, J = 6.6 Hz, 1H), 3.81 (ddd, J = 3.7, 2.0, 2.0 Hz, 1H), 1.84–1.78 (m, 2H), 1.51–1.46 (m, 2H), 1.43–1.14 (m, 10H), 0.89 (t, J = 6.9 Hz, 2H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 159.3, 142.4, 140.0, 138.9, 132.0, 131.7, 131.0, 130.8, 128.5, 128.1, 127.7, 127.2, 126.7, 120.7, 119.5, 115.2, 115.0, 112.8, 68.2, 51.2, 45.1, 31.8, 29.4, 29.3, 29.3, 26.1, 22.7, 14.1 ppm. HRMS (MALDI +ve) calcd for $C_{32}H_{32}N_2ONa$ [(M + Na)$^+$]: m/z = 483.2407; exp 483.2406. Analysis calcd (%) for $C_{32}H_{32}N_2O$ (460.62): C 83.44, H 7.00, N 6.08; found: C 83.28, H 6.90, N 6.12.

2-(2′,3′-Difluoro-4′-(octyloxy)-[1,1′-biphenyl]-4-yl)azulene-1,1(8aH)-dicarbonitrile (3g). Method 1: to a mixture of **13g** (3.35 g, 8.21 mmol) and $[C_7H_7]BF_4$ (1.53 g, 8.60 mmol) in CH_2Cl_2 (250 mL) at −78 °C under argon atmosphere was added NEt_3 (1.2 mL, 8.6 mmol) portion-wise over 30 min and the reaction mixture stirred at −78 °C for 2 h. Since there were still starting material and tropylium left unreacted, more NEt_3 was added (0.5 mL, 3.58 mmol) and the reaction mixture was left to stir for 1 h more and allowed to reach rt while being sonicated. Then it was quenched with HCl (100 mL, 2 M) and diluted with water (50 mL). Subsequently, the phases were separated and the water phase was extracted with CH_2Cl_2 (100 mL) and the combined organic phase was dried over $MgSO_4$ and the solvent was removed by rotary evaporation. The residue was treated with $[Ph_3C]BF_4$ (3.27 g, 9.89 mmol) in DCE (125 mL) under reflux for 2 h under an argon atmosphere, after which time the reaction mixture was cooled to 0 °C and diluted with toluene (125 mL). When the reaction mixture reached 0 °C, NEt_3 (1.5 mL, 10 mmol) was added, and the mixture was stirred overnight, while allowing to reach rt, and left to stir for 15 h. The solvent was removed *in vacuo* and the residue was subjected to flash column chromatography (40–50% CH_2Cl_2/heptane) and crystallized from CH_2Cl_2 and ethanol to give **3g** (1.104 g, 25%) as a yellow solid. Method 2: To a degassed solution of **15** (2.05 g, 5.36 mmol) in toluene (60 mL) and water (15 mL) were added $Pd(OAc)_2$ (76 mg, 0.339 mmol), RuPhos (262 mg, 0.561 mmol) and K_3PO_4 (2.51 g, 11.8 mmol) and **11g** (1.56 g, mmol). Degassed water (15 mL) was added and the biphasic mixture stirred for 18 h at 90 °C. Additional $Pd(OAc)_2$ (62 mg, 0.276 mmol), RuPhos (206 mg, 0.441 mmol) and K_3PO_4 (1.80 g, 8.48 mmol) and **11g** (1.04 g, mmol) were added and the mixture heated to 80 °C for a further 18 h. The contents of the vessel were diluted with water (100 mL) and the phases were separated. The aqueous phase was extracted with CH_2Cl_2 (100 mL) and the combined organic components were dried over $MgSO_4$, filtered and the solvent removed *in vacuo*. The crude residue was subjected to flash column chromatography (20% EtOAc/heptane) and a second flash column (gradient eluent 40–60% CH_2Cl_2/heptane) and then recrystallized from CH_2Cl_2/heptane to give **3g** (522 mg, 20%). R_f = 0.44 (50% CH_2Cl_2/heptane). Mp = Cr 79.9 (N 52.6) Iso; Iso 52.6 N 30.8 T_g °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.80 (d, J = 8.4 Hz, 2H), 7.62 (dd, J = 8.4, 1.3 Hz, 2H), 7.13 (td, J = 8.5, 2.3 Hz, 1H), 6.93 (s, 1H), 6.83 (td, J = 8.5, 1.6 Hz, 1H), 6.58 (dd, J = 11.2, 6.3 Hz, 1H), 6.49 (dd, J = 11.2, 6.1 Hz, 1H), 6.37 (d, J = 6.3 Hz, 0H), 6.32 (ddd, J = 10.2, 6.1, 2.1 Hz, 1H), 5.84 (dd, J = 10.2, 3.8 Hz, 1H), 4.09 (t, J = 6.6 Hz, 2H), 3.81 (ddd, J = 3.8, 2.1, 2.1 Hz, 1H), 1.85 (p, J = 6.6 Hz, 2H), 1.52–1.49 (m, 2H), 1.41–1.20 (m, 10H), 0.89 (t, J = 6.6 Hz, 3H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 149.2 (dd, J = 250.6, 11.2 Hz), 148.6 (dd, J = 8.2, 3.0 Hz), 142.0 (dd, J = 247.9, 14.9 Hz), 139.8, 138.8, 136.8 (dd, J = 2.4, 1.5 Hz), 132.6, 131.1 (d, J = 8.5 Hz), 129.7, 129.6 (d, J = 3.3 Hz), 127.8, 126.5, 123.6 (apparent t, J = 4.1 Hz), 121.7 (d, J = 10.6 Hz), 121.3, 119.6, 115.4, 112.9, 109.8 (dd, J = 3.3, 1.2 Hz), 70.1, 51.3, 45.3, 32.0, 29.5, 29.4, 29.3, 26.0, 22.8, 14.3 ppm. HRMS (MALDI +ve) calcd for $C_{32}H_{30}F_2N_2ONa$ [(M + Na)$^+$]: m/z = 519.2218, found m/z = 519.2217. Analysis calcd (%) for $C_{32}H_{30}F_2N_2O$ (496.60): C 77.40, H 6.09, N 5.64; found: C 77.59, H 5.88, N 5.70.

