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Reactive mesogens for ultraviolet-transparent liquid crystal polymer networks

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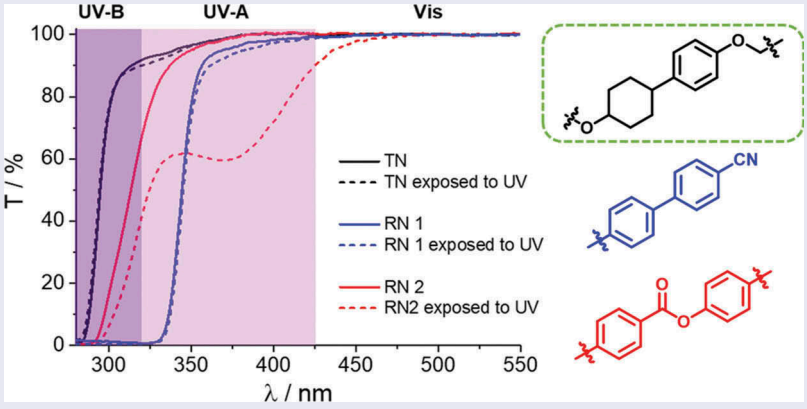
ABSTRACT

Transparency and stability to UV light are important and desirable properties for modern tunable optical elements and active soft robots. A library of novel reactive mesogens for liquid crystal polymer networks resilient and transparent to UV light has been synthetised and characterised. Phase behaviours of the reactive mesogens have been determined by polarised optical microscopy and differential scanning calorimetry. Liquid crystal polymer networks based on the combination of these novel reactive mesogens have been evaluated and compared to those based on common commercially available compounds. The results showed a twofold increase in transparency in a broad UV spectral region (200–400 nm) and importantly showed no degradation upon prolonged UV exposure contrary to the networks composed from commercial counterparts.



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Liquid crystals; reactive mesogens; liquid crystal polymer networks; UV transparent; liquid crystal elastomers

1. Introduction

Liquid crystalline materials have recently reached beyond applications in display technology, to extend to smart materials for advanced optics such as tunable filters, retarders, diffraction gratings and sensors [1–5]. The design and synthesis of sophisticated liquid crystal polymer networks (LCPNs) have also opened new perspectives for soft robotics and the development of light-driven soft robots [6,7].

In liquid crystal systems, light responsiveness is promoted by the use of photoactive molecules – either by doping native liquid crystals or by coupling them covalently to a polymer network. Light-induced molecular changes such as isomerisation, cyclisation and cycloaddition cause structural changes in these photoactive molecular switches, and these are transmitted to the material, which modifies its properties [8] and allows performing work, as anticipated by de Gennes in 1997 [9]. Photoswitches (azobenzenes, hydrazones, stilbenes, etc.) [10–13] and molecular motors [14,15] are the most widely used active molecules in LCPNs, and they usually absorb strongly in the UV. However, up-to-date LCPNs fabricated from commercially available reactive mesogens partially absorb light in the same spectral range as the photoswitches, thus limiting their operation and narrowing down the range of light-responsive switches that can be embedded due to two main reasons: (i) low transparency of LCPNs in the desired UV spectral range; (ii) low photostability of LCPNs to UV light. Low transparency sufficiently decreases the efficiency of photochemical processes since most of the light is absorbed by the predominant liquid crystal molecules of

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LCPNs and dissipated as heat. Regarding the issue of stability, LCPNs are mostly degraded or irremediably modified by photo-Fries rearrangement [16], the homolytic photo-cleavage followed by recombination which usually takes place in phenyl esters but that can also occur with various molecular moieties like diphenyl ether, amide, acetanilide, etc. [17].

In this work, we have overcome these two limitations in order to create materials which are transparent and resilient to UV light, including UV-A (315–400 nm) and UV-B (280–315 nm), and therefore are suitable as host media for UV photoactive molecules (switches and molecular motors). We describe the synthesis and characterisation of 12 reactive mesogens (mono- and diacrylates), which can be used as building blocks for LCPNs with enhanced photostability and UV transparency unmatched by commercially available analogues.

2. Experimental

2.1. Materials and instruments

All reactions are carried out under N_2. Tetrahydrofuran (THF) was purified and dried over Braun solvent purification system (MB-SPS-800), and other solvents (DMSO, DMF, CH_2Cl_2, heptane and ethanol) were purchased dry from Sigma-Aldrich and used without further purification. The chemical reagents were purchased from Synthon, abcr and Sigma-Aldrich and used as received. Analytical thin-layer chromatography was carried out on Merck silica gel 60 F_{254}. Products were revealed by ultraviolet light (254 or 366 nm) and stained with dyeing reagents (potassium permanganate aqueous solution). Flash chromatography was performed on Combiflash® Companion or with Merck silica gel 60 (230–400 mesh). ^{1}H and ^{13}C NMR spectra were recorded at ambient temperature on Bruker Ascend™ 400 spectrometers operating at 400 MHz ^{1}H. ^{13}C nucleus was observed with ^{1}H decoupling. Solvent residual signals were used as internal standard. Chemical shifts (δ) and coupling constants (*J*) are given in ppm and Hz, respectively. The peak patterns are indicated as the following format multiplicity (s: singlet; d: doublet; t: triplet; q: quartet; sept: septuplet; m: multiplet; dd: doublet of doublet; dt: doublet of triplet; dm: doublet of multiplet, etc.). The prefix br. indicates a broadened signal. Mass spectrometry was performed on MSVision spectrometer (micromass LCT). UV-vis spectra were measured on HR2000 + High-Resolution spectrometer (Ocean Optics). The phase behaviour was studied with a polarised optical microscope BX51 (Olympus) equipped with a heating stage (Instec). Differential scanning calorimetry (DSC) study was performed using Netzsch DCS-214 machine with heating/cooling speed 10 K/min.

2.2. Synthesis

General procedure 1 (**GP1**)

Phenol compound (1 eq.), alkyl halogen compound (1 eq.), K_2CO_3 (2.8 eq.) and KI (cat.) were dissolved in absolute ethanol (5 mL/1 mmol) and heated to reflux for 48 h. The organic phase was washed with a saturated solution of NaOH in water (5 mL/1 mmol), distilled water (5 mL/1 mmol) and brine (5 mL/1 mmol). The organic phase was dried over $MgSO_4$, and the solvent was evaporated under reduced pressure. The product was purified by flash chromatography on silica with the appropriate eluent.

General procedure 2 (**GP2**)

The alcohol (1 eq.) and NEt_3 (1.5 eq.) were dissolved in THF (5 mL/1 mmol) and stirred at 0°C. The acyl chloride (1.2 eq.) was added slowly while stirring at 0°C. After 1 h, the reaction was allowed to warm up to r.t. and was stirred for an additional 16 h. The resulting suspension was filtrated, and the filtrate was dried under reduced pressure. The residue was dissolved with CH_2Cl_2 (10 mL/1 mmol) and washed successively with distilled water (2× 10 mL/1 mmol) and brine (10 mL/1 mmol). The organic phase was dried over $MgSO_4$, and the solvent was evaporated under reduced pressure. The product was purified by flash chromatography on silica with the appropriate eluent.

General procedure 3 (**GP3**)

The alkyl halogen (1 eq.), potassium acrylate (2 eq. × number of halogen function), KI (0.4 eq. × number of halogen function) and 4-methoxyphenol (2 crystals) were dissolved in DMSO (5 mL/1 mmol) and stirred at 52°C for 72 h. The reaction was cooled down to r.t., and the product was precipitated with distilled water. The precipitate was filtrated and washed with distilled water. The solid was dissolved in CH_2Cl_2 (10 mL/1 mmol) and washed with distilled water (2× 10 mL/1 mmol) and brine (10 mL/1 mmol). The organic phase was dried over $MgSO_4$, and the solvent was evaporated under reduced pressure. The product was purified by flash chromatography on silica with the appropriate eluent.

6-(4′-((1s,4′r)-4-Propylcyclohexyl)phenoxy)hexan-1-ol (**1**).

1 was synthesised according to **GP1**. Trans-4-(4-propylcyclohexyl)phenol (5 g, 23 mmol) and 6-bromohexanol were used, respectively, as phenol and alkyl halogen compound. Flash chromatography with CH_2Cl_2/MeOH (99:1) as eluent yields 4.1 g of pure compound.

Yield = 56%. R_f (CH_2Cl_2/EtOAc, 8:2) = 0.44.

^{1}H NMR ($CDCl_3$, 400 MHz) δ = 0.86 (t, 3H, J = 7.25 Hz, -C**H$_3$**), 1.00 (2H, m, -C**H$_2$**-CH$_3$), 1.15–1.49 (11H, m, -C**H**-CH$_2$-, -CH$_2$-C**H$_2$**-CH-, -CH$_2$-C**H$_2$**-CH$_2$-), 1.56–1.83 (8H, m, -CH-C**H$_2$**-C**H$_2$**-CH-), 2.36

(1H, tt, J = 12.20, 3.23 Hz, Ar-C**H**), 3.60 (2H, t, J = 6.57 Hz, C**H$_2$**-OH), 3.89 (2H, t, J = 6.48 Hz, Ar-O-C**H$_2$**), 6.77 (2H, d, J = 8.55 Hz, Ar-**H**), 7.07 ppm (2H, d, J = 8.57 Hz, Ar-**H**).

6-(4′-((1s,4′r)-4-Pentylcyclohexyl)phenoxy)hexan-1-ol (**2**).

2 was synthesised according to **GP1**. Trans-4-(4-pentylcyclohexyl)phenol (5 g, 20 mmol) and 6-bromohexanol were used, respectively, as phenol and alkyl halogen compound. Flash chromatography with CH_2Cl_2/MeOH (99:1) as eluent yields 5 g of pure compound.

Yield = 71%. R_f (CH_2Cl_2/EtOAc, 8:2) = 0.44.

