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HOMO Energy-Level Lifting in p-Type O-Doped Graphenoids: Synthesis of Electrochromic Alkoxy-Decorated Xanthenoxanthenes

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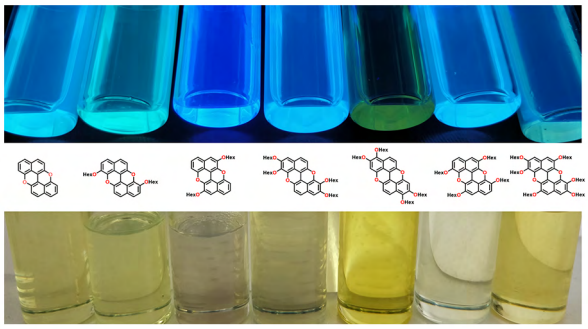

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Abstract A series of novel O-doped polycyclic aromatic hydrocarbons, bearing a different number of electron-donating alkoxy substituents, has been prepared using a novel copper-promoted anaerobic protocol for the cyclisation of highly electron rich *peri*-xanthenoxanthene molecular modules. The effect of the number and position of the alkoxy substituents on the optoelectronic properties has thus been investigated, unveiling p-type semiconducting properties. All molecules displayed a significant colour change upon oxidation, suggesting that these compounds can be used to devise chromogenic materials to engineer electrochromic devices.

Key words: polycyclic aromatic hydrocarbons, PXX, electrochromism, oxygen heterocycles, electrochromic devices

Introduction

In the compendium of semiconductor materials, heteroatom-embedded polycyclic aromatic hydrocarbons (PAHs) have gained increasing attention in a remarkably short time lapse, due to their tunable non-zero bandgaps and ability to form supramolecular π–π stacking motifs in the solid state, as well as their photochemical properties that often exceed those of pristine PAHs.[1] Amid the former family and in view of its excellent carrier-transport and electron injection properties, and chemical and thermal stability, *peri*-xanthenoxanthene (PXX, Figure 1)[2] has found its scope in a wide range of applications, ranging from emissive materials,[3] photocatalysis[4] to p-type molecular semiconductors.[5] Moreover, its electrochromic properties have been reported, showing a colour switch from yellow to blue upon applying a very low potential (1.25 V),[6] if compared to the non-doped analogues (4.0 V).[7] The recent development of a variant of the oxidative Pummerer O-annulation reaction[8] to prepare *peri*-substituted PXXs has allowed us to widen the scope of O-doped PAHs, featuring different geometries on both their peripheries and core structures.[9] Both size and edge of the PXX scaffold have been modified into ribbon-like structures, extending the *peri*-positions with π-annulated systems (Figure 1),[10] or multiple aryl ether groups embedded either through oxa- (armchair)[8a] or edge-type functionalisation (zig-zag).[11] Recently, dye-embedded PXXs, featuring a different number of either naphthalene- or perylene-diimide, have been reported by our group,[12] as well as PXX core modification, by replacement of C(sp^2) units with isoelectronic analogues.[13] The presence of O-atoms embodied in the structure has been shown to narrow the HOMO–LUMO gap

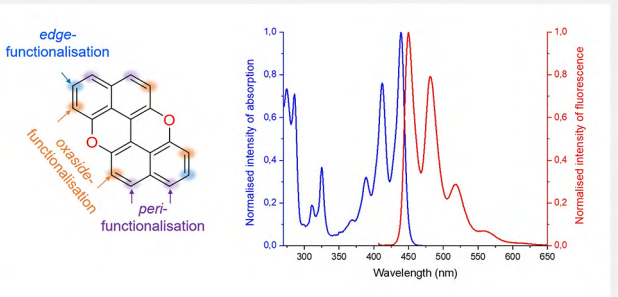


Figure 1 PXX structure and normalised absorption and emission (λ_{exc} = 405 nm) spectra in DMSO at r.t.

by rising the HOMO energy level, if compared to the all-C structures.[14] In this context, we envisaged that a further shrinking of the energy gap could be obtained upon decorating the PXX periphery with electron-donating alkoxy groups. Building on this idea, in this paper we put forward the synthesis of a series of alkoxy-functionalised PXX derivatives. A systematic study of the influence of the substitution position and the number of alkoxy-group on the optoelectronic (e.g., electrochemical and photophysical) properties has been performed. Hexyl chains were used a solubilising group to make the materials sufficiently processable in organic solvents. At last, spectroelectrochemical investigations were performed to unveil the electrochromic properties of the PXX-based molecular scaffolds in solution.

Results and Discussion

Molecular design and synthesis. Among all possible regioisomers, only symmetrical substituted PXXs were investigated, starting from commercially available dihydroxynaphthalenyl derivatives. Six different PXX-$(OHex)_n$ have been targeted, with a number of hexyloxy chains ranging from 2 to 6 (Figure 2). Similar to unsubstituted PXX, all symmetrical PXX-$(OHex)_n$ could be synthesised from a direct dimerisation/cyclisation from their hexyloxy-functionalised naphthalene-2-ol (Scheme 1, direct path d) or through a sequential route, via isolation of 1,1′-binaphthalene-2-ol bearing hexyloxy chains (Scheme 1, sequential path b, c). Starting from commercially available 2,7-dihydroxynaphthalene (compound **7** in Scheme 1), mono-hexylation was performed, followed by CuO-mediated oxidative C–C and C–O bond formation, to obtain derivative **1** with a modest 18% yield. By using the stepwise route, the $CuCl_2$/amine complex was used to get 7,7′-bis(hexyloxy)BINOL (**11**) in 50% yield, which was subsequently cyclised using CuI and PivOH in DMSO at 140 °C affording derivative **1** with an overall yield of 38% over the two steps (Scheme 1). Using the same reaction conditions as those employed for the synthesis of 1,3-(hexyloxy)naphthalene-2-ol, molecule **10** was obtained from 2,3-dihydroxynaphthalene **8** in 64% yield. In this case, the direct path involving the CuO-mediated dimerisation/cyclisation failed to produce **2**. Nevertheless, by using the sequential path, BINOL derivative **12** was obtained in 45% yield, and desired PXX-$(OHex)_2$ **2** produced in 50% yield using the CuI/PivOH cyclisation conditions (Scheme 1). For the preparation of derivative **3**, a different commercially available dihydroxynaphthalene was selected (Scheme 2). Spe-

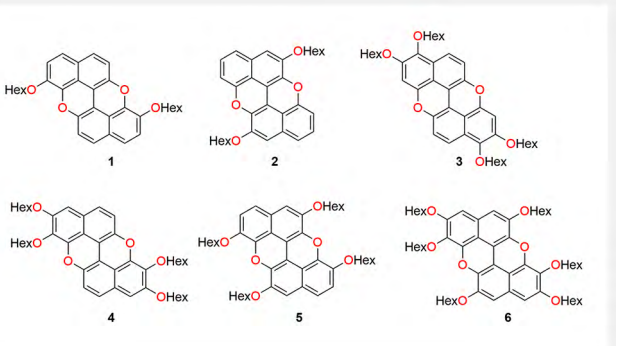
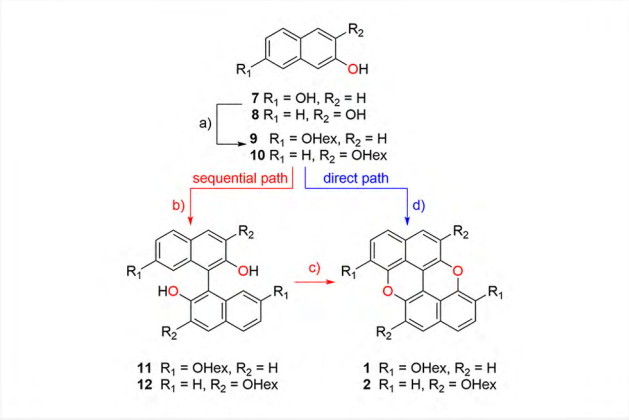
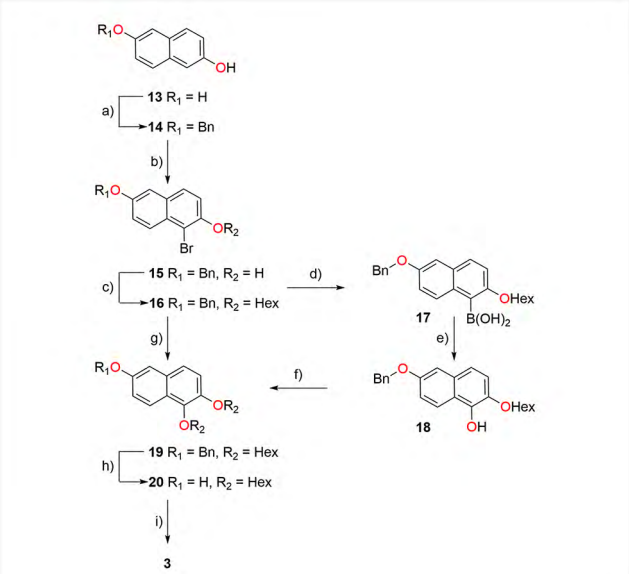


Figure 2 Target symmetrical PXX-$(OHex)_n$.