2-(2,3-Difluoro-4-(octyloxy)phenyl)azulene-1,1(8aH)-dicarbonitrile (3h). To a mixture of **13h** (6.58 g, 19.8 mmol) and $[C_7H_7]BF_4$ (3.62 g, 20.4 mmol) in CH_2Cl_2 (250 mL) at −78 °C under an argon atmosphere, was added NEt_3 (2.8 mL, 20.4 mmol) over 30 min, and the reaction mixture stirred at −78 °C for 2 h. Additional NEt_3 (0.5 mL, 3.58 mmol) was added and the reaction mixture was allowed to stir for a further 60 min. The reaction was quenched cold with HCl (50 mL, 2 M) and allowed to reach rt and diluted with water (50 mL). The phases were separated and the organic phase was washed with water (250 mL), dried over $MgSO_4$, filtered and the solvent removed under reduced pressure. The residue was taken up in CH_2ClCH_2Cl (125 mL) and treated with $[Ph_3C]BF_4$ (7.96 g, 24.1 mmol) and the vessel subjected to reflux for 2 h under argon. The reaction mixture was cooled to 0 °C and diluted with toluene (125 mL) and NEt_3 (3.4 mL, 24.4 mmol) was added. The mixture was stirred overnight, allowing the vessel to reach rt. The solvent was removed *in vacuo* and the residue was subjected to flash chromatography (30–50% CH_2Cl_2/heptane) to give **3h** (2.528 g, 30%) as a yellow solid. R_f = 0.60 (50% CH_2Cl_2/heptane). Mp = 95.0–97.9 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.52 (td, J = 8.5, 2.0 Hz, 1H), 7.04 (s, 1H), 6.92–6.81 (m, 1H), 6.57 (dd, J = 11.3, 6.4 Hz, 1H), 6.48 (dd, J = 11.3, 6.1 Hz, 1H), 6.37 (d, J = 6.4 Hz, 1H), 6.31 (ddd, J = 10.3, 6.1, 1.9 Hz, 1H), 5.80 (dd, J = 10.3, 3.8 Hz, 1H), 4.10 (t, J = 6.6 Hz, 2H), 3.74 (ddd, J = 3.8, 1.9, 1.9 Hz, 1H), 1.88–1.82 (m, 2H), 1.51–1.45 (m, 2H), 1.40–1.25 (m, 8H), 0.90 (t, J = 6.8 Hz, 3H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 150.51 (dd, J = 254.2, 11.8 Hz), 149.89 (dd, J = 8.2, 3.6 Hz), 142.05 (dd, J = 249.0, 14.8 Hz), 139.27, 135.90 (d, J = 14.9 Hz), 132.86 (dd. J = 4.3, 3.3 Hz), 131.08 (d, J = 1.6 Hz), 127.91, 121.71 (dd, J = 4.3, 3.6 Hz), 121.67, 119.45, 115.22, 112.95 (d, J = 9.1 Hz), 112.83, 109.34 (dd, J = 3.0, 1.2 Hz), 70.03, 50.36, 46.32, 31.91, 29.38, 29.31, 29.09, 25.95, 22.78, 14.22 ppm, 1C masked. HRMS (MALDI +ve) calcd for $C_{26}H_{26}F_2N_2O$ [(M)$^+$]: m/z = 420.2008; exp 420.2008; analysis calcd (%) for $C_{26}H_{26}F_2N_2O$ (420.20): C 74.26, H 6.23, N 6.66; found: C 74.14, H 6.35, N 6.54.