^{1}H NMR ($CDCl_3$, 400 MHz) δ = 0.89 (t, 3H, J = 6.98 Hz, -C**H$_3$**), 1.03 (2H, m, -C**H$_2$**-CH_3), 1.18–1.48 (15H, m, -C**H**-CH_2-, -CH_2-C**H$_2$**-CH-, -CH_2-C**H$_2$**-CH_2-), 1.56–1.89 (8H, m, -CH-C**H$_2$**-C**H$_2$**-CH-), 2.40 (1H, tt, J = 12.18, 3.21 Hz, Ar-C**H**), 3.66 (2H, t, J = 6.55 Hz, C**H$_2$**-OH), 3.93 (2H, t, J = 6.48 Hz, Ar-O-C**H$_2$**), 6.82 (2H, d, J = 8.63 Hz, Ar-**H**), 7.11 ppm (2H, d, J = 8.61 Hz, Ar-**H**).

6-(4′-((1s,4′r)-4-Heptylcyclohexyl)phenoxy)hexan-1-ol (**3**).

3 was synthesised according to **GP1**. Trans-4-(4-heptylcyclohexyl)phenol (2.8 g, 10 mmol, 1 eq.) and 6-bromohexanol were used, respectively, as phenol and alkyl halogen compound. Flash chromatography with CH_2Cl_2/MeOH (99:1) as eluent yields 2.5 g of pure compound.

Yield = 67%. R_f (CH_2Cl_2/EtOAc, 8:2) = 0.44.

^{1}H NMR ($CDCl_3$, 400 MHz) δ = 0.92 (t, 3H, J = 6.59 Hz, -C**H$_3$**), 1.04 (2H, m, -C**H$_2$**-CH_3), 1.20–1.53 (19H, m, -C**H**-CH_2-, -CH_2-C**H$_2$**-CH-, -CH_2-C**H$_2$**-CH_2-), 1.61–1.91 (8H, m, -CH-C**H$_2$**-C**H$_2$**-CH-), 2.43 (1H, m, Ar-C**H**), 3.65 (2H, t, J = 6.57 Hz, C**H$_2$**-OH), 3.95 (2H, t, J = 6.46 Hz, Ar-O-C**H$_2$**), 6.84 (2H, d, J = 8.19 Hz, Ar-**H**), 7.13 ppm (2H, d, J = 8.20 Hz, Ar-**H**).

(1r,4′r)-4′-(4-(Cyclohexyloxy)phenyl)cyclohexan-1-ol (**4**).

4 was synthesised according to **GP1**. Trans-4-(4-cyclohexyloxy)phenol (2 g, 10 mmol, 1 eq.) and bromohexane were used, respectively, as phenol and alkyl halogen compound. 2.7 g of the pure compound was obtained without further purification.

Yield = 97.5%. R_f (CH_2Cl_2/EtOAc, 8:2) = 0.40.

^{1}H NMR ($CDCl_3$, 400 MHz) δ = 0.90 (t, 3H, J = 6.57 Hz, -C**H$_3$**), 1.32–1.52 (8 H, m, -CH_2-C**H$_2$**-CH_2-, -CH_2-C**H$_2$**-CH_3), 1.57–2.10 (8 H, m, -CH-C**H$_2$**-C**H$_2$**-CH-OH), 2.44 (1 H, m, Ar-C**H**), 3.67 (1 H, m, C**H**-OH), 3.92 (2 H, t, J = 6.58 Hz, Ar-O-C**H$_2$**), 6.82 (2 H, d, J = 8.11 Hz, Ar-**H**), 7.10 ppm (2 H, d, J = 8.16 Hz, Ar-**H**).

(1r,4′r)-4-(4′-((6-Bromohexyl)oxy)phenyl)cyclohexan-1-ol (**5**).

5 was synthesised according to **GP1**. Trans-4-(4-cyclohexyloxy)phenol (2.2 g, 11 mmol, 1 eq.) and 1,6-dibromohexane (5 mL, 33 mmol, 3 eq) were used, respectively, as phenol and alkyl halogen compound. Instead of column chromatography, 200 mL of heptane was added to the oily residue to yield 2 g of the pure compound after filtration.

Yield = 51%. R_f (CH_2Cl_2/EtOAc, 8:2) = 0.42.

^{1} H NMR ($CDCl_3$, 400 MHz) δ = 1.38–1.55 (8H, m, -CH_2-C**H$_2$**-CH_2-), 1.78–2.10 (8H, m, -CH-C**H$_2$**-C**H$_2$**-**CH**-), 2.44 (1H, m, Ar-C**H**), 3.42 (2H, t, J = 6.81 Hz, C**H$_2$**-Br), 3.67 (1H, m, C**H**-OH), 3.93 (2H, t, J = 6.34 Hz, Ar-O-C**H$_2$**), 6.82 (2H, d, J = 8.69 Hz, Ar-**H**), 7.10 ppm (2H, d, J = 8.67 Hz, Ar-**H**).

1-((6-Bromohexyl)oxy)-4-((1r,4′r)-4′-(6-bromohexyloxy)cyclohexyl)benzene (**6**).

Trans-4-(4-cyclohexyloxy)phenol (0.7 g, 3.6 mmol, 1 eq.), 1,6-dibromohexane (11 mL, 73 mmol, 20 eq.) and NaH (0.26 g, 11 mmol, 3 eq.) were dissolved in 20 mL of THF and heated to reflux for 72 h. The reaction was quenched with a 15 mL solution of NH_4Cl (sat) in water and extracted with Et_2O (2× 50 mL). The organic phase was washed with 2× 50 mL of brine, the organic phase was dried over $MgSO_4$ and the solvent was evaporated under reduced pressure. The crude material was purified by flash chromatography on silica with hexane/EtOAc (9:1) as eluent yielding 0.9 g of the pure compound.

Yield = 48%. R_f (CH_2Cl_2) = 0.47.

^{1}H NMR (DMSO, 400 MHz) δ = 1.26–1.53 (16H, m, -CH_2-C**H$_2$**-CH_2-), 1.77–2.07 (8H, m, -CH-C**H$_2$**-C**H$_2$**-**CH**-), 2.39 (1H, m, Ar-C**H**), 3.22 (1H, m, -O-C**H**) 3.41 (2H, t, J = 6.41 Hz, C**H$_2$**-Br), 3.90 (2H, t, J = 6.43 Hz, Ar-O-C**H$_2$**), 6.81 (2H, d, J = 8.70 Hz, Ar-**H**), 7.10 ppm (2H, d, J = 8.69 Hz, Ar-**H**).

4-(4′-Hydroxycyclohexyl)benzonitrile (**7**).

4-(4′-Oxocyclohexyl)benzonitrile (1 g, 5 mmol, 1 eq.) and $NaBH_4$ (0.17 g, 4.5 mmol, 0.9 eq.) were dissolved in 50 mL of dry MeOH at 0°C. The mixture was allowed to warm up to r.t. and was stirred for 90 min. After this time, the reaction was quenched with 20 mL of distilled water, the methanol was removed under vacuum and 50 mL of CH_2Cl_2 was added. The organic phase was successively washed with 50 mL of NH_4Cl (sat) solution in water and 2× 50 mL of brine. The organic phase was dried over $MgSO_4$, and the solvent was evaporated under reduced pressure to give 0.9 g of the compound without further purification.

Yield = 89%. R_f (CH_2Cl_2/EtOAc, 8:2) = 0.3.

^{1}H NMR ($CDCl_3$, 400 MHz) δ = 1.51–2.17 (8H, m, -CH-C**H$_2$**-C**H$_2$**-**CH**-), 2.59 (1H, m, Ar-C**H**), 3.72 (1H, m, C**H**-OH), 7.31 (2H, d, J = 7.95 Hz, Ar-**H**), 7.61 ppm (2H, d, J = 7.87 Hz, Ar-**H**).

(1r,4′r)-4-(4′-(Hexyloxy)phenyl)cyclohexyl 6-bromohexanoate (**8**).

8 was synthesised according to **GP2. 4** (2.6 g) and 6-bromohexanoyl chloride were used, respectively, as alcohol and acyl chloride compound. Flash chromatography with hexane/CH_2Cl_2 (1:1) as eluent yields 2.17 g of the pure compound.

Yield = 51%. R_f (CH_2Cl_2) = 0.56.

^{1}H NMR ($CDCl_3$, 400 MHz) δ = 0.91 (t, 3H, J = 6.78 Hz, -C**H$_3$**), 1.21–1.70 (14H, m, -CH_2-C**H$_2$**-CH_2-, -CH_2-C**H$_2$**-CH_3), 1.77–2.12 (8H, m, -CH-C**H$_2$**-C**H$_2$**-CH-), 2.35 (2H, t, J = 7.41 Hz, C**H$_2$**-COO-), 2.49 (1H, m, Ar-C**H**), 3.45 (2H, t, J = 6.77 Hz, C**H$_2$**-Br), 3.95 (2H, t, J = 6.59 Hz, Ar-O-C**H$_2$**), 4.81 (1H, m, C**H**-O-), 6.86 (2H, d, J = 8.62 Hz, Ar-**H**), 7.13 ppm (2H, d, J = 8.61 Hz, Ar-**H**).

4-(4′-Cyanophenyl)cyclohexyl 6-bromohexanoate (**9**).

9 was synthesised according to **GP2. 7** (0.9 g) and 6-bromohexanoyl chloride were used, respectively, as alcohol and acyl chloride compound. Flash chromatography with EtOAc/CH_2Cl_2 (2:8) as eluent yields 1.2 g of the pure compound.

Yield = 70%. R_f (CH_2Cl_2/EtOAc, 9:1) = 0.2.

^{1}H NMR ($CDCl_3$, 400 MHz) δ = 1.27–1.65 (6H, m, -CH_2-C**H$_2$**-CH_2-), 1.69–2.14 (8H, m, -CH-C**H$_2$**-C**H$_2$**-CH-), 2.33 (2H, t, J = 7.40 Hz, C**H$_2$**-COO-), 2.59 (1H, m, Ar-C**H**), 3.42 (2H, t, J = 6.72 Hz, C**H$_2$**-Br), 4.79 (1H, m, C**H**-O-), 7.30 (2H, d, J = 8.32 Hz, Ar-**H**), 7.59 ppm (2H, d, J = 8.32 Hz, Ar-**H**).