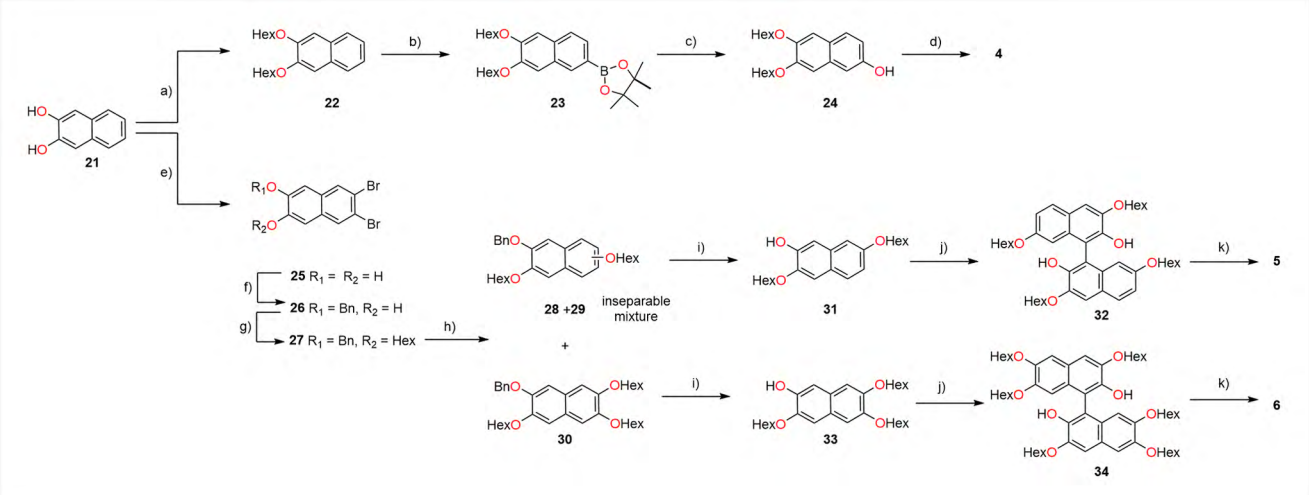


Scheme 1 Synthetic path for the preparation of PXX-$(OHex)_2$. a) HexI, K_2CO_3, DMF, 100 °C, 34% (**9**), 64% (**10**); b) $CuCl_2$, α-phenylethylamine, MeOH/CH_2Cl_2, r.t., 50% (**11**), 45% (**12**); c) CuI, PivOH, DMSO, 140 °C, 77% (**1**), 50% (**2**); d) CuO, $PhNO_2$, reflux, 18% (**1**).



Scheme 2 Synthetic paths for the preparation of **3**. a) NaH, BnBr, DMF, 100 °C, 28%; b) NBS, CH_2Cl_2, r.t., 78%; c) HexI, K_2CO_3, DMF, 100 °C, 78%; d) Mg, $B(OMe)_3$, THF, −94 °C, 64%; e) NaOH, H_2O_2, THF, 0 °C, 70%; f) HexI, K_2CO_3, DMF, 140 °C, 59%; g) Cs_2CO_3, Me_4Phen, CuI, HexOH, 130 °C, 34%; h) NaH_4HCO_2, Pd/C, THF/MeOH, reflux, 87%; i) CuO, $PhNO_2$, reflux, 80%.

cifically, 2,6-dihydroxynaphthalene **13** was mono-benzylated at first, then it was regioselectively brominated using NBS at r.t. Next, compound **15** was alkylated with HexI to give the desired bromo intermediate **16** (Scheme 2). Two different methodologies were attempted for preparing precursor **19**. The first route relies on the borylation of **16** by metal/halogen exchange using Mg in refluxing THF and addition of $B(OMe)_3$. Oxidation of the boronic acid with H_2O_2 under basic conditions followed by hexylation, gave tri-functionalised naphthalene **19**, with an overall yield of 26% over 3 steps. The second route exploited the Ullmann's copper-catalysed ether synthesis. Using CuI with 3,4,7,8-tetramethyl-9,10-phenanthroline as a ligand, Cs_2CO_3 as a base, and 1-hexanol as a solvent and coupling partner, the desired trihexyloxy naphthalene **19** was obtained with 34% yield in only one step, proving the synthetic efficiency of this method when compared to the sequential borylation/oxidation/hexylation route. Finally, hydrogenolysis of the benzyl group using NH_4HCO_2 afforded targeted 5,6-bis(hexyloxy)naphthalene-2-ol **20**, which was finally dimerised/cyclised using CuO to yield **3** in good yields. 2,3-Dihydroxynaphthalene **21** was chosen as a suitable module for the synthesis of targeted tetra-hexyloxy derivatives (**4** and **5**), as well as for hexa-hexyloxy PXX **6**. To prepare molecule **4**, 2,3- dihydroxynaphthalene was bis-hexylated, followed by a borylation using $[Ir(COD)OMe]_2$ as a catalyst, 4,4′-di-*tert*-butyl-2,2′-dipyridyl (dttbpy) and HBpin as a boron source.[15] Following the same procedure as that used in the case of derivative **17**, oxidation of the boronic acid afforded **24**, which was unsuccessfully reacted using the $CuCl_2$/amine conditions for the BINOL synthesis. Surprisingly, when naphthol **24** was refluxed in $PhNO_2$ with an excess of CuO, the desired tetra-hexyloxy PXX derivative **4** was obtained in 38% yield (Scheme 3). The preparation of both molecules **5** and **6** shares the first three synthetic steps. Tetrabromination of 2,3-dihydroxynaphthalene **21**, followed by treatment with $SnCl_2{\cdot}2H_2O$, yielded 6,7-dibromo-2,3-dihydroxynaphthalene **25** in an overall yield of 37%. Next, mono-benzylation followed by the hexylation of the remaining hydroxyl group gave derivative **27** in 93% yield. When the Ullman ether synthesis conditions were used, tri-hexyloxy naphthalene **30** was obtained as the major product, along with an inseparable mixture of 2-(benzyloxy)-3,6-bis(hexyloxy) and 2-(benzyloxy)-3,7-bis(hexyloxy) naphthalene (namely **28** and **29**). Due to the impossibility to purify the two species, **28** and **29** were subjected as a mixture to hydrogenolysis of the benzyl group to afford the two corresponding hydroxy-modified regioisomers, namely 3,6- and 3,7-bis(hexyloxy)naphthalene-2-ol. After several purification cycles on silica gel chromatographic columns, a pure fraction of the less polar species was obtained, which revealed to correspond to 3,7-bis(hexyloxy)naphthalene-2-ol **31**. Dimerisation of **31** to its BINOL derivative **32** using di-μ-hydroxo-bis[(*N,N,N′,N′*-tetramethylethylenediamine) copper(II)] chloride (Cu-TMEDA) was achieved in 77% yield. However, when the latter was heated in DMSO with CuI/PivOH or in m-xylene with CuCl/NMI mixtures, only degradation was observed. The degradation product probably derives from the over-oxidation reactions occurring in the presence of O_2. Thus, a new O_2-free protocol for the production of PXX had to be investigated. When a stoichiometric amount of Cu-TMEDA was added to BINOL derivative **32** in degassed m-xylene at 140 °C for 1 hour, the desired modified PXX derivative **5** was obtained in 56% yield. Similar to molecule **32**, also BINOL derivative



Scheme 3 Synthetic paths for the preparation of **4–6**. a) HexI, K_2CO_3, acetone, reflux, 97%; b) $[Ir(COD)OMe]_2$, dtbbpy, HBPin, THF, MW, 120 °C, 19%; c) NaOH, H_2O_2, THF, 0 °C, 67%; d) CuO, $PhNO_2$, reflux, 38%; e) Br_2, AcOH, reflux/$SnCl_2{\cdot}2H_2O$, HCl, AcOH, reflux, 37%; f) $NaHCO_3$, BnBr, DMF, 100 °C, 39%; g) HexI, K_2CO_3, DMF, 110 °C, 93%; h) Cs_2CO_3, Me_4Phen, CuI, HexOH, 130 °C, 34% (**28** + **29**), 40% (**30**); i) NH_4HCO_2, Pd/C, THF/MeOH, r.t., 45% (**31**), 93% (**33**); j) Cu-TMEDA, CH_2Cl_2, r.t., 77% (**32**), 81% (**34**); k) Cu-TMEDA, m-xylene, degas, 140 °C, 56% (**5**), 69% (**6**).