2-(4-Octylphenyl)azulene-1,1-(8aH)-dicarbonitrile (3i). To a mixture of **13i** (10.01 g, 35.70 mmol) and $[C_7H_7]BF_4$ (6.35 g, 35.7 mmol) in CH_2Cl_2 (250 mL), at −78 °C under an argon atmosphere, was added NEt_3 (5 mL, 35.9 mmol) over 30 min, and the resulting mixture allowed to stir at −78 °C for 2 h. Saturated aqueous NH_4Cl (100 mL) and water (100 mL) were added to the vessel and the contents allowed to reach ambient temperature. The phases were separated and the organic phase was washed with water (200 mL) and brine (200 mL). The organic phase was dried over $MgSO_4$, filtered, and the removal of the solvent gave the crude mixture (13.08 g). Of this crude material (12.84 g, 34.65 mmol) was dissolved in $ClCH_2CH_2Cl$ (200 mL) and treated with $[Ph_3C]BF_4$ (13.73 g, 41.58 mmol), whilst being subjected to reflux for 2 h under argon. After cooling the vessel, toluene (200 mL) was added and the vessel placed in an ice bath, where NEt_3 (6.3 mL, 45 mmol) was added and the mixture was stirred overnight, whilst being allowed to reach rt. Aqueous NH_4Cl (100 mL) was added to the vessel and the phases separated. The organic phase was washed with water

(100 mL) and brine (100 mL), dried with $MgSO_4$, filtered and absorbed onto Celite. The material was purified by dry column vacuum chromatography (gradient elution from heptane to toluene in 10% steps) followed by recrystallization from boiling ethanol to give **3i** (1.73 g, 14%). The material was stored in the freezer, as it decomposes at ambient temperature. R_f = 0.65 (50% toluene/heptane). Mp = 54.4–58.6 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.58 (d, J = 8.4 Hz, 2H), 7.20 (d, J = 8.4 Hz, 2H), 6.77 (s, 1H), 6.49 (dd, J = 11.2, 6.4 Hz, 1H), 6.39 (dd, J = 11.2, 6.1 Hz, 1H), 6.31–6.05 (m, 2H), 5.75 (dd, J = 10.3, 3.8 Hz, 1H), 3.71 (ddd, J = 3.8, 1.9, 1.9 Hz, 1H), 2.57 (t, J = 7.7 Hz, 2H), 1.62–1.52 (m, 2H), 1.34–1.01 (m, 10H), 0.81 (t, J = 7.0 Hz, 3H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 145.7, 140.5, 139.1, 131.4, 131.1, 130.7, 129.5, 128.0, 127.8, 126.3, 120.6, 119.6, 115.4, 113.0, 51.3, 45.3, 36.0, 32.0, 31.3, 29.6, 29.5, 29.4, 22.8, 14.3 ppm. HRMS (MALDI +ve) calcd for $C_{26}H_{27}N_2$ [(M − H)$^+$]: m/z = 367.2169; exp 367.2169; analysis calcd (%) for $C_{26}H_{28}N_2$ (368.52): C 84.74, H 7.66, N 7.60; found: C 84.69, H 7.58, N 7.60.

General procedure for 14a–e. To a solution of **7** (either **a–e**) in DMSO (20 mL), under an argon atmosphere, was added NaN_3 (1.5–2 molar equivalents) and the contents of the reaction vessel were heated to 50 °C for 2 h. The cooled reaction mixture was poured into ice-water (*ca.* 50 g) and extracted with Et_2O (3 × 75 mL). The combined organics were washed with water (100 mL), dried over $MgSO_4$, filtered and the volatiles removed *in vacuo*. Purification by flash column chromatography (1% EtOAc/toluene) gave **14** (either **a–e**) as a white solid.

*4-((5-Azidopentyl)oxy)benzonitrile (**14a**).* R_f = 0.41. Mp = 29.1–30.5 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.57 (d, J = 7.6 Hz, 2H), 6.93 (d, J = 7.6 Hz, 2H), 4.01 (t, J = 6.3 Hz, 2H), 3.32 (t, J = 6.7 Hz, 2H), 1.84 (p, J = 6.3 Hz, 2H), 1.68 (p, J = 6.7 Hz, 2H), 1.65–1.51 (m, 2H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 162.4, 134.1, 119.4, 115.3, 104.0, 68.1, 51.4, 28.7, 28.7, 23.5 ppm. HRMS (ESP +ve) calcd for $C_{12}H_{14}N_4ONa$ ([M + Na]$^+$): m/z = 231.1060; exp 253.1060.