(1r,4′r)-4-(4′-((6-Bromohexyl)oxy)phenyl)cyclohexyl 6-bromohexanoate (**10**).

10 was synthesised according to **GP2. 5** (1.3 g) and 6-bromohexanoyl chloride were used, respectively, as alcohol and acyl chloride compound. Flash chromatography with EtOAc/CH_2Cl_2 (2:8) as eluent yields 0.85 g of the pure compound.

Yield = 45%. R_f (CH_2Cl_2) = 0.56.

^{1}H NMR ($CDCl_3$, 400 MHz) δ = 1.45–1.77 (14H, m, -CH_2-C**H$_2$**-CH_2-), 1.80–2.10 (8H, m, -CH-C**H$_2$**-C**H$_2$**-CH-), 2.33 (2H, t, J = 7.42 Hz, C**H$_2$**-COO-), 2.46 (1H, m, Ar-C**H**), 3.42 (4H, t, J = 6.77 Hz, C**H$_2$**-Br), 3.93 (2H, t, J = 6.37 Hz, Ar-O-C**H$_2$**), 4.78 (1H, m, C**H**-O-), 6.82 (2H, d, J = 8.62 Hz, Ar-**H**), 7.10 ppm (2H, d, J = 8.58 Hz, Ar-**H**).

6-(4-((1r,4′r)-4′-Hydroxycyclohexyl)phenoxy)hexyl acrylate (**11**).

11 was synthesised according to **GP3. 5** (1 g) was used as alkyl halogen compound. Flash chromatography with EtOAc/CH_2Cl_2 (2:8) as eluent yields 1 g of the pure compound.

Yield = 51%. R_f (CH_2Cl_2/EtOAc, 9:1) = 0.32.

^{1}H NMR ($CDCl_3$, 400 MHz) δ = 1.38–1.56 (8H, m, -CH_2-C**H$_2$**-CH_2-), 1.70–1.79 (4H, m, -CH-C**H$_2$**-C**H$_2$**-C**H**-), 1.82–2.10 (4H, m, -CH-C**H$_2$**-C**H$_2$**-C**H**-), 2.44 (1H, m, Ar-C**H**), 3.67 (1H, m, C**H**-OH), 3.93 (2H, t, J = 6.41 Hz, Ar-O-C**H$_2$**), 4.16 (2H, t, J = 6.66 Hz, C**H$_2$**-OOC), 5.81 (1H, dd, J = 10.42, 1.51 Hz, Acr-H), 6.12 (1H, dd, J = 17.31, 10.41 Hz, Acr-H), 6.40 (1 H, dd, J = 17.32, 1.46 Hz, Acr-H), 6.82 (2 H, d, J = 8.62 Hz, Ar-**H**), 7.10 ppm (2H, d, J = 8.64 Hz, Ar-**H**). ^{13}C NMR ($CDCl_3$, 100 MHz) δ = 25.89 (CH_2), 25.92 (CH_2), 28.70 (CH_2), 29.35 (CH_2), 32.81 (CH_2), 36.12 (CH_2), 42.66 (CH_2), 64.68 (C-O), 67.87 (C-O), 70.81 (C-OH), 114.45 (C=C), 127.70 (C=C), 128.72 (C=C), 130.65 (C=C), 138.72 (C=C), 157.48 (C=C), 166.47 ppm (C=O). MS(ESI) (m/z): calcd for $C_{21}H_{30}NaO_4^+$ (M+Na^+): 369.2036, found: 369.2020. See Figure S1.

6-(4-((1s,4′r)-4′-Propylcyclohexyl)phenoxy)hexyl acrylate (**12**).

12 was synthesised according to **GP2. 1** (3.8 g) and acryloyl chloride were used, respectively, as alcohol and acyl chloride compound. Flash chromatography with heptane/EtOAc (9:1) as eluent yields 4 g of the pure compound.

Yield = 89%. R_f (CH_2Cl_2) = 0.51.

^{1}H NMR ($CDCl_3$, 400 MHz) δ = 0.82 (t, 3H, J = 7.26 Hz, -C**H$_3$**), 1.05–1.50 (13H, m, -C**H**-CH_2-, -CH_2-C**H$_2$**-CH-, -CH_2-C**H$_2$**-CH_2-), 1.56–1.88 (8 H, m, -CH-C**H$_2$**-C**H$_2$**-CH-), 2.41 (1H, m, Ar-C**H**), 3.93 (2H, t, J = 6.42 Hz, Ar-O-C**H$_2$**), 4.17 (2H, t, J = 6.67 Hz, C**H$_2$**-OOC), 5.81 (1H, dd, J = 10.41, 1.53 Hz, Acr-H), 6.12 (1H, dd, J = 10.41, 17.32 Hz, Acr-H), 6.40 (1H, dd, J = 17.33, 1.5 Hz, Acr-H), 6.81 (2H, d, J = 8.63 Hz, Ar-**H**), 7.11 ppm (2H, d, J = 8.63 Hz, Ar-**H**). ^{13} C NMR ($CDCl_3$, 100 MHz) δ = 14.56 (CH_3), 20.18 (CH_2), 25.90 (CH_2), 25.94 (CH_2), 28.71 (CH_2), 29.37 (CH_2), 33.77 (CH_2), 34.72 (CH_2), 37.17 (CH_2), 39.88 (CH_2), 43.87 (CH_2), 64.69 (C-O), 67.84 (C-O), 114.36 (C=C), 127.72 (C=C), 128.73 (C=C), 130.62 (C=C), 140.14 (C=C), 157.27 (C=C), 166.44 ppm (C=O). MS(ESI) (m/z): calcd for $C_{24}H_{36}NaO_3^+$ (M+Na^+): 395.2557, found: 395.2551. See Figure S2.

6-(4-((1s,4′r)-4′-Pentylcyclohexyl)phenoxy)hexyl acrylate (**13**).

13 was synthesised according to **GP2. 2** (2.8 g) and acryloyl chloride were used, respectively, as alcohol and acyl chloride compound. Flash chromatography with heptane/EtOAc (9:1) as eluent yields 2.8 g of the pure compound.

Yield = 87%. R_f (CH_2Cl_2) = 0.51.

^{1}H NMR ($CDCl_3$, 400 MHz) δ = 0.87 (t, 3 H, J = 6.94 Hz, -C**H$_3$**), 1.04 (2 H, m, -C**H$_2$**-CH_3), 1.18–1.38 (11 H, m, -C**H**-CH_2-, -CH_2-C**H$_2$**-CH-, -CH_2-C**H$_2$**-CH_2-), 1.40–1.57 (4 H, m, -C**H**-CH_2-, -CH_2-C**H$_2$**-CH-, -CH_2-C**H$_2$**-CH_2-), 1.65–1.92 (8 H, m, -CH-C**H$_2$**-C**H$_2$**-

CH-), 2.40 (1 H, m, Ar-C**H**), 3.91 (2 H, t, J = 6.40 Hz, Ar-O-C**H$_2$**), 4.16 (2 H, t, J = 6.67 Hz, C**H$_2$**-OOC), 5.81 (1 H, dd, J = 10.35, 1.39 Hz, Acr-H), 6.12 (1 H, dd, J = 17.35, 10.46 Hz, Acr-H), 6.40 (1 H, dd, J = 17.30, 1.54 Hz, Acr-H), 6.81 (2 H, d, J = 8.55 Hz, Ar-**H**), 7.10 ppm (2 H, d, J = 8.61 Hz, Ar-**H**). ^{13} C NMR ($CDCl_3$, 100 MHz) δ = 14.27 (CH_3), 22.86 (CH_2), 25.91 (CH_2), 25.94 (CH_2), 26.81 (CH_2), 28.71 (CH_2), 29.38 (CH_2), 32.36 (CH_2), 33.81 (CH_2), 34.73 (CH_2), 37.46 (CH_2), 37.54 (CH_2), 43.88 (CH_2), 64.69 (C-O), 67.85 (C-O), 114.36 (C=C), 127.73 (C=C), 128.73 (C=C), 130.63 (C=C), 140.15 (C=C), 157.27 (C=C), 166.46 ppm (C = O). MS (ESI) (m/z): calcd for $C_{26}H_{40}NaO_3^+$ (M+Na^+): 423.2870, found: 423.2868. See Figure S3.

6-(4-((1 s,4′r)-4′-Heptylcyclohexyl)phenoxy)hexyl acrylate (**14**).

14 was synthesised according to **GP2. 3** (2.5 g) and acryloyl chloride were used, respectively, as alcohol and acyl chloride compound. Flash chromatography with heptane/EtOAc (9:1) as eluent yields 2.6 g of the pure compound.

Yield = 91%. R_f (CH_2Cl_2) = 0.51.