34 was obtained by dimerisation of **33** as the only product, due to the extent of steric hindrance of the *ortho* OHex group if compared to the hydroxy one. As for molecule **32**, commonly employed conditions for the production of PXX (CuI/Piv in DMSO, CuO in $PhNO_2$ and CuCl/NMI in *m*-xylene) did not afford the desired hexalkoxy-decorated PXX, but only degradation products were observed. Hence, we decided to apply the O_2-free protocol to synthesise **6**, which was thus obtained in 69% yield. To assess the nature of the newly synthesised species, full characterisation by means of NMR and mass spectroscopies was performed.

Electrochemical studies. To gain insight into the electrochemical behaviour of the PXX-$(OHex)_n$ derivatives, CV analyses were performed in CH_2Cl_2 using n-Bu_4NPF_6 as a supporting electrolyte (Figure S84). Reference unsubstituted PXX presents a clear reversible redox peak centred at 0.354 V against ferrocenium/ferrocene (Fc^+/Fc), as previously reported by Kobayashi et al.[16] and later by us.[4a] All the newly synthesised PXX-$(OHex)_n$ derivatives displayed electrochemical reversibility at all measured scan rates for their first oxidation process ($E_{1/2}^{ox,0/+1}$), indicating a good chemical and thermal stability of the monocationic species. The values of the oxidation peaks against Fc^+/Fc are reported in Table 1. In the case of tetra-hexyloxy derivatives **3** and **5**, a second reversible oxidation peak ($E_{1/2}^{ox,+1/+2}$) centered at 0.717 and 0.594 V, respectively, was observed. When compared to the first oxidation event of PXX ($E_{1/2}^{ox,0/+1}$ = 0.354 V), the peripheral functionalisation with two hexyloxy chains caused a lessening of the oxidation potential to 0.163 and 0.326 V for **1** and **2**, respectively. Moving to the tetra-hexyloxy derivatives, the first oxidation event for derivative **4** is centered at 0.256 V, whilst lower potentials were needed to oxidise regioisomers **3** (0.158 V) and **5** (0.135 V). Surprisingly, hexa-hexyloxy species **6** displayed a relatively high oxidation potential of 0.302 V, which is only 52 meV lower than that of PXX.

Table 1 Redox potentials and HOMO–LUMO gap values of 10^{-4} M solution of PXX and compounds **1–5** in *V* vs. Fc/Fc^+ with 0.1 M n-Bu_4NPF_6 as supporting electrolyte in aerated CH_2Cl_2.

	PXX	1	2	3	4	5	6
$E_{1/2}^{ox,0/+1}$	0.354	0.163	0.326	0.158	0.256	0.135	0.302
$E_{1/2}^{ox,+1/+2}$	–	–	–	0.717	–	0.594	–
E_{gap}[a]	3.171	3.108	3.283	2.973	3.174	3.193	3.231

[a]HOMO energy levels were determined by CV and LUMO energy levels were calculated using the optical bandgap as estimated from the photophysical data reported in Table 2 (calculated using the optical bandgap: $E_{LUMO} = E_{HOMO} + E_g^{00}$).

Photophysical studies. Investigations of the photophysical properties of the PXX derivatives were evaluated by UV-vis absorption and fluorescence analysis (Table 2 and Figure 3). All derivatives present similar absorption and emission envelops, with three distinctive vibronic peaks arising from the PXX aromatic core. Upon insertion of the hexyloxy groups, a hypsochromic shift is observable for derivatives **2, 4**, and **6**, whereas **1** and **3** experience a bathochromic shift, whose extent ranges from 8 nm for **1** to 31 nm for **3**. From these data, it is clear that the PXX derivatives bearing the hexyloxy chains in the *peri*-position experience the major changes in the electronic transition. For instance, the UV-vis absorption envelop of tetra-hexyloxy derivative **5** resembles that of PXX, with the same absorption maximum, indicating a similar HOMO–LUMO gap (3.174 V for **5** vs. 3.171 V for PXX). In addition, its emission maximum overlaps that of PXX, with a small difference in the Stokes shift, 6 and 5 nm observed for **4** and unsubstituted PXX, respectively. All the derivatives show a similar emission pattern, with two main peaks of similar relative intensities and a third peak over 500 nm. As expected, PXX derivative **3** showed the most red-shifted emission spectrum, with an emission maximum of 488 nm, 39 nm more than the unsubstituted PXX. Pristine PXX showed the maximum fluorescence quantum yield (Φ_{Fl}), and a decrease of the Φ_{Fl} value upon increasing the number of hexyloxy chains was detected, from 0.43 in the case of **2** to 0.27 for **6**. Combining the electrochemical and photophysical analyses, it was possible to estimate the frontier orbital diagram reported in Figure 4, as well as the values obtained by computational analysis in *vacuum*. Upon substitution, both HOMO and LUMO energy levels slightly increased in energy to a different extent, depending on the number and position of the hexyloxy chains. Despite a 100 meV increase of both its orbitals, molecule **4** shows almost the same energy gap as PXX, which is consistent with the similar absorption and emission spectra reported in Figure 3. In the case of molecule **3**, possessing the most notable colour change, the HOMO energy level value rose by 219 meV, while the LUMO level decreased by 21 meV. Despite the highest degree of functionalisation, and as observed by CV, hexa-hexyloxy derivative **6** does not show any dramatic change in its absorption and emission properties when compared to its unsubstituted parent PXX.

Table 2 Absorption maxima λ_{abs}, molar extinction coefficients ε_{max}, fluorescence maxima λ_{em}, fluorescence quantum yields Φ_{Fl}, Stokes shift, and optical bandgap (E_g^{opt}) in PhMe.

	λ_{abs} (nm)	ε_{max} ($cm^{-1} \cdot M^{-1}$)	λ_{em} (nm)	Φ_{Fl}[a]	Stokes shift (nm)	E_g^{opt} (eV)
PXX	444	1.79×10^4	449	0.45	5	2.731
1	452	7.95×10^3	463	0.31	11	2.655
2	424	1.21×10^4	436	0.43	12	2.834
3	475	9.57×10^3	488	0.34	13	2.510
4	444	1.54×10^4	450	0.38	6	2.728
5	433	4.51×10^3	454	0.25	21	2.737
6	430	5.94×10^3	445	0.27	15	2.756

[a] Coumarin 345 in EtOH was used as reference.

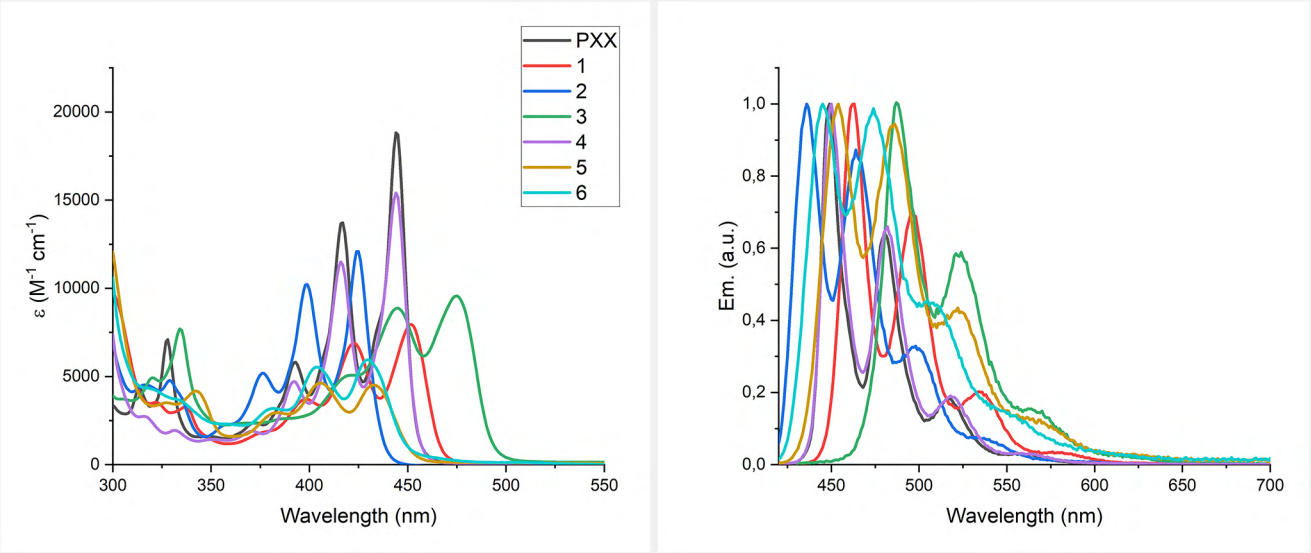


Figure 3 Absorption spectra (left) and normalised fluorescence spectra (right) of PXX-$(OHex)_n$ derivatives in PhMe at r.t.