*4-((6-Azidohexyl)oxy)benzonitrile (**14b**).* R_f = 0.42. Mp = 37.4–40.5 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.57 (d, J = 8.8 Hz, 2H), 6.93 (d, J = 8.8 Hz, 2H), 4.00 (t, J = 6.4 Hz, 2H), 3.29 (t, J = 6.8 Hz, 2H), 1.82 (p, J = 6.4 Hz, 2H), 1.64 (p, J = 6.8 Hz, 2H), 1.57–1.42 (m, 4H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 162.5, 134.1, 119.4, 115.3, 103.9, 68.3, 51.5, 29.0, 28.9, 26.6, 25.7 ppm. HRMS (ESP +ve) calcd for $C_{13}H_{16}N_4ONa$ ([M + Na]$^+$): m/z = 267.1217; exp 267.1216.

*4-((8-Azidooctyl)oxy)benzonitrile (**14c**).* R_f = 0.44. Mp = 33.9–36.5 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.57 (d, J = 8.8 Hz, 2H), 6.93 (d, J = 8.8 Hz, 2H), 3.99 (t, J = 6.5 Hz, 2H), 3.26 (t, J = 6.6 Hz, 2H), 1.80 (p, J = 6.5 Hz, 2H), 1.63–1.56 (m, 2H), 1.53–1.16 (m, 8H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 162.5, 134.1, 119.4, 115.3, 103.8, 68.5, 51.6, 29.3, 29.2, 29.1, 28.9, 26.8, 26.0 ppm. HRMS (ESP +ve) calcd for $C_{15}H_{20}N_4ONa$ ([M + Na]$^+$): m/z = 295.1529; exp 295.1530.

*4-((9-Azidononyl)oxy)benzonitrile (**14d**).* R_f = 0.49. Mp = 42.5–43.2 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.57 (d, J = 8.8 Hz, 2H), 6.93 (d, J = 8.8 Hz, 2H), 3.99 (t, J = 6.56 Hz, 2H), 3.26 (t, J = 6.8 Hz, 2H), 1.79 (t, J = 6.56 Hz, 2H), 1.60 (t, J = 6.8 Hz, 2H), 1.51–1.25 (m, 10H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 162.6, 134.1, 119.5, 115.3, 103.8, 68.5, 51.6, 29.5, 29.3, 29.2, 29.1, 29.0, 26.8, 26.0 ppm. HRMS (ESP +ve) calcd for $C_{16}H_{22}N_4ONa$ ([M + Na]$^+$): m/z = 309.1687; exp 309.1686.

*4-((10-Azidodecyl)oxy)benzonitrile (**14e**).* R_f = 0.49. Mp = 46.7–47.7 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.57 (d, J = 8.9 Hz, 2H), 6.93 (d, J = 8.9 Hz, 2H), 3.99 (t, J = 6.6 Hz, 2H), 3.26 (t, J = 6.9 Hz, 2H), 1.80 (p, J = 6.6 Hz, 2H), 1.60 (p, J = 6.9 Hz, 2H), 1.48–1.31 (m, 12H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 162.4, 134.0, 119.3, 115.2, 103.7, 68.4, 51.5, 29.4, 29.4, 29.3, 29.1, 29.0, 28.8, 26.7, 25.9 ppm. HRMS (ESP +ve) calcd for $C_{17}H_{24}N_4ONa$ ([M + Na]$^+$): m/z = 323.1842; exp 323.1842.

*1,1-Dicyano-2-(4-(1-(5-(4-cyanophenoxy)pentyl)-1H-1,2,3-triazol-4-yl)phenyl)-1,8a-dihydroazulene (**4a**).* To a degassed solution of **15** (51 mg, 0.182 mmol), **14a** (96 mg, 0.417 mmol) and Hünig's base (10 drops) in toluene (4 mL) was added CuI (8 mg, 0.021 mmol) and the contents stirred for 2 days at rt. The solvent was removed under reduced pressure and the residue purified by flash column chromatography (10% EtOAc/CH_2Cl_2) to furnish **4a** as a yellow solid (91 mg, 98%). R_f = 0.60 (5% EtOAc/CH_2Cl_2). Mp = 183.6–185.5; 186.9–188.7 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.92 (d, J = 8.4 Hz, 2H), 7.82 (s, 1H), 7.80 (d, J = 8.4 Hz, 2H), 7.56 (d, J = 8.8 Hz, 2H), 6.93 (s, 1H), 6.90 (d, J = 8.8 Hz, 2H), 6.57 (dd, J = 11.3, 6.4 Hz, 1H), 6.48 (dd, J = 11.3, 6.1 Hz, 1H), 6.36 (d, J = 6.4 Hz, 1H), 6.31 (ddd, J = 10.2, 6.1, 1.9 Hz, 1H), 5.82 (dd, J = 10.2, 3.7 Hz, 1H), 4.46 (t, J = 7.0 Hz, 2H), 3.99 (t, J = 6.2 Hz, 2H), 3.80 (ddd, J = 3.7, 1.9, 1.9 Hz, 1H), 2.06 (p, J = 7.0 Hz, 2H), 1.87 (p, J = 6.2 Hz, 2H), 1.59–1.53 (m, 2H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 162.3, 146.9, 139.7, 138.8, 134.1, 132.5, 132.2, 131.1, 131.1, 130.2, 127.8, 126.9, 126.4, 121.3, 120.2, 119.5, 119.4, 115.3, 112.9, 104.1, 51.2, 50.4, 45.2, 30.1, 28.5, 23.2 ppm. HRMS (MALDI +ve) calcd for $C_{32}H_{27}N_6O$ ([M + H]$^+$): m/z = 511.2244; exp 511.2244. Analysis calcd (%) for $C_{32}H_{26}N_6O$ (510.60): C 75.27, H 5.13, N 16.46; found: C 75.27, H 4.78, N 16.26.