^{1} H NMR ($CDCl_3$, 400 MHz) δ = 0.90 (t, 3 H, J = 6.75 Hz, -C**H$_3$**), 1.04–1.52 (21 H, m, -C**H**-CH_2-, -CH_2-C**H$_2$**-CH-, -CH_2-C**H$_2$**-CH_2-), 1.62–1.96 (8 H, m, -CH-C**H$_2$**-C**H$_2$**-CH-), 2.41 (1 H, m, Ar-C**H**), 3.94 (2 H, t, J = 6.40 Hz, Ar-O-C**H$_2$**), 4.17 (2 H, t, J = 6.67 Hz, C**H$_2$**-OOC), 5.82 (1 H, dd, J = 10.35, 1.39 Hz, Acr-H), 6.12 (1 H, dd, J = 17.32, 10.42 Hz, Acr-H), 6.40 (1 H, dd, J = 17.33, 1.52 Hz, Acr-H), 6.82 (2 H, d, J = 8.65 Hz, Ar-**H**), 7.11 ppm (2 H, d, J = 8.59 Hz, Ar-**H**). ^{13} C NMR ($CDCl_3$, 100 MHz) δ = 14.28 (CH_3), 22.85 (CH_2), 25.90 (CH_2), 25.94 (CH_2), 27.16 (CH_2), 28.71 (CH_2), 29.38 (CH_2), 29.54 (CH_2), 30.12 (CH_2), 32.07 (CH_2), 33.81 (CH_2), 34.73 (CH_2), 37.47 (CH_2), 37.60 (CH_2), 43.88 (CH_2), 64.69 (C-O), 67.85 (C-O), 114.36 (C=C), 127.72 (C=C), 128.73 (C=C), 130.62 (C=C), 140.15 (C=C), 157.27 (C=C), 166.45 ppm (C = O). MS(ESI) (m/z): calcd for C_{28} $H_{44}NaO_3^+$ (M+ Na^+): 451.3183, found: 451.3183. See Figure S4.

(1 r,4′r)-4-(4′-(Hexyloxy)phenyl)cyclohexyl 6-(acryloyloxy)hexanoate (**15**).

15 was synthesised according to **GP3. 8** (1 g) was used as alkyl halogen compound. Flash chromatography with EtOAc/CH_2Cl_2 (2:8) as eluent yields 0.47 g of the pure compound.

Yield = 48%. R_f (CH_2Cl_2) = 0.29.

^{1} H NMR ($CDCl_3$, 400 MHz) δ = 0.90 (t, 3 H, J = 6.92 Hz, -C**H$_3$**), 1.27–1.64 (14 H, m, -C**H**-CH_2-, -CH_2-C**H$_2$**-CH-, -CH_2-C**H$_2$**-CH_2-), 1.91–2.08 (8 H, m, -CH-C**H$_2$**-C**H$_2$**-CH-), 2.31 (2 H, t, J = 7.42 Hz, C**H$_2$**-COO), 2.45 (1 H, m, Ar-C**H**), 3.92 (2 H, t, J = 6.58 Hz, Ar-O-C**H$_2$**), 4.16 (2 H, t, J = 6.61 Hz, C**H$_2$**-O), 5.82 (1 H, dd, J = 10.42, 1.51 Hz, Acr-H), 6.12 (1 H, dd, J = 17.34, 10.43 Hz, Acr-H), 6.41 (1 H, dd, J = 17.32, 1.56 Hz, Acr-H), 6.83 (2 H, d, J = 8.64 Hz, Ar-**H**), 7.10 ppm (2 H, d, J = 8.66 Hz, Ar-**H**). ^{13} C NMR ($CDCl_3$, 100 MHz) δ = 14.28 (CH_3), 22.85 (CH_2), 25.90 (CH_2), 25.94 (CH_2), 27.16 (CH_2), 28.71 (CH_2), 29.38 (CH_2), 29.54 (CH_2), 30.12 (CH_2), 32.07 (CH_2), 33.81 (CH_2), 34.73 (CH_2), 37.47 (CH_2), 37.60 (CH_2), 43.88 (CH_2), 64.69 (C-O), 67.85 (C-O), 114.36 (C=C), 127.72 (C=C), 128.73 (C=C), 130.62 C=C), 140.15 (C=C), 157.27 (C=C), 166.45 ppm (C = O). MS(ESI) (m/z): calcd for $C_{27}H_{40}NaO_5^+$ (M+ Na^+): 467.2768, found: 467.2775. See Figure S5.

4-(4′-Cyanophenyl)cyclohexyl 6-(acryloyloxy)hexanoate (**16**).

16 was synthesised according to **GP3. 9** (1.2 g) was used as alkyl halogen compound. Flash chromatography with EtOAc/CH_2Cl_2 (2:8) as eluent to give 1 g of the pure desired compound.

Yield = 85%. R_f (CH_2Cl_2) = 0.29.

^{1} H NMR ($CDCl_3$, 400 MHz) δ = 1.38–1.58 (6H, m, -CH_2-C**H$_2$**-CH_2-), 1.62–1.44 (4 H, m, -CH-C**H$_2$**-C**H$_2$**-CH-), 1.90–2.13 (4 H, m, -CH-C**H$_2$**-C**H$_2$**-CH-), 2.32 (2 H, t, J = 7.44 Hz, C**H$_2$**-COO-), 2.58 (1 H, m, Ar-C**H**), 4.16 (2 H, t, J = 7.44 Hz, C**H$_2$**-O), 4.78 (1 H, m, C**H**-O-), 5.82 (1 H, dd, J = 10.42, 1.53 Hz, Acr-H), 6.11 (1 H, dd, J = 17.33, 10.42 Hz, Acr-H), 7.28 (2 H, d, J = 8.26 Hz, Ar-**H**), 7.58 ppm (2 H, d, J = 8.22 Hz, Ar-**H**). ^{13} C NMR ($CDCl_3$, 100 MHz) δ = 24.80 (CH_2), 25.63 (CH_2), 28.46 (CH_2), 31.90 (CH_2), 31.94 (CH_2), 34.61 (CH_2), 43.61 (CH_2), 64.48 (C-O), 72.41 (C-COO), 110.23 (C=C), 119.12 (CN), 127.77 (C=C), 128.67 (C=C), 130.71 (C=C), 132.46 (C=C), 151.75 (C=C), 166.40 (C = O), 173.16 ppm (C = O). MS(ESI) (m/z): calcd for C_{22} $H_{27}NNaO_4^+$ (M+ Na^+): 392.1832, found: 392.1829. See Figure S6.

(1 r,4′r)-4-(4′-((6-(Acryloyloxy)hexyl)oxy)phenyl)cyclo hexyl hexanoate (**17**).

17 was synthesised according to **GP2. 11** (0.1 g) and hexanoyl chloride were used, respectively, as alcohol and acyl chloride compound. Flash chromatography with heptane/EtOAc (9:1) as eluent yields 0.11 g of the pure compound.

Yield = 86%. R_f (CH_2Cl_2) = 0.20.

^{1} H NMR ($CDCl_3$, 400 MHz) δ = 0.90 (3 H, t, J = 6.88 Hz, CH_3), 1.26–1.56 (14 H, m, -CH_2-C**H$_2$**-CH_2-, -CH_2-C**H$_2$**-CH_3), 1.56–1.83 (4 H, m, -CH-C**H$_2$**-C**H$_2$**-**CH**-), 1.91–2.09 (4 H, m, -CH-C**H$_2$**-C**H$_2$**-**CH**-), 2.28 (2 H, t, J = 7.54 Hz, C**H$_2$**-COO), 2.47 (1 H, m, Ar-C**H**), 3.94 (2 H, t, J = 6.39 Hz, Ar-O-C**H$_2$**), 4.16 (2 H, t, J = 6.66 Hz, C**H$_2$**-OOC), 4.78 (1 H, m, C**H**-OOC), 5.81 (1 H, dd, J = 10.33, 1.42 Hz, Acr-H), 6.12 (1 H, dd, J = 17.33, 10.41 Hz, Acr-H), 6.40 (1 H, dd, J = 17.32,

1.49 Hz, Acr-H), 6.82 (2 H, d, J = 8.66 Hz, Ar-**H**), 7.10 ppm (2 H, d, J = 8.66 Hz, Ar-**H**). ^{13} C NMR ($CDCl_3$, 100 MHz) δ = 14.08 (CH_3), 22.47 (CH_2), 24.92 (CH_2), 25.90 (CH_2), 25.93 (CH_2), 28.71 (CH_2), 29.35 (CH_2), 31.44 (CH_2), 32.23 (CH_2), 32.59 (CH_2), 34.85 (CH_2), 42.59 (CH_2), 64.68 (C-O), 67.88 (C-O), 72.82 (C-COO), 114.49 (C=C), 127.69 (C=C), 128.73 (C=C), 130.64 (C=C), 138.43 (C=C), 157.54 (C=C), 166.45 (C = O), 173.61 ppm (C = O). MS(ESI) (m/z): calcd for $C_{27}H_{40}NaO_5^+$ (M+ Na^+): 467.2768, found: 467.2750. See Figure S7.

(1 r,4 r)-4-(4-(Hexyloxy)phenyl)cyclohexyl acrylate (**18**).

18 was synthesised according to **GP2. 3** (0.05 g) and acryloyl chloride were used, respectively, as alcohol and acyl chloride compound. Flash chromatography with heptane/EtOAc (9:1) as eluent to give 50 mg of the pure compound.

Yield = 84%. R_f (CH_2Cl_2) = 0.40.

^{1}H NMR ($CDCl_3$, 400 MHz) δ = 0.90 (3 H, t, J = 7.03 Hz, -CH_3), 1.20–1.54 (8 H, m, -CH_2-C**H$_2$**-CH_2-, CH_2-CH_3), 1.57–1.84 (4 H, m, -CH-C**H$_2$**-C**H$_2$**-**CH**-), 1.87–2.21 (4 H, m, -CH-C**H$_2$**-C**H$_2$**-**CH**-), 2.47 (1 H, m, Ar-C**H**), 3.93 (2 H, t, J = 6.56 Hz, Ar-O-C**H$_2$**), 4.86 (1 H, m, C**H**-OOC), 5.82 (1 H, dd, J = 10.41, 1.58 Hz, Acr-H), 6.12 (2 H, dd, J = 17.29, 10.38 Hz, Acr-H), 6.41 (2 H, dd, J = 17.32, 1.51 Hz, Acr-H), 6.83 (2 H, d, J = 8.67 Hz, Ar-**H**), 7.11 ppm (2H, d, J = 8.63 Hz, Ar-**H**). ^{13} C NMR ($CDCl_3$, 100 MHz) δ = 14.19 (CH_3), 22.77 (CH_2), 25.90 (CH_2), 29.46 (CH_2), 31.75 (CH_2), 32.20 (CH_2), 32.85 (CH_2), 42.59 (CH_2), 68.15 (C-O), 73.32 (C-O), 114.53 (C=C), 127.68 (C=C), 129.18 (C=C), 130.46 (C=C), 138.29 (C=C), 157.67 (C=C), 165.95 ppm (C = O). MS(ESI) (m/z): calcd for $C_{21}H_{30}NaO_3^+$ (M+ Na^+): 353.2087, found: 353.2110. See Figure S8.