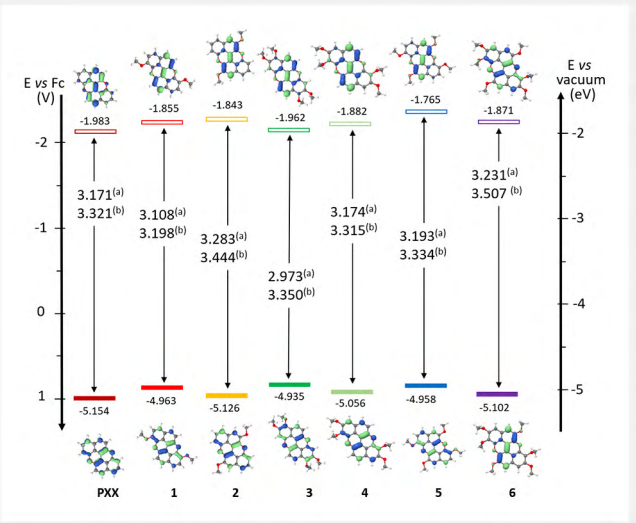


Figure 4 Frontier orbital energies for PXX-$(OHex)_n$. a) Experimental data. b) Calculated energy gap in eV. Hexyl groups in the optimised structures were omitted for clarity.

Electrochromic studies. To shed further light on the potentialities of the electrochromic properties of the molecules, spectroelectrochemistry investigations in $CHCl_3$ were performed (Figure 5). UV-vis absorption spectra of all PXX-$(OHex)_n$ were recorded at the neutral state (0 V), oxidised state (+1.0 V) and back to neutral state by using a negative potential (−0.5 V) at which no electrochemical reaction occurred. However, even after a prolonged period under reductive potential, the obtained spectrum did not overlap the original neutral one, indicating a non-reversible oxidation process (Figure 5). Upon oxidation, a broad absorption band of relatively weak intensity appeared at a high wavelength for all obtained PXX-$(OHex)_n$. Interestingly, molecule **3** was the only one showing a high-intensity blue-shifted absorption maximum. Depending on the position of these absorption maxima and broad band, solution of PXX-$(OHex)_n$ switched colour upon oxidation from yellow to red-brownish for PXX, to magenta for **1** and **2**, to purple for **4, 5**, and **6**, and to green for **3**. Given the significant colour change at low oxidation potentials, these PXX-$(OHex)_n$ are interesting candidates for electrochromic applications. Thus, their incorporation in prototype devices has been investigated. As a representative example, molecule **2**, with the lowest-lying HOMO level, was used to prepare electrochromic films to be integrated in a coplanar device architecture. A 10 mg/mL chloroform solution of the substrate was spray-coated onto squared-masked PET-ITO, to produce a 1 cm^2 square on one side and a complementary window of 0.5 cm width on the other side to differentiate ionised and neutral states at the same time on the same device. A 0.1 M solution of $LiClO_4$ in ethylene glycol was used as an electrolyte. The colour change for the device before (0 V) and after oxidation (+1.5 V) as well as after reduction (−1.5 V) is depicted in Figure 6. When the applied voltage was increased to 1.5 V, the colour changed from yellow to magenta, the same as was already observed for the solution during the spectroelectrochemistry experiments. The corresponding UV-vis transmittance spectra are shown in Figure 7. When potential square-wave cycles were applied to the device, the PXX-modified film exhibited a moderate contrast of the optical transmittance change ($\Delta T\%$) up to 9% at 536 nm. The switching time was calculated as the time required for reaching 90% of the full change in transmittance after switching potential.[17] The switching time was calculated as 11.6 s for the

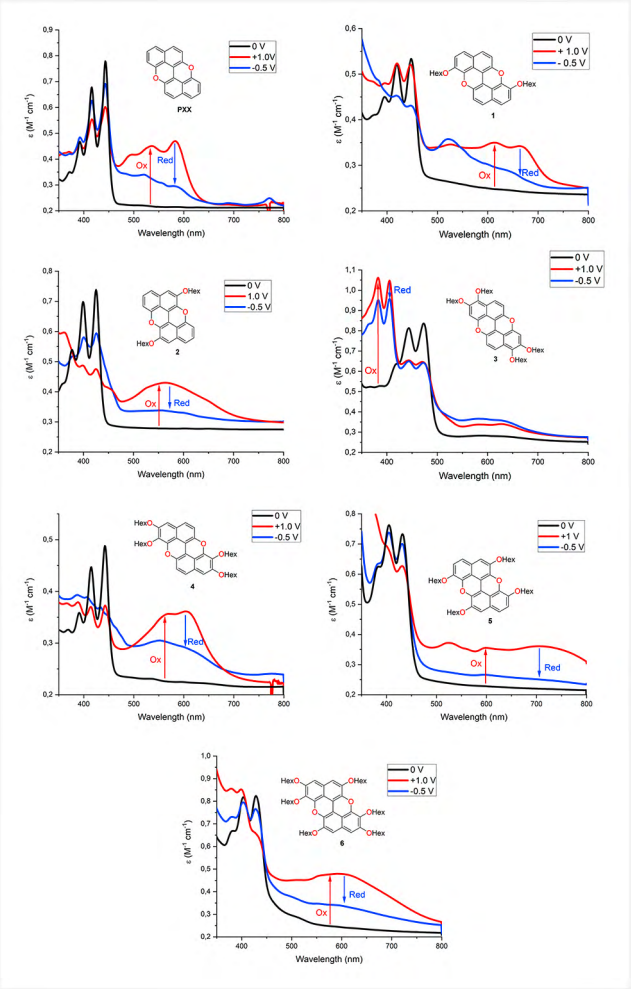


Figure 5 Electrochromic spectra of PXX-$(OHex)_n$ upon oxidation (+1.0 V) and reduction to the neutral state (−0.5 V) in aerated $CHCl_3$ solution.

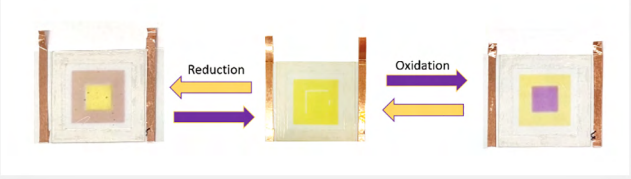


Figure 6 Pictures taken of a prototype electrochromic device using **2** as testing material. Device in its neutral state (middle), upon oxidation (+1.5 V, right), and upon reduction (−1.5 V, left).

reduction (from magenta to yellow) and 7.4 s for oxidation (from yellow to magenta). A very small variation of $\Delta T\%$ was observed upon increasing the number of cycles (Figure 7), indicating good stability of the molecule upon repetitive oxidation cycles.

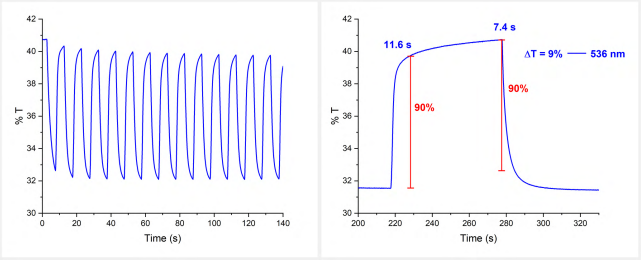


Figure 7 Electrochromic switching studies for the ECD based on the **2** film between −2.0 V and +2.0 V with a residence time of 5 s (left) and 60 s (right).

Conclusions

We have successfully synthesised and isolated six different O-doped PXX derivatives decorated with electron-donating hexyloxy chains. A new O_2-free cyclisation method, based on Cu-TMEDA oxidant, was developed to prepare these derivatives under anaerobic conditions, overcoming the problem of the overoxidation products. Computational investigations and CV analysis showed a decrease of the oxidation potential upon functionalisation, although we could not establish a direct correlation between the degree of functionalisation and oxidation potential values. However, the functionalisation position was observed to be crucial for a fine-tuning of the oxidation potential, with the *peri*-positions displaying the strongest effect on the destabilisation of the HOMO energy level. All the newly prepared molecules demonstrated a multicoloured electrochromic behaviour, which was investigated both in solution and in the solid state. Electrochemical and spectral results showed moderate electrochromic contrast upon oxidation/reduction; therefore, a prototype electrochromic device (ECD) with a coplanar architecture was made from derivative **2**. The ECD presented a stable electrochromic behaviour, switching colour from pale yellow to magenta, paving the way for the exploitation of these materials in ECDs.