*1,1-Dicyano-2-(4-(1-(6-(4-cyanophenoxy)hexyl)-1H-1,2,3-triazol-4-yl)phenyl)-1,8a-dihydroazulene (**4b**).* To a degassed solution of **15** (104 mg, 0.371 mmol), **14b** (117 mg, 0.478 mmol) and Hünig's base (10 drops) in toluene (4 mL) was added CuI (10 mg, 0.053 mmol) and the contents stirred for 2 days at rt. The solvent was removed under reduced pressure and the residue was subjected to flash column chromatography (10% EtOAc/CH_2Cl_2) and subsequently crystallized (CH_2Cl_2/heptane) to furnish **4b** (141 mg, 72%) as a yellow solid. R_f = 0.66 (5% EtOAc/CH_2Cl_2). Mp = 54.0–55.7 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.92 (d, J = 8.6 Hz, 2H), 7.82 (s, 1H), 7.80 (d, J = 8.6 Hz, 2H), 7.55 (d, J = 8.9 Hz, 2H), 6.94 (s, 1H), 6.91 (d, J = 8.9 Hz, 2H), 6.58 (dd, J = 11.2, 6.5 Hz, 1H), 6.48 (dd, J = 11.2, 6.1 Hz, 1H), 6.36 (d, J = 6.5 Hz, 1H), 6.31 (ddd, J = 10.2, 6.1, 2.1 Hz, 1H), 5.83 (dd, J = 10.2, 3.8 Hz, 1H), 4.44 (t, J = 7.1 Hz, 2H), 3.98 (t, J = 6.3 Hz, 2H), 3.80 (ddd, J = 3.8, 2.1, 2.1 Hz, 1H), 2.01 (p, J = 7.1 Hz, 2H), 1.85–1.77 (m, 2H), 1.58–1.50 (m, 2H), 1.48–1.40 (m, 2H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 162.4, 146.9, 139.7, 138.8, 134.1, 132.5, 132.3, 131.1, 131.1, 130.2, 127.8, 126.9, 126.4, 121.3, 120.1, 119.6, 119.4, 115.3, 112.9, 103.9, 68.1, 51.3, 50.5, 45.3, 30.3, 28.9, 26.3, 25.6 ppm. MS (ESP +ve): m/z = 525 ([M + H]$^+$). Analysis calcd (%) for $C_{33}H_{28}N_6O$ (524.63): C 75.55, H 5.38, N 16.02; found: C 75.57, H 5.39, N 16.00.

1,1-Dicyano-2-(4-(1-(8-(4-cyanophenoxy)octyl)-1H-1,2,3-triazol-4-yl)phenyl)-1,8a-dihydroazulene (4c). To a degassed solution of **15** (66 mg, 0.235 mmol), **14c** (87 mg, 0.318 mmol) and Hünig's base (10 drops) in toluene (4 mL) was added CuI (7 mg, 0.037 mmol) and the contents stirred for 2 days at rt. The solvent was removed under reduced pressure and the residue purified by flash column chromatography (10% EtOAc/CH_2Cl_2) to furnish **4c** (65 mg, 50%) as a yellow solid. $R_f = 0.75$ (5% EtOAc/CH_2Cl_2). Mp = 148.6–152.4 °C. ^{1}H NMR (500 MHz, $CDCl_3$): $\delta = 7.93$ (d, $J = 8.5$ Hz, 2H), 7.81 (s, 1H), 7.79 (d, $J = 8.5$ Hz, 2H), 7.56 (d, $J = 8.8$ Hz, 2H), 6.93 (s, 1H), 6.91 (d, $J = 8.8$ Hz, 2H), 6.57 (dd, $J = 11.3$, 6.4 Hz, 1H), 6.48 (dd, $J = 11.3$, 6.1 Hz, 1H), 6.36 (d, $J = 6.4$ Hz, 1H), 6.31 (ddd, $J = 10.2$, 6.1, 2.0 Hz, 1H), 5.83 (dd, $J = 10.2$, 3.8 Hz, 1H), 4.42 (t, $J = 7.1$ Hz, 2H), 3.97 (t, $J = 6.5$ Hz, 2H), 3.80 (ddd, $J = 3.8$, 2.0, 2.0 Hz, 1H), 2.00–1.96 (m, 2H), 1.81–1.75 (m, 2H), 1.53–1.32 (m, 8H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): $\delta =$ 162.5, 146.8, 139.7, 138.78, 134.1, 132.5, 132.3, 131.1, 130.1, 127.8, 126.9, 126.4, 121.3, 120.1, 119.6, 119.4, 115.3, 115.3, 112.9, 103.8, 68.4, 51.2, 50.6, 45.2, 30.4, 29.2, 29.0, 29.0, 26.5, 25.9 ppm, 1C masked. HRMS (MALDI +ve) calcd for $C_{35}H_{33}N_6O$ ($[M + H]^+$): $m/z = 553.2710$; exp 553.2716. Analysis calcd (%) for $C_{35}H_{32}N_6O$ (552.68): C 76.06, H 5.84, N 15.21; found: C 75.93, H 5.88, N 15.11.