(1 r,4′r)-4-(4′-((6-(Acryloyloxy)hexyl)oxy)phenyl)cyclo hexyl 6-(acryloyloxy)hexanoate (**19**).

19 was synthesised according to **GP3. 10** (0.8 g) was used as alkyl halogen compound. Flash chromatography with CH_2Cl_2/MeOH (99:1) as eluent yields 315 mg of the pure compound.

Yield = 41%. R_f (CH_2Cl_2) = 0.11.

^{1}H NMR ($CDCl_3$, 400 MHz) δ = 1.40–1.69 (14 H, m, -CH_2-C**H$_2$**-CH_2-), 1.69–2.14 (8 H, m, -CH-C**H$_2$**-C**H$_2$**-**CH**-), 2.32 (2H, t, J = 7. 24 Hz, C**H$_2$**-COO), 2.46 (1H, m, Ar-C**H**), 3.92 (2H, t, J = 6.44 Hz, Ar-O-C**H$_2$**), 4.16 (4H, t, J = 6.63 Hz, C**H$_2$**-OOC), 4.78 (1H, m, C**H**-OOC), 5.81 (2H, d, J = 10.42 Hz, Acr-H), 6.11 (2H, dd, J = 17.33, 10.43 Hz, Acr-H), 6.40 (2H, dd, J = 17.25 Hz, Acr-H), 6.82 (2H, d, J = 8.61 Hz, Ar-**H**), 7.10 ppm (2H, d, J = 8.63 Hz, Ar-**H**). ^{13}C NMR ($CDCl_3$, 100 MHz) δ = 24.84 (CH_2), 25.64 (CH_2), 25.89 (CH_2), 25.92 (CH_2), 28.47 (CH_2), 28.71 (CH_2), 29.35 (CH_2), 32.22 (CH_2), 32.57 (CH_2), 34.67 (CH_2), 42.57 (CH_2), 64.51 (C-O), 64.68 (C-O), 67.88 (C-O), 72.98 (C-O), 114.49 (C=C), 127.68 (C=C), 128.68 (C=C), 128.72 (C=C), 130.65 (C=C), 130.69 (C=C), 138.38 (C=C), 157.55 (C=C), 166.41 (C = O), 166.46 (C = O), 173.22 ppm (C = O). MS(ESI) (m/z): calcd for $C_{30}H_{42}NaO_7^+$ (M+ Na^+): 537.2823, found: 537.2805. See Figure S9.

6-(4-((1 r,4′r)-4′-((6-(acryloyloxy)hexyl)oxy)cyclohexyl)phenoxy)hexyl acrylate (**20**).

20 was synthesised according to **GP3. 6** (0.2 g) was used as alkyl halogen compound. Flash chromatography with heptane/EtOAc (9:1) as eluent yields 157 mg of the pure compound.

Yield = 80%. R_f (CH_2Cl_2) = 0.20.

^{1}H NMR ($CDCl_3$, 400 MHz) δ = 1.33–1.68 (16H, m, -CH_2-C**H$_2$**-CH_2-), 1.69–2.20 (8H, m, -CH-C**H$_2$**-C**H$_2$**-**CH**-), 2.45 (1H, m, Ar-C**H**), 3.25 (1H, m, C**H**-O), 3.48 (2H, t, J = 6.63 Hz,), 3.93 (2H, t, J = 6.41 Hz, Ar-O-C**H$_2$**), 4.16 (4H, m, C**H$_2$**-OOC), 5.82 (2H, d, J = 10.39 Hz, Acr-H), 6.11 (2H, dd, J = 17.34, 10.42 Hz, Acr-H), 6.40 (2H, d, J = 17.34 Hz, Acr-H), 6.81 (2H, d, J = 8.66 Hz, Ar-**H**), 7.10 ppm (2H, d, J = 8.66 Hz, Ar-**H**). ^{13} C NMR ($CDCl_3$, 100 MHz) δ = 25.90 (CH_2), 25.94 (CH_2), 25.97 (CH_2), 26.08 (CH_2), 28.72 (CH_2), 28.75 (CH_2), 29.37 (CH_2), 30.25 (CH_2), 32.89 (CH_2), 32.94 (CH_2), 43.01 (CH_2), 64.69 (C-O), 64.75 (C-O), 67.88 (C-O), 68.15 (C-O), 114.43 (C=C), 127.69 (C=C), 128.73 (C=C), 128.77 (C=C), 130.60 (C=C), 130.65 (C=C), 138.97 (C=C), 157.45 (C = O), 166.47 ppm (C = O). MS(ESI) (m/z): calcd for $C_{30}H_{44}NaO_6^+$ (M+ Na^+): 523.3030, found: 523.3023. See Figure S10.

(1 r,4′r)-4-(4′-((6-(Acryloyloxy)hexyl)oxy)phenyl) cyclohexyl 4-((6-(acryloyloxy)hexyl)oxy)benzoate (**21**).

11 (80 mg, 0.23 mmol, 1 eq.), *N,N′*-dicyclohexylcarbodiimide (143 mg, 0.7 mmol, 3 eq.), DMAP (3 mg, 0.023 mmol, 0.1 eq) and 4-((6-(acryloyloxy)hexyl)oxy) benzoic acid (67 mg, 0.23 mmol, 1 eq) were dissolved in 5 mL of dry CH_2Cl_2 and stirred 24 h at 30°C. 20 mL of CH_2Cl_2 were added to the solution before washing with 2× 20 mL of distilled water and 20 mL of brine. The organic phase was dried with $MgSO_4$, and the solvent was evaporated under reduced pressure. The crude material was then purified by flash chromatography on silica with heptane/EtOAc (8:2) as eluent to yield 60 mg of the pure compound.

Yield = 42%. R_f (CH_2Cl_2) = 0.13.

^{1}H NMR ($CDCl_3$, 400 MHz) δ = 1.42–1.71 (16H, m, -CH_2-C**H$_2$**-CH_2-), 1.72–1.89 (4H, m, -CH-C**H$_2$**-C**H$_2$**-**CH**-), 1.89–2.27 (4H, m, -CH-C**H$_2$**-C**H$_2$**-**CH**-), 2.52 (1H, m, Ar-C**H**), 3.94 (2H, t, J = 6.40 Hz, Ar-O-C**H$_2$**),

4.01 (2H, t, J = 6.42 Hz, C**H$_2$**-O), 4.18 (4H, m, C**H$_2$**-O), 4.99 (1H, m, COO-C**H**), 5.81 (2H, d, J = 10.42 Hz, Acr-H), 6.12 (2H, dd, J = 17.31, 10.41 Hz, Acr-H), 6.40 (2H, d, J = 17.31 Hz, Acr-H), 6.84 (2H, d, J = 8.67 Hz, Ar-**H**), 6.90 (2H, d, J = 8.92 Hz, Ar-**H**), 7.13 (2H, d, J = 8.43 Hz, Ar-**H**), 7.99 ppm (2H, d, J = 8.86 Hz, Ar-**H**). ^{13} C NMR ($CDCl_3$, 100 MHz) δ = 25.85 (CH_2), 25.87 (CH_2), 25.91 (CH_2), 25.94 (CH_2), 28.72 (CH_2), 28.69 (CH_2), 28.72 (CH_2), 29.15 (CH_2), 29.36 (CH_2), 32.36 (CH_2), 32.64 (CH_2), 42.66 (CH_2), 64.62 (C-O), 64.69 (C-O), 67.89 (C-O), 68.10 (C-O), 73.34 (C-O), 114.10 (C=C), 114.51 (C=C), 123.21 (C=C), 127.72 (C=C), 128.70 (C=C), 128.73 (C=C), 130.65 (C=C), 130.70 (C=C), 131.68 (C=C), 138.47 (C=C), 157.56 (C=C), 162.88 (C = O), 166.05 (C = O),166.46 ppm (C = O). MS(ESI) (m/z): calcd for $C_{37}H_{48}NaO_8^+$ (M+ Na^+): 643.3241, found: 643.3243. See Figure S11.

(1 r,4′r)-4-(4′-((6-(Acryloyloxy)hexyl)oxy)phenyl) cyclohexyl 4-((6-(acryloyloxy)hexyl)oxy)-2-methylbenzoate (**22**).

4-((6-(acryloyloxy)hexyl)oxy)-2-methylbenzoic acid (221 mg, 0.72 mmol, 1 eq.), triethylamine (0.3 mL, 2.2 mmol, 3 eq.) and 2,4,6-trichlorobenzoyl chloride (0.14 mL, 0.87 mmol, 1.2 eq.) were dissolved in 3 mL of dry THF and stirred 2 h at r.t. The reaction mixture was filtrated under inert atmosphere. **11** (0.3 g, 0.87 mmol, 1.2 eq.) and DMAP (0.133 g, 1.1 mmol, 1.5 eq.) were dissolved in 3 mL of dry THF and added to the first mixture. The reaction was stirred for 16 h at r.t. and filtrated before being condensed under reduced pressure. The residue was dissolved in 100 mL of CH_2Cl_2 and washed with 2× 100 mL of distilled water and 100 mL of brine. The organic phase was then dried with $MgSO_4$, and the solvent was evaporated under reduced pressure. The crude material was then purified by flash chromatography on silica with CH_2Cl_2/EtOAc (9:1) as eluent to yield 220 mg of the pure desired compound.

Yield = 48%. R_f (CH_2Cl_2) = 0.13.