Experimental Section

TLC was performed using pre-coated aluminium sheets using 0.20 mm silica gel 60 with fluorescent indicator F254 manufactured by Merck. Column chromatography was carried out using silica gel 60 (particle size 40 – 60 µm) from Applichem or using neutral Al_2O_3 supplied by Carlo Erba Reagents. Melting points (m. p.) were measured, uncorrected, on a Stuart SMP1 analogue melting point apparatus. NMR spectra were recorded using a Bruker Fourier 300 MHz spectrometer equipped with a dual (^{13}C, ^1H) probe, a Bruker Fourier 400 MHz equipped with a broadband multinuclear (BBO) probe, a Bruker AV III HDX 700 NMR spectrometer (Bruker BioSpin, Rheinstetten, Germany). ^1H spectra were

obtained at 500, 400 or 300 MHz and ^{13}C at 126, 101 or 75 MHz with complete decoupling for proton. All spectra were obtained at r.t. unless otherwise specified. Chemical shifts were reported in ppm according to tetramethylsilane using the solvent residual signal as an internal reference. The splitting of peaks is described as s (singlet), d (doublet), t (triplet), dd (doublet of doublets), and m (multiplet). IR spectra were recorded on a Shimadzu IR Affinity 1S FTIR spectrometer in ATR mode with a diamond mono-crystal at Cardiff University. MS: HRMS spectra were recorded on a Waters LCT HR TOF mass spectrometer in the positive or negative ion modes at Cardiff University on a maXis UHR ESI-Qq-TOF mass spectrometer (Bruker Daltonics, Bremen, Germany) in the positive or negative ion mode by direct infusion. The sum formulas of the detected ions were determined using Bruker Compass DataAnalysis 4.1 based on the mass accuracy ($\Delta m/z \leq 5$ ppm) and isotopic pattern matching (SmartFormula algorithm). HRLDMS spectra were acquired on a timsTOF fleX ESI/MALDI dual source-trapped ion mobility separation – Qq-TOF mass spectrometer (Bruker Daltonics, Bremen, Germany) in the positive ion mode. The sum formulas of the detected ions were determined using Bruker Compass DataAnalysis 5.3 based on the mass accuracy ($\Delta m/z \leq 5$ ppm) and isotopic pattern matching (SmartFormula algorithm). UV-vis absorption spectra were recorded on Agilent Cary 5000 UV-vis-NIR Spectrophotometer running in double-beam mode with a matched pair of quartz absorbance cuvettes (1 × 1 cm). All absorption measurements were performed at 21 °C unless specified otherwise. Steady-state photoluminescence (PL): PL excitation and emission spectra, absolute quantum yield, and decay curves were recorded on an FLS1000 PL spectrometer from Edinburgh Instruments. The spectrometer was equipped with excitation and emission double-grating Czerny–Turner monochromators, a continuous 400 W xenon lamp, and a photomultiplier detector with extended near-IR sensitivity (PMT-980), thermoelectric cooled to −20 °C with a Peltier element. For fluorescence decay measurement, the spectrometer was fitted with a picosecond pulsed light-emitting diode (EPLED-295) or with a picosecond pulsed diode laser (EPL-405). CV experiments were performed at r.t. in dry argon-purged CH_2Cl_2 (dried over activated molecular sieves prior to use) using an Autolab PGSTAT204 potentiostat. Dry argon was bubbled through the sample solution for at least 15 min prior to each measurement and the headspace was continuously flushed throughout the experiment. A prebubbler filled with CH_2Cl_2 was used to prevent solvent evaporation. Glassy carbon (3 mm diameter) was used as a working electrode, Pt wire as an auxiliary electrode, and an Ag/AgCl electrode was used as a reference. The glassy carbon electrode was sequentially polished on a pad using 15, 3 and 1 µm diamond slurry and washed with deionized water and methanol before each experiment; the Pt wire was flame-cleaned. Tetrabutylammonium hexafluorophosphate was recrystallised twice from absolute ethanol prior to use and it was added to the solution as a supporting electrolyte at a concentration of 0.1 M. Ferrocene (sublimed at reduced pressure) is used as an internal reference. Spectroelectrochemical characterisation was performed using a thin-layer quartz cuvette (path length of 0.5 mm) equipped with an optically transparent platinum minigrid working electrode, platinum wire as an auxiliary electrode, and an Ag/AgCl as the reference electrode. Degassing of solution/solvent mixtures was done by bubbling nitrogen through the solution with sonication followed by sealing the system under an inert atmosphere. Anhydrous conditions were achieved through heating of round-bottom flasks to 100 °C in the oven overnight, and allowing to cool under vacuum, followed by purging with nitrogen. Anhydrous solvents were dried over activated molecular sieves for at least 24 h prior to use. Low temperatures were achieved using low-temperature baths: −84 °C with ethyl acetate/liquid nitrogen, −94 °C with Acetone/liquid nitrogen while monitoring the temperature with a low-temperature thermometer, 0 °C with ice/H_2O. The inert atmosphere was maintained using nitrogen-filled balloons equipped with a syringe and needle which was used to pierce the silicone stoppers used to seal the flask's necks. Chemicals were purchased from Sigma Aldrich, TCI, Alfa Aesar, or Fluorochem and used as supplied. The computational results presented were achieved using the Vienna Scientific Cluster (VSC), at the B3LYP-D3/6 – 311 G** level of theory, using Gaussian 16 package.[18]

Procedures

General Procedure for the Synthesis of Mono-hexyloxy Naphthols

A suspension of dihydroxynaphthalene (3.20 g, 20.0 mmol) and K_2CO_3 (2.76 g, 20 mmol) in DMF (20 mL) was heated at 100 °C for 3 h. Hexyl iodide (2.95 mL, 20.0 mmol) was added and stirred at 100 °C for 16 h. H_2O was added (200 mL) and the suspension filtered and washed with H_2O.

7-(Hexyloxy)naphthalen-2-ol (9)

Purification by silica gel chromatography (PE/CH_2Cl_2 7 : 3) afforded **9** as a white solid (1.635 g, 6.7 mmol, 34%). M.f.: $C_{16}H_{20}O_2$. MW: 244.33 g/mol. M.p.: 92 °C. IR (neat) ν_{max}: 3211, 2939, 1627, 1448, 1355, 1201, 1026, 862, 831, 620, 467 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$) δ 7.65 (d, J = 8.8 Hz, 2 H), 7.03 (d, J = 2.5 Hz, 1 H), 7.00 (dd, J = 8.8, 2.5 Hz, 1 H), 6.97 (d, J = 2.5 Hz, 1 H), 6.93 (dd, J = 8.8, 2.5 Hz, 1 H), 4.86 (s, 1 H), 4.05 (t, J = 6.6 Hz, 2 H), 1.89 – 1.79 (m, 2 H), 1.55 – 1.45 (m, 2 H), 1.42 – 1.30 (m, 4 H), 0.92 (t, J = 7.0 Hz, 3 H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 157.94, 153.99, 136.12, 129.71, 129.33, 124.42, 116.78, 115.15, 108.86, 105.55, 68.14, 31.75, 29.35, 25.92, 22.76, 14.20. HRMS (ES+) calcd. for $C_{16}H_{21}O_2$ $[M + H]^+$ 245.1542, found 245.1544 (error 0.8 ppm).

3-(Hexyloxy)naphthalen-2-ol (10)

Purification by silica gel chromatography (PE/CH_2Cl_2 1 : 1 to CH_2Cl_2) afforded **10** as a white solid. (3.147 g, 12.9 mmol, 64%). M.f.: $C_{16}H_{20}O_2$. MW: 244.33 g/mol. M.p.: 45 °C. IR (neat) ν_{max}: 2920, 1638, 1508, 1487, 1458, 1387, 1256, 1163, 1113, 851, 741, 619, 474 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$) δ 7.72 – 7.64 (m, 2 H), 7.36 – 7.31 (m, 2 H), 7.29 (s, 1 H), 7.12 (s, 1 H), 6.00 (s, 1 H), 4.16 (t, J = 6.5 Hz, 2 H), 2.03 – 1.73 (m, 2 H), 1.60 – 1.45 (m, 2 H), 1.45 – 1.32 (m, 4 H), 1.03 – 0.87 (t, J = 7.0 Hz, 3 H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 147.25, 146.33, 129.97, 129.45, 126.87, 126.75, 124.62, 124.21, 109.53, 106.65, 68.92, 31.38, 28.83, 25.52, 22.38, 13.76. HRMS (ES^-) calcd. for $C_{16}H_{19}O_2$ $[M - H]^-$ 243.1385, found 243.1378 (error −2.9 ppm).