1,1-Dicyano-2-(4-(1-(9-(4-cyanophenoxy)nonyl)-1H-1,2,3-triazol-4-yl)phenyl)-1,8a-dihydroazulene (4d). To a degassed solution of **15** (49 mg, 0.175 mmol), **14d** (49 mg, 0.179 mmol) and Hünig's base (10 drops) in toluene (4 mL) was added CuI (7 mg, 0.037 mmol) and the contents stirred for 2 days at rt. The solvent was removed under reduced pressure and the residue was subjected to flash column chromatography (10% EtOAc/CH_2Cl_2) followed by crystallization to give pure **4d** (49 mg, 49%) as a yellow solid. $R_f = 0.77$ (5% EtOAc/CH_2Cl_2). Mp = 131.9–148.4 °C. ^{1}H NMR (500 MHz, $CDCl_3$): $\delta = 7.94$ (d, $J = 8.4$ Hz, 2H), 7.81–7.79 (m, 3H), 7.57 (d, $J = 8.77$ Hz, 2H), 6.93–6.91 (m, 3H), 6.58 (dd, $J = 11.3$, 6.3 Hz, 1H), 6.49 (dd, $J = 11.3$, 6.1 Hz, 1H), 6.36 (d, $J = 6.3$ Hz, 1H), 6.32 (ddd, $J = 10.2$, 6.1, 2.0 Hz, 1H), 5.83 (dd, $J = 10.2$, 3.8 Hz, 1H), 4.42 (t, $J = 7.1$ Hz, 2H), 3.98 (t, $J = 6.5$ Hz, 2H), 3.81 (ddd, $J = 3.8$, 2.0, 2.0 Hz, 1H), 1.99–1.96 (m, 2H), 1.78 (p, $J = 6.5$ Hz, 2H), 1.44–1.41 (m, 2H), 1.37–1.34 (m, 8H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): $\delta = 162.4$, 146.7, 139.6, 138.7, 134.0, 132.3, 132.2, 131.0, 130.9, 130.0, 127.7, 126.8, 126.3, 121.1, 119.9, 119.5, 119.3, 115.2, 112.7, 103.7, 68.3, 51.1, 50.5, 45.1, 30.3, 29.3, 29.2, 29.0, 28.9, 26.5, 25.9 ppm. HRMS (MALDI +ve) calcd for $C_{36}H_{35}N_6O$ (M^+): $m/z = 566.2789$; exp 566.2794. Analysis calcd (%) for $C_{36}H_{34}N_6O$ (566.71): C 76.30, H 6.05, N 14.83; found: C 75.92, H 5.70, N 14.71.