^{1}H NMR ($CDCl_3$, 400 MHz) δ = 1.38–1.75 (16H, m, -CH_2-C**H$_2$**-CH_2-), 1.75–1.87 (4H, m, -CH-C**H$_2$**-C**H$_2$-CH**-), 1.94–2.27 (4H, m, -CH-C**H$_2$**-C**H$_2$-CH**-), 2.53 (1H, m, Ar-C**H**), 2.60 (3H, s, CH_3) 3.94 (2H, t, J = 6.38 Hz, Ar-O-C**H$_2$**), 3.99 (2H, t, J = 6.41 Hz, C**H$_2$**-O), 4.18 (4H, m, C**H$_2$**-O), 4.97 (1H, m, COO-C**H**), 5.82 (2H, d, J = 10.41 Hz, Acr-H), 6.12 (2H, dd, J = 17.34, 10.42 Hz, Acr-H), 6.40 (2H, d, J = 17.31 Hz, Acr-H), 6.73 (2H, m, Ar-**H**), 6.83 (2H, d, J = 8.68 Hz, Ar-**H**), 7.13 (2H, d, J = 8.43 Hz, Ar-**H**), 7.92 ppm (H, m, Ar-**H**). ^{13} C NMR ($CDCl_3$, 100 MHz) δ = 22.53 (CH_2), 25.84 (CH_2), 25.86 (CH_2), 25.90 (CH_2), 25.93 (CH_2), 28.69 (CH_2), 28.71 (CH_2), 29.17 (CH_2), 29.35 (CH_2), 32.42 (CH_2), 32.66 (CH_2), 42.66 (CH_2), 64.62 (C-O), 64.68 (C-O), 67.88 (C-O), 67.90 (C-O), 73.15 (C-O), 111.45 (C=C), 114.50 (C=C), 117.53 (C=C), 122.40 (C=C), 127.71 (C=C), 128.70 (C=C), 128.73 (C=C), 130.64 (C=C), 130.68 (C=C), 133.00 (C=C), 138.47 (C=C), 142.92 (C=C), 157.55 (C=C), 161.81 (C = O), 166.45 (C = O), 166.89 ppm (C = O). MS(ESI) (m/z): calcd for $C_{38}H_{50}NaO_8^+$ (M+ Na^+): 657.3398, found: 657.3409. See Figure S12.

6-(4-((1 r,4 r)-4-(Acryloyloxy)cyclohexyl)phenoxy) hexyl acrylate (**23**). (**GP2**)

23 was synthesised according to **GP2. 11** (100 mg) and acryloyl chloride were used, respectively, as alcohol and acyl chloride compound. Flash chromatography with heptane/EtOAc (9:1) as eluent yields 100 mg of the pure desired compound.

Yield = 89%. R_f (CH_2Cl_2) = 0.24.

^{1}H NMR ($CDCl_3$, 400 MHz) δ = 1.39–1.62 (8H, m, -CH_2-C**H$_2$**-CH_2-), 1.66–1.84 (4H, m, -CH-C**H$_2$**-C**H$_2$-CH**-), 1.88–2.18 (4H, m, -CH-C**H$_2$**-C**H$_2$-CH**-), 2.49 (1H, m, Ar-C**H**), 3.93 (2H, t, J = 6.42 Hz, Ar-O-C**H$_2$**), 4.16 (2H, t, J = 6.67 Hz, C**H$_2$**-OOC), 4.85 (1H, m, C**H**-OOC), 5.81 (2H, dd, J = 10.42, 1.5 Hz, Acr-H), 6.12 (2H, dd, J = 17.31, 10.40 Hz, Acr-H), 6.40 (2H, dm, J = 17.32 Hz, Acr-H), 6.82 (2H, d, J = 8.70 Hz, Ar-**H**), 7.11 ppm (2H, d, J = 8.65 Hz, Ar-**H**). ^{13} C NMR ($CDCl_3$, 100 MHz) δ = 25.89 (CH_2), 25.92 (CH_2), 28.70 (CH_2), 29.34 (CH_2), 32.18 (CH_2), 32.56 (CH_2), 42.57 (CH_2), 64.67 (C-O), 67.88 (C-O), 73.28 (C-O), 114.50 (C=C), 127.68 (C=C), 128.72 (C=C), 129.16 (C=C), 130.45 (C=C), 130.63 (C=C), 138.37 (C=C), 157.56 (C=C), 165.91 (C = O), 166.44 ppm (C = O). MS(ESI) (m/z): calcd. for $C_{24}H_{32}NaO_5^+$ (M+ Na^+): 423.2142, found: 423.2111. See Figure S13.

Preparation of LCPNs

Three photopolymerisable LC mixtures (TN, RN1 and RN2) were prepared by mixing monomers (see Table 2) with 0.5 wt% of the photo-initiator (Irgaqure 651) in dichloromethane. Dichloromethane was slowly evaporated, and mixtures were dried at 80°C overnight. The mixtures TN, RN1 and RN2 form nematic phase with clearing temperature 31°C, 62°C and 57°C, respectively.

The mixture was introduced into a 2-µm-thick quartz cell by capillary forces in the isotropic state and cooled down to polymerisation temperature which was 25°C for TN and 50°C for RN1 and RN2. Unidirectional LC alignment has been achieved by poly(vinyl alcohol) (~31 kDa, from Sigma-Aldrich) layers coated on quartz substrates and rubbed unidirectionally with a velvet cloth. Once filled, the cells were cross-polymerised by exposing to UV light (LED 365 nm, intensity ~100 mW/cm^2) for 5 min. The cells were finally post-cured at 60°C overnight.

3. Results and discussion

3.1. Design of the reactive mesogens

We have designed and synthesised a number of LC monomers having minimal aromatic conjugation in order to shift the absorption band hypsochromically. Moreover, we have excluded from the design any moieties that could lead to photo-Fries rearrangement. We have used cyclohexylbenzene as rigid mesomorphic core since its absorbance is sufficiently blue-shifted, and the aromatic moiety improves the compatibility with various organic compounds. Bicyclohexyl-based LC core has not been used in the general design because of poor compatibility with aromatic compounds despite its largely blue-shifted absorbance band. We have also designed a monomer with a nitrile moiety **16** which has a higher dipole moment and therefore is more sensitive to external electric fields. It is also worth noting that during the synthesis of targeted molecules we have synthetised nine new intermediates which can be used as starting materials to build up libraries of new reactive mesogens. Overall, we have designed and synthetised eight new monomers in gram scale and five new cross-linkers suitable for LCPN synthesis which are transparent and resilient to UV light.

3.2. Synthesis of the reactive mesogens

Cyclohexylbenzene-based LC monomers **12, 13** and **14** have been synthetised starting, respectively, from 4-(4-propylcyclohexyl)phenol, 4-(4-pentylcyclohexyl)phenol and 4-(4-heptylcyclohexyl)phenol. These compounds have been synthesised by Williamson reaction with 6-bromohexanol to yield **1, 2** and **3** which have been transformed into polymerisable acrylates by the reaction with acryloyl chloride to yield **12, 13** and **14** in gram scale (Figure 1).

Compound **15** has been synthesised starting from 4-(4′-hydroxycyclohexyl)phenol which gives **4** in quantitative yield after the Williamson reaction with bromohexane. Here, we took advantage of the reduced reactivity of the secondary alcohol compared to phenol in order to asymmetrically functionalise 4-(4′-hydroxycyclohexyl)phenol with an alkyl tail. Compound **4** has been transferred to acrylic monomer consequently by the reaction with bromohexanoyl chloride yielding **8** and then with potassium acrylate yielding monomer **15** in gram scale (Figure 2).

To avoid the reduction of the nitrile group, compound **7** has been synthesised by reduction of 4-(4′-oxocyclohexyl)benzonitrile in mild conditions. The resulting alcohol has been converted into monoacrylate **16** in gram scale following the procedure for compound **15** (Figure 3).

Compound **17** has been synthetised in the same way as compound **15**. 4-(4′-Hydroxycyclohexyl)phenol reacts with 1,6-dibromohexane to give **5** which further reacts with potassium acrylate leading to **11**. Compound **11** was then acylated with hexanoyl chloride, resulting in **17** with a 86% yield (Figure 4). Notably, this approach allows for gram-scale production of the intermediate **11** which is a versatile functional precursor for the synthesis of mono- and diacrylates.

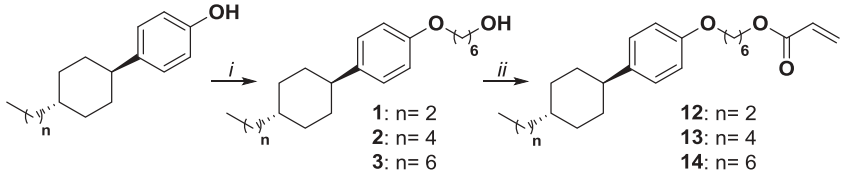

Figure 1. Synthesis of compounds **1, 2, 3, 12, 13** and **14**. *i*: K_2CO_3, KI, 6-bromohexanol, EtOH, reflux 48 h; *ii*: NEt_3, acryloyl chloride, THF, 0°C 1 h, r.t. 16 h.

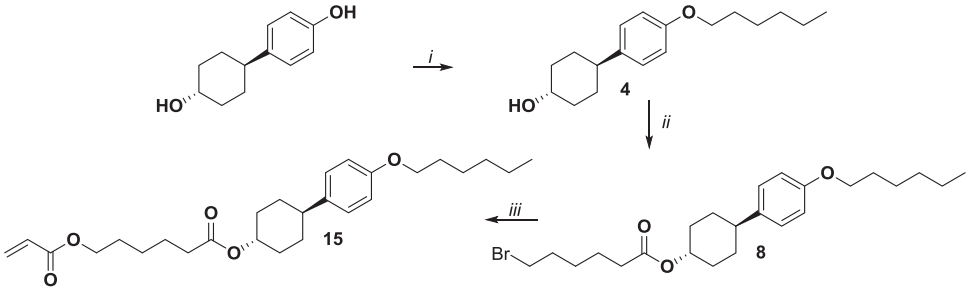

Figure 2. Synthesis of compound **15**. *i*: K_2CO_3, KI, bromohexane, EtOH, reflux 48 h; *ii*: 6-bromohexanoyl chloride, NEt_3, THF, 0°C 1 h, r.t. 16 h; *iii*: potassium acrylate, KI, DMSO, 52°C 72 h.