General Procedure for the Synthesis of Di-hexylated binoles

To a solution of $CuCl_2$ (807 mg, 6.00 mmol) in dry MeOH (30 mL), α-methylbenzylamine (0.967 mL, 7.5 mmol) was added at 0 °C and the resulting green/blue reaction was degassed for 1 h at 0 °C. A solution of (hexyloxy)naphthol (733.0 mg, 3.00 mmol) in dry CH_2Cl_2 (30 mL) was added and the reaction was stirred at r.t. for 16 h. The reaction was quenched with aq. HCl 1 M (30 mL) and extracted with CH_2Cl_2 (3 × 50 mL). The combined organic phases were dried over $MgSO_4$, filtered and evaporated in vacuo.

7,7′-Bis(hexyloxy)-[1,1′-binaphthalene]-2,2′-diol (11)

Purification by silica gel chromatography (PE/CH_2Cl_2 1 : 1 to CH_2Cl_2) afforded **11** as a white solid (368.1 mg, 0.76 mmol, 50%). M.f.: $C_{32}H_{38}O_4$. MW: 486.65 g/mol. M.p.: 85 °C. IR (neat) ν_{max}: 3337, 2953, 1464, 1448, 1265, 1248, 1171, 1115, 1074, 1018, 935, 899, 826, 740, 419 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$) δ 7.78 (d, J = 8.9 Hz, 2 H), 7.72 (d, J = 8.8 Hz, 2 H), 7.17 (d, J = 8.8 Hz, 2 H), 7.04 (dd, J = 8.9, 2.3 Hz, 2 H), 6.50 (d, J = 2.3 Hz, 2 H), 5.31 (s, 2 H), 3.84 – 3.61 (m, 4 H), 1.73 – 1.53 (m, 4 H), 1.44 – 1.17 (m, 12 H), 0.90 (t, J = 6.8 Hz, 6 H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 158.55, 153.33, 134.96, 130.87, 129.86, 124.69, 116.34, 115.09, 110.44, 104.16, 67.85, 31.61, 28.99, 25.70, 22.61, 14.06. HRMS (AP^+) calcd. for $C_{32}H_{39}O_4$ $[M + H]^+$ 487.2848, found 487.2853 (error 1.0 ppm).

3,3′-Bis(hexyloxy)-[1,1′-binaphthalene]-2,2′-diol (12)

Purification by silica gel chromatography (PE/CH_2Cl_2 1 : 1 to CH_2Cl_2) afforded **12** as a white powder (109 mg, 0.224 mmol, 45%). M.f.: $C_{32}H_{38}O_4$. MW: 486.65 g/mol. M.p.: 140 °C. IR (neat) ν_{max}: 3547, 2920, 2358, 1463, 1247, 1114, 827, 740, 621, 460 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$) δ 7.68 (d, J = 7.68 Hz, 2 H), 7.26 – 7.18 (m, 4 H), 7.10 – 7.04 (m, 4 H), 5.93 (s, 2 H), 4.20 – 4.15 (m, 4 H), 1.89 – 1.80 (m, 4 H), 1.50 – 1.40 (m, 4 H), 1.35 – 1.28 (m, 8 H), 0.82 (t, J = 7.0 Hz, 6 H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 146.68, 143.83, 129.22, 129.04, 126.97, 124.88, 124.51, 124.08, 114.70, 106.83, 69.05, 31.70, 29.21, 25.89, 22.73, 14.16. HRMS (ES^+) calcd. for $C_{32}H_{38}O_4Na$ $[M + Na]^+$ 509.2668, found 509.2676 (error 1.6 ppm).

General Procedure for the Synthesis of PXX-$(Hex)_2$

Procedure A: A suspension of mono-hexylated binol (487.0 mg, 1.00 mmol) and CuO (795 mg, 10.0 mmol) in $PhNO_2$ (5 mL) was refluxed under open-air conditions for 3 h. The reaction was filtered on a pad of silica and Celite and washed with CH_2Cl_2.

Procedure B: A solution of mono-hexylated binol (243 mg, 0.5 mmol), CuI (286 mg, 1.5 mmol) and pivalic acid (102 mg, 1.0 mmol) in DMSO (5 mL) was heated for 3 h at 140 °C under open-air conditions. The reaction was filtered, washed with CH_2Cl_2 and volatile solvents were removed in vacuo.

1,7-Bis(hexyloxy)xantheno[2,1,9,8-*klmna*]xanthene (1)

Procedure A: Purification by silica gel chromatography (PE to PE/CH_2Cl_2 2 : 1) afforded **1** as a yellow solid (43.1 mg, 0.089 mmol, 18%).

Procedure B: Purification by silica gel chromatography (PE/CH_2Cl_2 1 : 1 to CH_2Cl_2) afforded **1** as a yellow solid (186 mg, 0.386 mmol, 77%).

M.f.: $C_{32}H_{34}O_4$. MW: 482.62 g/mol. M.p.: 186 °C. IR (neat) ν_{max}: 2933, 2360, 1500, 1327, 1228, 1084, 814, 765, 750 cm^{-1}. ^1H NMR (500 MHz, THF-d_8) δ 7.26 (d, J = 9.1 Hz, 2 H), 7.08 (d, J = 8.9 Hz, 2 H), 7.02 (d, J = 8.9 Hz, 2 H), 6.81 (d, J = 9.1 Hz, 2 H), 4.08 (t, J = 6.5 Hz, 4 H), 1.82 – 1.76 (m, 4 H), 1.57 – 1.51 (m, 4 H), 1.40 – 1.37 (m, 8 H), 0.93 (t, J = 7.0 Hz, 6 H). ^{13}C NMR (126 MHz, THF-d_8) δ 145.28, 142.94, 141.51, 127.62, 127.40, 123.61, 121.31, 119.49, 116.46, 111.54, 71.24, 32.78, 30.75, 26.80, 23.72, 14.58. HRMS (AP^+) calcd. for $C_{32}H_{34}O_4$ $[M]^+$ 482.2457, found 482.2439 (error −1.8 ppm).

5,11-Bis(hexyloxy)xantheno[2,1,9,8-klmna]xanthene (2)

Procedure B: Purification by silica gel chromatography afforded **2** as a yellow solid (239 mg, 0.495 mmol, 50%). M.f.: $C_{32}H_{34}O_4$. MW: 482.62 g/mol. M.p.: 204 °C. IR (neat) ν_{max}: 2927, 1606, 1456, 1325, 1273, 1236, 1217, 1172, 1155, 1074, 736 cm^{-1}. ^1H NMR (500 MHz, THF-d_8) δ 7.05 (dd, J = 8.1, 7.5 Hz, 2 H), 7.00 (d, J = 8.1 Hz, 2 H), 6.86 (s, 2 H), 6.57 (d, J = 7.5 Hz, 2 H), 4.08 (t, J = 6.6 Hz, 4 H), 1.89 – 1.85 (m, 4 H), 1.58 – 1.52 (m, 4 H), 1.44 – 1.37 (m, 8 H), 0.94 (t, J = 7.0 Hz, 6 H). ^{13}C NMR (126 MHz, THF-d_8) δ 153.44, 149.54, 137.21, 133.50, 128.62, 119.96, 117.12, 113.14, 107.84, 106.89, 69.71, 32.73, 30.13, 26.81, 23.68, 14.57. HRMS (ES^+) calcd. for $C_{32}H_{34}O_4$ $[M]^+$ 482.2457, found 482.2450 (error −1.5 ppm).

6-(Benzyloxy)naphthalen-2-ol (14)

To a solution of 2,6-dihydroxynaphthalene **13** (9.61 g, 60.0 mmol) was added sodium hydride (2.401 g, 60% in mineral oil, 60.0 mmol) in three portions. When no more H_2 production was observable (ca. 2.5 h), benzyl bromide (7.2 mL, 60 mmol) was added dropwise and the reaction was heated at 100 °C for 16 h. After cooling to r.t., H_2O was added (400 mL) and the precipitate was filtered and washed with H_2O (400 mL) and MeOH (500 mL) to remove soluble the bis-functionalised product. Purification by silica gel chromatography (CH_2Cl_2) afforded **14** as a white solid (4.150 g, 16.58 mmol, 28%). M.f.: $C_{17}H_{14}O_2$. MW: 250.30 g/mol. M.p.: 144 °C. IR (neat) ν_{max}: 3256, 2359, 2342, 1602, 1512, 1452, 1373, 1222, 1153, 1008, 849, 743, 696, 624 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$) δ 7.62 (t, J = 9.1 Hz, 2 H), 7.50 (d, J = 7.5 Hz, 2 H), 7.44 – 7.32 (m, 3 H), 7.23 – 7.19 (m, 2 H), 7.11 – 7.06 (m, 2 H), 5.16 (s, 2 H), 4.78 (s, 1 H). ^{13}C NMR (75 MHz, $CDCl_3$) 155.41, 151.93, 137.13, 130.08, 129.81, 128.76, 128.69, 128.15, 127.99, 127.73, 119.84, 118.18, 109.84, 107.57, 70.23. HRMS (ES+) calcd. for $C_{17}H_{15}O_2$ $[M + H]^+$ 251.1072, found 251.1070 (error −0.2 ppm).