1,1-Dicyano-2-(4-(1-(10-(4-cyanophenoxy)deconyl)-1H-1,2,3-triazol-4-yl)phenyl)-1,8a-dihydroazulene (4e). To a degassed solution of **15** (73 mg, 0.260 mmol), **14e** (112 mg, 0.373 mmol) and Hünig's base (10 drops) in toluene (4 mL) was added CuI (15 mg, 0.079 mmol) and the contents stirred for 2 days at rt. The solvent was removed under reduced pressure and the residue was subjected to flash column chromatography (10% EtOAc/CH_2Cl_2) followed by crystallization to give pure **4e** (73 mg, 48%) as a yellow solid. $R_f = 0.80$ (5% EtOAc/CH_2Cl_2). Mp = 111.1–115.1 °C. ^{1}H NMR (500 MHz, $CDCl_3$): $\delta = 7.94$ (d, $J = 8.4$ Hz, 2H), 7.81–7.79 (m, 3H), 7.56 (d, $J = 8.9$ Hz, 1H), 6.93–6.91 (m, 3H), 6.58 (dd, $J = 11.2$, 6.4 Hz, 1H), 6.49 (dd, $J = 11.2$, 6.0 Hz, 1H), 6.36 (d, $J = 6.4$ Hz, 1H), 6.32 (ddd, $J = 10.4$, 6.1, 1.8 Hz, 1H), 5.83 (dd, $J = 10.4$, 3.7 Hz, 1H), 4.42 (t, $J = 7.0$ Hz, 2H), 3.98 (t, $J = 6.4$ Hz, 2H), 3.81 (ddd, $J = 3.7$, 1.8, 1.8 Hz, 1H), 2.16–1.89 (m, 2H), 1.81–1.75 (m, 2H), 1.49–1.16 (m, 12H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): $\delta = 146.8$, 139.8, 138.8, 134.1, 132.5, 132.4, 131.1, 131.1, 130.1, 127.9, 126.9, 126.4, 121.3, 120.1, 119.6, 119.5, 115.3, 115.3, 112.9, 103.8, 68.5, 51.3, 50.7, 45.3, 30.5, 29.5, 29.4, 29.4, 29.1, 29.1, 26.6, 26.1 ppm. HRMS (MALDI +ve) calcd for $C_{37}H_{36}N_6O$ (M^+): $m/z = 580.2945$; exp 580.2951.

1,1-Dicyano-2-(4-octyl-(1H-1,2,3-triazol-4-yl)phenyl)-1,8a-dihydroazulene (4j). To a degassed solution of **16** (98 mg, 0.350 mmol), octylazide (106 mg, 0.683 mmol) and Hünig's base (10 drops) in toluene (4 mL) was added CuI (11 mg, 0.058 mmol) and the contents stirred for 2 days at rt. The solvent was removed under reduced pressure and the residue was subjected to flash column chromatography (10% EtOAc/CH_2Cl_2) followed by crystallization to give pure **4j** (147 mg, 97%) as a yellow solid. $R_f = 0.84$ (5% EtOAc/CH_2Cl_2). Mp = 126.1–130.6 °C. ^{1}H NMR (500 MHz, $CDCl_3$): $\delta = 7.94$ (d, $J = 8.4$ Hz, 2H), 7.81 (s, 1H), 7.79 (d, $J = 8.4$ Hz, 2H), 6.93 (s, 1H), 6.57 (dd, $J = 11.2$, 6.3 Hz, 1H), 6.48 (dd, $J = 11.2$, 6.1 Hz, 1H), 6.35 (d, $J = 6.3$ Hz, 1H), 6.34–6.28 (m, 1H), 5.83 (dd, $J = 10.2$, 3.6 Hz, 1H), 4.41 (t, $J = 7.2$ Hz, 2H), 3.80 (ddd, $J = 3.7$, 1.9, 1.9 Hz, 1H), 1.99–1.91 (m, 2H), 1.97–1.95 (m, 2H), 1.42–1.18 (m, 8H), 0.87 (t, $J = 6.8$ Hz, 3H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): $\delta = 146.6$, 139.7, 138.7, 132.3, 130.9, 130.9, 129.9, 127.7, 126.7, 126.3, 121.1, 120.0, 119.5, 115.2, 112.7, 51.1, 50.6, 45.1, 31.7, 30.4, 29.1, 29.0, 26.5, 22.6, 14.1 ppm, 1C masked. HRMS (MALDI +ve) calcd for $C_{28}H_{30}N_5$ ($[M + H]^+$): $m/z = 436.2496$; exp 436.2495. Analysis calcd (%) for $C_{28}H_{29}N_5$ (435.58): C 77.21, H 6.71, N 16.08; found: C 77.15, H 6.80, N 15.94.