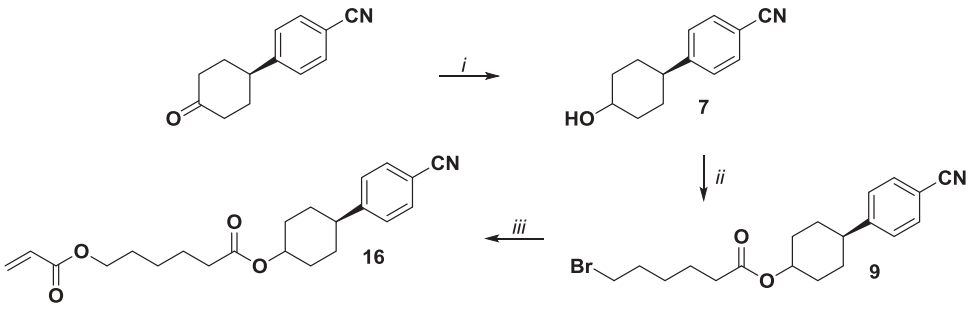

Figure 3. Synthesis of compound **16**. *i*: $NaBH_4$, MeOH, r.t. 90 min. *ii*: 6-bromohexanoyl chloride, NEt_3, THF, 0°C 1 h, r.t. 16 h; *iii*: potassium acrylate, KI, DMSO, 52°C 72 h.

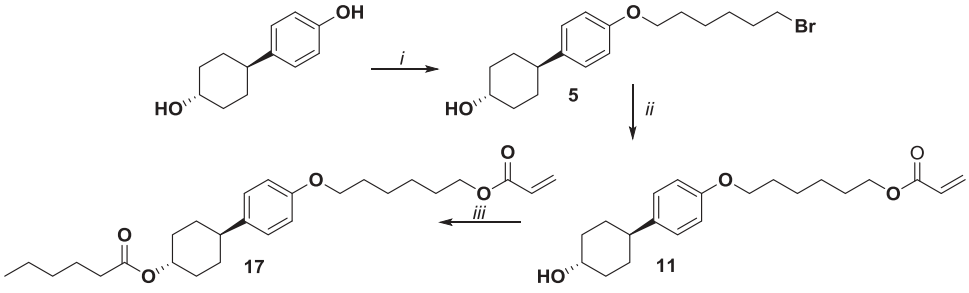

Figure 4. Synthesis of compound **17**. *i*: K_2CO_3, KI, 1,6-dibromohexane, EtOH, reflux 48 h; *ii*: potassium acrylate, KI, DMSO, 52°C 72 h; *iii*: hexanoyl chloride, NEt_3, THF, 0°C 1 h, r.t. 16 h.

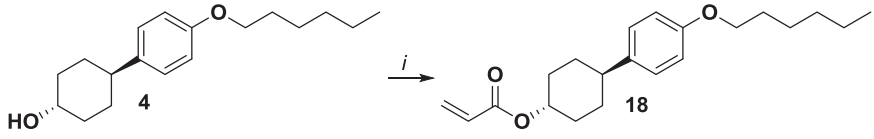

Figure 5. Synthesis of **18**. *i*: NEt_3, acryloyl chloride, THF, 0°C 1 h, r.t. 16 h.

Compound **18** has been synthetised starting from **4** which has been acylated with acryloyl chloride to yield the desired compound with 84% yield (Figure 5).

Cross-linker **19** has been synthetised by acylation of compound **5**, with bromohexanoyl chloride followed by reaction with potassium acrylate (Figure 6).

Cross-linker **20** has been synthetised starting with 4-(4′-hydroxycyclohexyl)phenol which has been deprotonated by NaH in order to allow the reaction of both alcohol with 1,6-dibromohexane to give **6**. Compound **6** has been reacted with potassium acrylate, resulting in **20** in 80% yield (Figure 7).

Cross-linkers **21, 22** and **23** have been all synthetised starting from compound **11**. Compound **21** has been produced with a 42% yield by Steglich esterification starting from 4-((6-(acryloyloxy)hexyl)oxy)benzoic

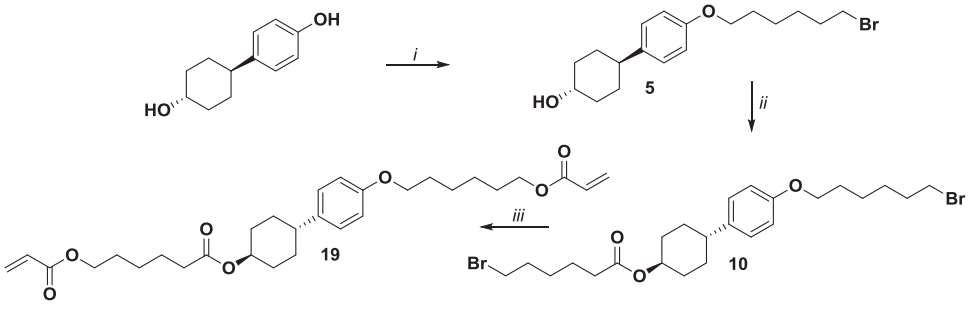

Figure 6. Synthesis of 19. *i*: K_2CO_3, KI, 1,6-dibromohexane, EtOH, reflux 48 h; *ii*: 6-bromohexanoyl chloride, NEt_3, THF, 0°C 1 h, r.t. 16 h; *iii*: potassium acrylate, KI, DMSO, 52°C 72 h.

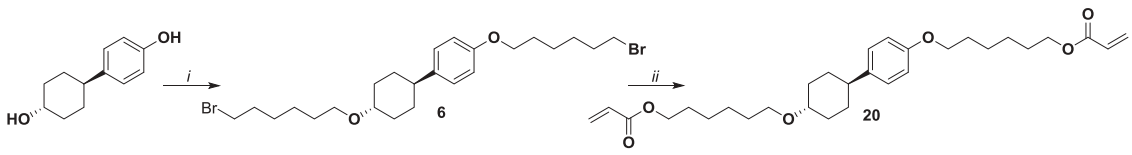

Figure 7. Synthesis of **20**. *i*: NaH, 1,6-dibromohexane, THF reflux 78 h; *ii*: potassium acrylate, KI, DMSO, 52°C 72 h.

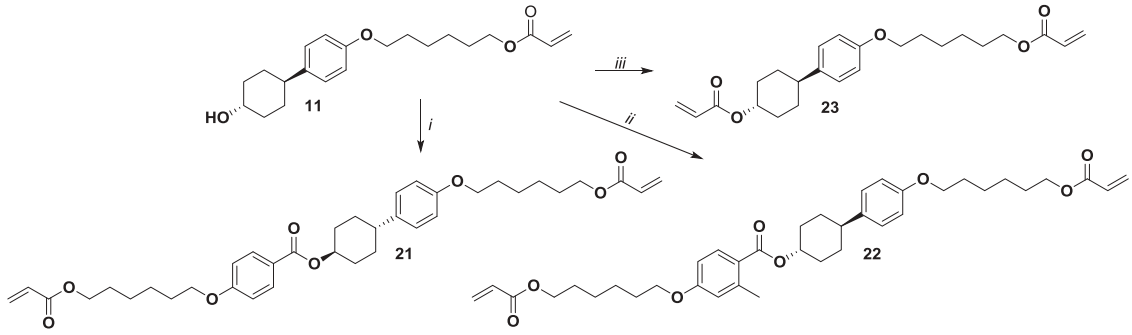

Figure 8. Synthesis of **21, 22** and **23**. *i*: DCC, DMAP, 4-((6-(acryloyloxy)hexyl)oxy)benzoic acid, CH_2Cl_2, 30°C 24 h. *ii*: 4-((6-(acryloyloxy) hexyl)oxy)-2-methylbenzoic acid, triethylamine, 2,4,6-trichlorobenzoyl chloride, DMAP THF 18 h r.t.; *iii*: NEt_3, acryloyl chloride, THF, 0°C 1 h, r.t. 16 h.

acid (Figure 8). The same reaction has been carried out under similar conditions with 4-((6-(acryloyloxy)hexyl) oxy)-2-methylbenzoic acid resulting in **22** with only 1–2% yield, likely due to the hindrance of the carboxylic acid. To overcome this limitation, we have used Yamaguchi esterification of 4-((6-(acryloyloxy)hexyl) oxy)-2-methylbenzoic acid with the Yamaguchi reagent. The resulting anhydride has been reacted with **11** in the presence of a stoichiometric amount of DMAP, which is used as an acyl transfer agent, to produce **22** with 48% yield (Figure 8). The cross-linker **23** has been obtained in 89% yield by acylation of **11** with acryloyl chloride (Figure 8).

3.3. Characterisation of the reactive mesogens

Phase behaviour of the synthesised mono- and diacrylates has been determined by polarised optical microscopy, and enthalpies of phase transitions have been measured by DSC and gathered in Table 1. Monoacrylates **12–14** and **18** melt to isotropic liquid; however, nematic monotropic mesophase has been observed upon cooling. Upon cooling, compound **14** forms smectic A phase (Figure 9). Diacrylates **20–22** form smectic phases, while the others melt to isotropic liquids. Diacrylate **20** forms monotropic smectic C phase upon cooling as revealed by schlieren texture in the cell with homeotropic boundary conditions (Figure S14(a)). Compound **21** forms smectic A phase with characteristic focal conic texture (Figure S14(b)). Diacrylate **22** first melts to disordered smectic X phase (Figure S14(c)) and then to nematic phase existing in quite broad temperature range. It should be noted that despite the fact that some of the compounds are not liquid crystalline, they can be used in mixtures with the other LC monomers or low molar mass liquid crystals to form UV-transparent LCPNs. To demonstrate the improvement of phase behaviour, we designed few monomeric compositions (see Table S1) that are in nematic state at room temperature, e.g. a mixture of monomers **13** and **14** (1:1 by weight) forms nematic phase up to 27.5°C. Moreover, such monomers can be polymerised into side-chain LC polymers where their

Table 1. Summary of phase behaviour, enthalpy of LC phase transition and maximum absorption wavelength (λ_{max}) of the synthesised reactive mesogens. Monotropic LC phases are indicated in the brackets.