6-(Benzyloxy)-1-bromonaphthalen-2-ol (15)

To a solution of 6-(benzyloxy)naphthalene-2-ol **14** (2.44 g, 10.0 mmol) in DMF (20 mL) was added NBS (1.78 g, 10.0 mmol) and the resulting mixture was stirred at r.t. for 16 h. Aq. HCl 6 M (10 mL) was added and the solution was extracted with CH_2Cl_2 (3 × 100 mL). The combined organic phases were dried over $MgSO_4$, filtered and evaporated in vacuo. Purification by silica gel chromatography (PE/CH_2Cl_2 1 : 1) afforded **15** as a white solid (2.557 g, 7.77 mmol, 78%). M.f.: $C_{17}H_{13}O_2Br$. MW: 329.19 g/mol. M.p.: 113 °C. IR (neat) ν_{max}: 3308, 2359, 1609, 1506, 1371, 1353, 1229, 1172, 993, 903, 852, 815, 702, 692, 513 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 7.95 (d, J = 9.18 Hz, 1 H), 7.61 (d, J = 8.88 Hz, 1 H), 7.48 (d, J = 7.32 Hz, 2 H), 7.41 (t, J = 7.38 Hz, 2 H), 7.37 – 7.31 (m, 2 H), 7.22 (d, J = 8.88 Hz, 1 H), 7.19 (d, J = 2.40 Hz, 1 H), 6.42 (s, 1 H), 5.74 (s, 1 H), 5.17 (s, 2 H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 146.19, 143.69, 135.61, 129.07, 128.95, 128.76, 128.27, 128.01, 127.07, 125.72, 125.61, 124.83, 107.05, 105.06, 71.44. HRMS (EI^+) calcd. for $C_{17}H_{13}O_2Br$ $[M]^+$ 328.0099, found 328.0097 (error −0.6 ppm).

6-(Benzyloxy)-1-bromo-2-(hexyloxy)naphthalene (16)

A suspension of 6-(benzyloxy)-1-bromonapthalen-2-ol **15** (1.324 g, 4.03 mmol) and K_2CO_3 (3.44 g, 25.0 mmol) anhydrous DMF (6 mL) was heated at 110 °C for 2 h under N_2. Hexyl iodide (2.40 mL, 3.45 g, 16.3 mmol) was added and the reaction was stirred at 100 °C for 16 h. The suspension was cooled to r.t. and poured into ice/H_2O (200 mL) and stirred for 1 h. The organic phase was extracted with CH_2Cl_2 (4 × 30 mL). Combined organic phases were dried over $MgSO_4$, filtered and evaporated in vacuo. Purification by silica gel chromatography (PE to PE/CH_2Cl_2 3 : 2) afforded **16** as a white-yellowish solid (873 mg, 3.14 mmol, 78%). M.f.: $C_{23}H_{25}O_2Br$. MW: 413.36 g/mol. M.p.: 63 °C. IR (neat) ν_{max}: 3530, 1514, 1485, 1452, 1391, 1159, 1107, 1013, 947, 921, 874, 858, 739, 702, 455 cm^{-1}. ^1H NMR (400 MHz, CD_2Cl_2) δ 8.15 (dd, J = 9.0, 5.5 Hz, 1 H), 7.69 (d, J = 8.9 Hz, 1 H), 7.51 – 7.47 (m, 2 H), 7.44 – 7.30 (m, 4 H), 7.23 (m, 2 H), 5.17 (s, 2 H), 4.14 (t, J = 6.5 Hz, 2 H), 1.90 – 1.81 (m, 2 H), 1.58 – 1.53 (m, 2 H), 1.39 (m, 4 H), 0.96 – 0.93 (m, 3 H). ^{13}C NMR (100 MHz, CD_2Cl_2) δ 156.27, 152.71, 137.56, 131.31, 129.20, 129.13, 128.59, 128.31, 128.20, 128.05, 121.14, 116.62, 110.01, 107.99, 71.02, 70.70, 32.16, 30.05, 26.28, 23.22, 14.42. HRMS (AP+) calcd. For $C_{23}H_{26}O_2Br$ $[M + H]^+$ 413.1116, found 413.1100 (error −3.9 ppm).

(6-(Benzyloxy)-2-(hexyloxy)naphthalene-1-yl)boronic acid (17)

Magnesium turnings (25 mg, 1.0 mmol) were added to a solution of 6-(benzyloxy)-1-bromo-2-(hexyloxy)naphthalene **16** (413 mg, 1.00 mmol) in THF (2.0 mL) and the reaction was heated at reflux until almost all the metal disappeared (ca. 3 h). The reaction was cooled to −94 °C, trimethylborate (225 µL, 2.00 mmol) was added and the reaction was stirred at r.t. for 16 h before being quenched with H_2O (2 mL and 2 drops of aq. HCl 1 M). The white precipitate was filtered and the solid was dissolved in a minimum amount of CH_2Cl_2, precipitated with hexane, filtered and dried in vacuo to afford **17** as a white solid (242 mg, 0.64 mmol, 64%). M.f.: $C_{23}H_{27}BO_4$. MW: 378.28 g/mol. M.p.: 139 °C. IR (neat) ν_{max}: 3313, 1734, 1595, 1466, 1365, 1338, 1217, 1014, 827, 711 cm^{-1}. ^1H NMR (300 MHz, DMSO-d_6) δ 8.22 (s, 2 H), 7.72 (d, J = 8.9 Hz, 1 H), 7.62 (d, J = 9.1 Hz, 1 H), 7.50 (d, J = 7.1 Hz, 2 H), 7.40 (t, J = 7.1 Hz, 2 H), 7.36 – 7.31 (m, 2 H), 7.27 (d, J = 8.9 Hz, 1 H), 7.18 (dd, J = 9.1, 2.6 Hz, 1 H), 5.18 (s, 2 H), 4.03 (t, J = 6.4 Hz, 2 H), 1.74 – 1.65 (m, 2 H), 1.54 – 1.38 (m, 2 H), 1.38 – 1.22 (m, 4 H), 0.89 (t, J = 6.9 Hz, 3 H). ^{13}C NMR (75 MHz, DMSO-d_6) δ 156.72, 154.24, 137.17, 131.20, 129.42, 128.90, 128.45, 128.01, 127.82, 127.74, 118.74, 115.54, 107.55, 69.17, 68.92, 31.10, 29.21, 25.19, 22.14, 13.98 (1 carbon signal missing, probably due to coupling with boron). HRMS (ES^+) calcd. for $C_{23}H_{28}BO_4$ $[M + H]^+$ 378.2117, found 378.2126 (error 2.4 ppm).

6-(Benzyloxy)-2-(hexyloxy)naphthalene-1-ol (18)

A solution of (6-(benzyloxy)-2-(hexyloxy)naphthalen-1-yl) boronic acid **17** (200 mg, 0.53 mmol) in THF (15 mL) was cooled to 0 °C, then H_2O_2 (0.6 mL, 30% in H_2O) and aq. NaOH 1 M (0.6 mL, 0.6 mmol) were added. After 10 min, the reaction was stirred at r.t. until no more starting material was detectable by TLC (ca. 15 min). The reaction was diluted with Et_2O (30 mL) and extracted with Et_2O (3 × 20 mL). The combined organic phases were washed with brine, dried over $MgSO_4$, filtered and evaporated in vacuo. Purification by sil-

ica gel chromatography (PE/CH_2Cl_2 3 : 1 to 3 : 1) afforded **18** as a white solid (128.1 mg, 0.37 mmol, 70%). M.f.: $C_{23}H_{26}O_3$. MW: 350.46 g/mol. M.p.: 75 °C. IR (neat) ν_{max}: 3537, 2947, 2864, 1603, 1446, 1355, 1267, 1219, 1166, 1002, 782, 707, 694, 451 cm^{-1}. ^1H NMR (400 MHz, CD_2Cl_2) δ 8.10 (d, *J* = 9.1 Hz, 1 H), 7.56 – 7.50 (m, 2 H), 7.48 – 7.41 (m, 2 H), 7.38 (ddd, *J* = 7.2, 3.6, 1.2 Hz, 1 H), 7.30 (d, *J* = 8.9 Hz, 1 H), 7.28 – 7.21 (m, 2 H), 7.19 (d, *J* = 2.4 Hz, 1 H), 6.18 (s, 1 H), 5.17 (s, 2 H), 4.14 (t, *J* = 6.6 Hz, 2 H), 1.91 – 1.81 (m, 2 H), 1.58 – 1.46 (m, 2 H), 1.46 – 1.34 (m, 4 H), 0.97 (t, *J* = 7.0 Hz, 3 H). ^{13}C NMR (101 MHz, $CDCl_2$) δ 156.21, 140.87, 139.89, 137.65, 131.08, 128.94, 128.35, 128.05, 123.23, 119.91, 118.90, 118.47, 115.80, 107.21, 71.02, 70.37, 32.05, 30.01, 26.12, 23.06, 14.26. HRMS (ES^+) calcd. for $C_{23}H_{27}O_3$ $[M + H]^+$ 351.1960, found 351.1962 (error 0.6 ppm).