2-(2-(Cyclohepta-2,4,6-trien-1-ylidene)-1-(4′-(octyloxy)-[1,1′-biphenyl]-4-yl)ethylidene)malononitrile (17). To a stirred solution of **3f** (418 mg, 0.908 mmol) in CH_2Cl_2 (50 mL) at rt under an argon atmosphere, was added $AlCl_3$ (341 mg, 2.56 mmol). After continued stirring for approximately 20 min, TLC analysis indicated the presence of unreacted **3f** and more $AlCl_3$ (183 mg, 1.37 mmol) was added to the vessel and the reaction allowed to stir a further 20 min. The mixture was cooled on an ice bath and quenched by addition of ice-water (100 mL) and the phases separated. The aqueous phase was extracted with CH_2Cl_2 (2 × 50 mL) and the combined organic phases dried over $MgSO_4$ and filtered. The solution was diluted with heptane (100 mL) and the CH_2Cl_2 was removed by rotary evaporation while being kept at 0 °C. The solution was placed in a freezer resulting in the crystallization of **17**, which was isolated as a dark red solid (368 mg, 88%). This material was stored in the freezer to prevent ring-closure back to **3f**. Mp = 105–109 °C. ^{1}H NMR (500 MHz, $CDCl_3$): $\delta = 7.35$ (d, $J = 8.2$ Hz, 2H), 7.35 (d, $J = 8.7$ Hz, 2H), 7.10 (d, $J = 8.2$ Hz, 2H), 6.91 (d, $J = 8.7$ Hz, 2H), 6.12 (s, 1H), 5.80 (dd, $J = 11.4$, 1.5, 1H), 5.65 (dd, $J = 12.2$, 2.1 Hz, 1H), 5.59–5.49 (m, 2H), 5.46–5.42 (m, 1H), 5.10 (dd, $J = 12.2$, 7.8 Hz, 1H), 3.69 (t, $J = 6.5$ Hz, 2H), 1.68–1.63 (m, 2H), 1.39–1.34 (m, 2H), 1.33–1.18 (m, 8H), 0.92 (t, $J = 7.0$ Hz, 3H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): $\delta = 167.8$, 160.1, 152.9, 143.7, 142.2, 135.2, 134.7, 134.2, 133.3, 133.2, 132.7, 132.1, 129.3, 128.6, 128.4, 127.6, 119.8, 115.3, 78.4, 68.1, 32.2, 29.8, 29.7, 29.7, 26.4, 23.1, 14.4 ppm, 1C masked. HRMS (MALDI +ve) calcd for $C_{32}H_{32}N_2ONa$ $[(M + Na)^+]$: $m/z = 483.2407$, found $m/z = 483.2412$. Analysis calcd (%) for $C_{32}H_{32}N_2O$ (496.62): C 83.49, H 7.00, N 6.08; found: C 83.38, H 7.11, N 6.14.

*2-(2-(Cyclohepta-2,4,6-trien-1-ylidene)-1-(2′,3′-difluoro-4′-hydroxy-[1,1′-biphenyl]-4-yl)ethylidene)malononitrile (**18**).* To a stirred solution of **3g** (210 mg, 0.423 mmol) in CH_2Cl_2 (50 mL) at rt, under an argon atmosphere, was added $AlCl_3$ (1.010 g, 7.58 mmol) and the mixture was stirred for 20 min. TLC analysis indicated the presence of unreacted **3g** and more $AlCl_3$ (540 mg, 4.05 mmol) was added, whereby the reaction was allowed to stir a further 20 min. The mixture was cooled on an ice bath and quenched by addition of ice-water (100 mL) after which the phases were separated. The aqueous phase was extracted with CH_2Cl_2 (2 × 50 mL) and the combined organic phases was dried with $MgSO_4$ and filtered. Heptane was added (100 mL), and the solution concentrated under reduced pressure at 0 °C, whereby the solution was placed at −18 °C for 16 h, resulting in the crystallization of **18** (85 mg, 52%) as a dark red solid. This material was stored in the freezer to prevent ring-closure back to **3g**. Mp = 129.7–131.0 (color change to yellow), 168 (decomposes) °C. ^1H NMR (500 MHz, $CDCl_3$): $\delta = 7.61$ (d, $J = 7.9$ Hz, 2H), 7.47 (d, $J = 7.9$ Hz, 2H), 7.13 (td, $J = 8.3, 2.2$ Hz, 1H), 6.90–6.84 (m, 1H), 6.75–6.69 (m, 1H), 6.45–6.37 (m, 2H), 6.35 (s, 1H), 6.33–6.27 (m, 1H), 5.94 (d, $J = 4.6$ Hz, 1H), 5.60 (br s, 1H, exchanges D_2O) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = ppm ^{13}C NMR (125 MHz, $CDCl_3$): $\delta = 168.4$, 154.1, 148.4 (dd, $J = 250.4, 11.4$ Hz), 145.0 (dd, $J = 11.3, 2.0$ Hz), 142.3, 137.7 (dd, $J = 2.5, 1.6$ Hz), 135.6, 135.3, 135.2, 134.5, 134.1, 133.7, 129.9 (d, $J = 3.3$ Hz), 128.6, 124.3 (dd, $J = 3.8, 3.8$ Hz), 121.4 (d, $J = 9.8$ Hz), 118.9, 115.1, 114.6, 112.6 (dd, $J = 3.6, 1.0$ Hz) ppm, 2Cs masked. HRMS (MALDI +ve) calcd for $C_{32}H_{31}F_2N_2O$ $[(M + H)^+]$: $m/z = 358.1147$, found $m/z = 385.1142$.

Acknowledgements

The Danish Council for Independent Research | Technology and Production Sciences (#12-126668) and University of Copenhagen are acknowledged for financial support. Dr Theis Brock-Nannestad, University of Copenhagen, is thanked for helpful discussions.

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