Compound	Acrylic functionality	Phase behaviour	ΔH, kJ/mol	λ_{max}, nm
11	1	Cr 62.0 I	-	276
12	1	Cr 43.3 (N 14.6) I	0.63	276
13	1	Cr 31.9 (N 18.5) I	0.80	276
14	1	Cr 38.0 (N 32.8 SmA 27.7) I	0.74/3.49	276
15	1	Cr 49.5 I	-	277
16	1	Cr 71.6 I	-	263
17	1	Cr 49.3 I	-	276
18	1	Cr 56.4 (N 23.5) I	0.22	277
19	2	Cr 47.9 I		276
20	2	Cr 15.4 (SmC −8.5) I	5.10	277
21	2	Cr 90.6 SmA 106.8 I	6.14	256
22	2	Cr 47.8 SmX 51.5 N 65.4 I	0.79/1.02	257
23	2	Cr 50.8 I	-	277

Table 2. Chemical compositions (in wt.%) of the test network (TN) and reference networks (RN1 and RN2) and their total transparencies in different UV spectral regions.

	TN	RN1	RN2
Composition, wt%	12 (8%) 13 (24%) 14 (48%) 22 (20%)	C6BPhCN (80%) RM-257 (20%)	C6BP (20%) C6BP6 (60%) RM-257 (20%)
Transparency in UV-A (315–400 nm), %	96.7	62.8	92.6
Transparency in UV-B (280–315 nm), %	48.9	0	18.6
Transparency in broad UV range (280–400 nm), %	72.8	31.4	55.6
Resilience to UV[a]	+	+	-

[a]1 hour of exposure to UV light (312 nm, 5.8 mWcm^{-2}).

monomeric phase behaviour will completely altered by the fact that the monomers are now connected in the macromolecule.

Figure 10 shows the absorbance spectra of all reactive mesogens synthesised in the work. It is clearly seen from the spectra that all compounds are transparent in the UV-A spectral region. Absorbance in UV-B is still present which is mostly associated with the presence of aromatic benzene rings in the structure of reactive mesogens; however, electron-withdrawing substitution like nitril (for compound **16**) or carboxylic groups (for compounds **21** and **22**) sufficiently shifts the maxima of absorbance bathochromically by 14–19 nm.

3.4. UV-transparent LCPNs

We have designed a monomeric mixture containing monoacrylates **12**–**14** and cross-linker **22** to demonstrate the advantages of LCPNs prepared from the new library of reactive mesogens. This monomeric mixture is liquid crystalline at room temperature forming a nematic mesophase with clearing temperature 31°C. Fluidity at r.t. significantly simplifies processing of LC mixtures, and we envision that it will be particularly attractive for microfluidic production of LCPN droplets and shells. The test network (TN) with unidirectional planar alignment (Figure S15) has been produced by photopolymerisation at room temperature. Reference networks have been prepared from widely used commercially available reactive mesogens (Figure 11(a)). Reference network 1 (RN1) consists of cyanobiphenyl-

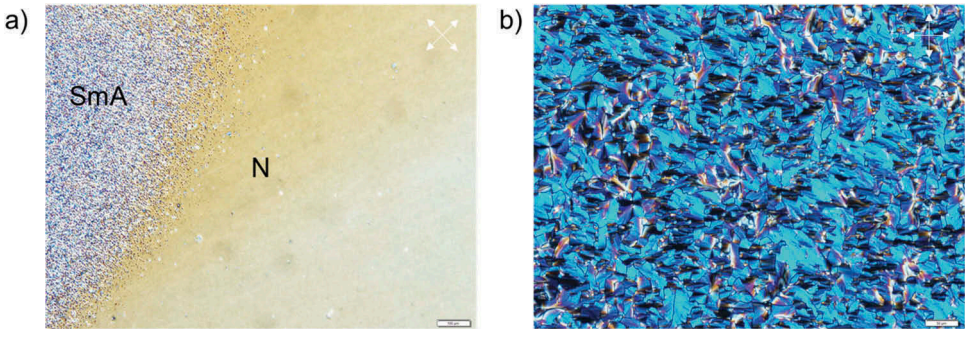

Figure 9. Polarised optical microscopy images of LC textures of compound **14** demonstrating the transition from smectic A to nematic (a) upon cooling, and fan-like texture of smectic A obtained at 22°C (b). Planar boundary conditions. Scale bars correspond to 100 and 50 µm, respectively. Polariser and analyser are shown as white arrows.

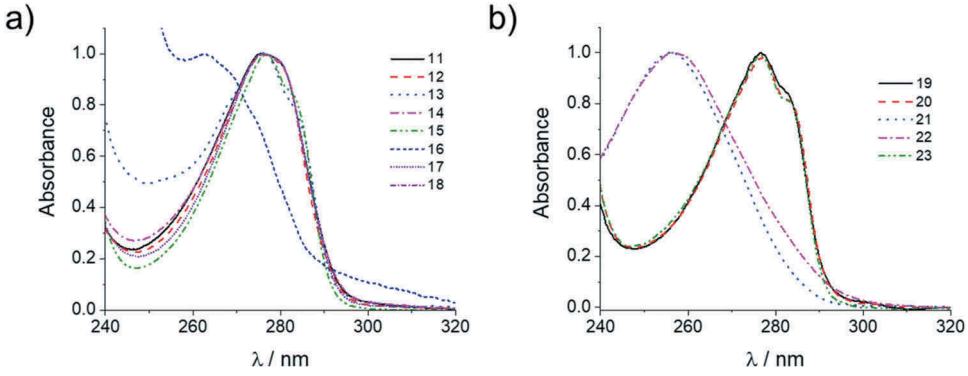

Figure 10. Normalised absorbance spectra of mono- (a) and diacrylates (b). Spectra are measured in CH_2Cl_2 at room temperature.

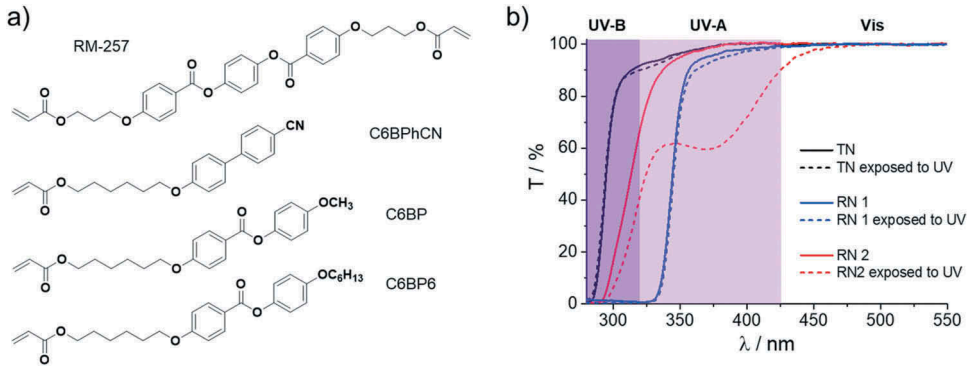

Figure 11. (a) Chemical structures of commercially available reactive mesogens used for the production of reference networks RN1 and RN2. (b) Transmittance spectra of the studied LCPNs before and after exposure to UV light (312 nm, 5.8 mWcm^{-2}) for 1 h.

based monoacrylate and cross-linker RM-257. Reference network 2 (RN2) is composed of alkyloxyphenyl benzoate-based monoacrylates and RM-257.

Spectroscopic characterisation of RN1 shows that the network acts as a cut-off filter below 340 nm, due to the absorption of the cyanobiphenyl fragments of the network leading to only 62.8% of transmittance in UV-A region and complete blocking of UV-B light (transmittance here is calculated as the area under the spectral curve in the given spectral range) (Figure 11(b), Table 2). Photostability test performed at 312 nm demonstrates the resilience of RN1 to UV light likely due to its high absorption. Network RN2 is characterised by overall higher transparency, 92.6% and 18.6% in UV-A and UV-B, respectively. Nevertheless, RN2 degrades upon UV exposure (312 nm) by photo-Fries rearrangement (Figure 11(b) dashed line). The TN network, consisting of the newly synthesised reactive mesogens presented in this work, displays the best optical performances associated with 96.7% and 48.9% transparency in UV-A and UV-B, respectively, and high stability to UV light (Figure 11(b)). We believe that the optical window of networks composed of the monomers described here will enable effective use of broad range of photoactive dopants (cinnamates, stilbenes, overcrowded alkenes, etc.), and generally, it provides a new toolbox for UV-stable and UV-transparent optical materials.

4. Conclusion

A new library of reactive mesogens (mono- and diacrylates) as building blocks for liquid crystal polymers and networks has been synthesised and characterised. The library has been used for the design and fabrication of UV-transparent LCPNs with remarkable stability to UV light. The use of these novel reactive mesogens sufficiently increases the transparency of the LCPNs in a broad UV spectral region (280–400 nm) in comparison with LCPNs based on commercially available compounds and results in materials resistant to prolonged UV exposure. Overall, the LC materials we designed are an attractive media for the integration of photoactive compounds (photoswitches and molecular motors) while preserving their effective photochemical and photophysical performance. Moreover, LCPNs based on these reactive mesogens can also find applications for a wide range of optical elements and devices (e.g. retarders, filters, coatings, etc.) where UV stability and transparency are critical.

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Disclosure statement

No potential conflict of interest has been reported by the authors.

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