6-(Benzyloxy)-1,2-bis(hexyloxy)naphthalene-1-ol (19)

Procedure A: To a flame-dried Schlenk flask filled with 6-(benzyloxy)-1-bromo-2-(hexyloxy)naphthalene **16** (412 mg, 1.00 mmol), CuI (26.5 mg, 0.14 mmol), 3,4,7,8-tetramethyl-1,10-phenanthroline (70.3 mg, 0.30 mmol) and Cs_2CO_3 (559.2 mg, 1.72 mmol) under N_2 was added anhydrous 1-hexanol (1.0 mL, 8.0 mmol). The reaction was heated at 130 °C for 20 h before being cooled to r.t., filtered on a pad of silica and washed with CH_2Cl_2. Purification by silica gel chromatography (PE to PE/CH_2Cl_2 2 : 3) afforded **19** a white solid (147.6 mg, 0.34 mmol, 34%).

Procedure B: To a flame-dried Schlenk flask, 6-(benzyloxy)-2-(hexyloxy)naphthalene-1-ol **18** (77.8 mg, 0.22 mmol), K_2CO_3 (167 mg, 1.2 mmol) and anhydrous DMF (1 mL) were added and the reaction was stirred under N_2 at 100 °C for 1 h. 1-Iodohexane (0.2 mL, 1.35 mmol) was added and the mixture was stirred at 100 °C for 16 h. In order to push the reaction towards completion, the reaction was stirred at 140 °C for another 26 h. The suspension was poured into H_2O (50 mL) and extracted with CH_2Cl_2 (3 × 30 mL). The combined organic phases were dried over $MgSO_4$, filtered and evaporated in vacuo. Purification by silica gel chromatography (PE/CH_2Cl_2 1 : 1) afforded **19** as a white solid (56.0 mg, 0.13 mmol, 59%).

M.f.: $C_{29}H_{38}O_3$. MW: 434.62 g/mol. M.p.: 62 °C. IR (neat) ν_{max}: 2926, 2858, 2360, 1595, 1456, 1350, 1323, 1246, 1174, 1016, 731, 696 cm^{-1}. ^1H NMR (400 MHz, CD_2Cl_2) δ 8.10 (d, *J* = 9.2 Hz, 1 H), 7.55 – 7.50 (m, 2 H), 7.48 – 7.35 (m, 4 H), 7.27 (d, *J* = 8.9 Hz, 1 H), 7.24 (dd, *J* = 9.2, 2.4 Hz, 1 H), 7.20 (d, *J* = 2.4 Hz, 1 H), 5.17 (s, 2 H), 4.17 (t, *J* = 6.7 Hz, 2 H), 4.11 (t, *J* = 6.5 Hz, 2 H), 1.93 – 1.83 (m, 4 H), 1.63 – 1.53 (m, 4 H), 1.46 – 1.37 (m, 8 H), 0.98 (t, *J* = 7.0 Hz, 6 H). ^{13}C NMR (101 MHz, CD_2Cl_2) δ 155.68, 146.45, 143.13, 137.26, 130.81, 128.53, 127.93, 127.63, 125.08, 123.36, 122.19, 118.96, 117.80, 106.89, 73.70, 70.21, 69.99, 31.82, 31.71, 30.50, 29.83, 25.93, 25.90, 22.73, 22.71, 13.90, 13.88. HRMS (ES^+) calcd. for $C_{29}H_{39}O_3$ $[M + H]^+$ 435.2899, found 435.2900 (error 0.2 ppm).

5,6-*Bis*(hexyloxy)naphthalene-2-ol (20)

A solution of 6-(benzyloxy)-1,2-bis(hexyloxy)naphthalene **19** (142.4 mg, 0.328 mmol), NH_4HCO_2 (417 mg, 6.61 mmol) and Pd/C (10% w/w, 164.7 mg) in a mixture THF/MeOH (3 mL/3 mL) was refluxed for 2 h with an empty balloon above the condenser to collect the produced hydrogen. After cooling to r.t., the reaction was filtered through Celite and washed with CH_2Cl_2. Purification by silica gel chromatography (CH_2Cl_2) afforded **20** as a greenish oil (98.0 mg, 0.285 mmol, 87%). M.f.: $C_{22}H_{32}O_3$. MW: 344.50 g/mol. M.p.: Oil. IR (neat) ν_{max}: 2928, 1603, 1510, 1466, 1360, 1261, 1092, 763, 750 cm^{-1}. ^1H NMR (400 MHz CD_2Cl_2) δ 8.07 (d, *J* = 9.0 Hz, 1 H), 7.35 (d, *J* = 8.9 Hz, 1 H), 7.26 (d, *J* = 9.0 Hz, 1 H), 7.15 – 7.11 (m, 1 H), 7.09 (d, *J* = 1.8 Hz, 1 H), 6.16 (s, 1 H), 4.19 (t, *J* = 6.7 Hz, 2 H), 4.12 (t, *J* = 6.5 Hz, 2 H), 1.95 – 1.83 (m, 4 H), 1.59 – 1.52 (m, 4 H), 1.47 – 1.29 (m, 8 H), 1.02 – 0.90 (m, 6 H). ^{13}C NMR (101 MHz, CD_2Cl_2) δ 153.04, 146.56, 143.28, 131.51, 125.26, 123.90, 122.55, 118.57, 118.37, 109.67, 74.46, 70.79, 32.22, 32.13, 30.85, 30.23, 26.32, 26.30, 23.14, 23.13, 14.32, 14.30. HRMS (ES^+) calcd. for $C_{22}H_{33}O_3$ $[M + H]^+$ 345.2430, found 345.2427 (error −0.9 ppm).

2,3,8,9-Tetrakis(hexyloxy)xantheno[2,1,9,8-*klmna*]xanthene (3)

A suspension of 5,6-bis(hexyloxy)naphthalen-2-ol **20** (22.0 mg, 63.9 µmol) and CuO (51.2 mg, 0.64 mmol) in $PhNO_2$ (1 mL) was refluxed under open-air conditions for 1.5 h. The reaction was filtered on a pad of silica and Celite and washed with CH_2Cl_2. Purification by silica gel chromatography (PE to PE/CH_2Cl_2 2 : 1) afforded **3** as a yellow solid (17.5 mg, 25.6 µmol, 80%). M.f.: $C_{44}H_{58}O_6$. MW: 682.94 g/mol. M.p.: 116 °C. IR (neat) ν_{max}: 2951, 2920, 1628, 1506, 1344, 1274, 1227, 1159, 1051, 987, 766, 750, 611 cm^{-1}. ^1H NMR (500 MHz, THF-d_8) δ 7.45 (d, *J* = 9.2 Hz, 2 H), 6.84 (d, *J* = 9.2 Hz, 2 H), 6.58 (s, 2 H), 4.03 – 3.98 (m, 8 H), 1.82 – 1.76 (m, 8 H), 1.57 – 1.50 (m, 8 H), 1.41 – 1.37 (m, 16 H), 0.93 (t, *J* = 6.5 Hz, 12 H). ^{13}C NMR (126 MHz, THF-d_8) δ 150.28, 149.50, 144.07, 138.37, 127.24, 121.92, 118.20, 117.48, 111.71, 101.55, 73.83, 70.78, 32.92, 32.78, 31.53, 30.75, 27.03, 26.94, 23.75, 23.73, 14.62, 14.58. HRMS (ES^+) calcd. for $C_{44}H_{59}O_6$ $[M + H]^+$ 683.4312, found 683.4313 (error 0.1 ppm).

2,3-*Bis*(hexyloxy)naphthalene (22)

Naphthalen-2,3-diol **21** (8.0 g, 50 mmol) and K_2CO_3 (27.6 g, 200 mmol) were heated at 80 °C in acetone (120 mL) for 10 min. 1-Iodohexane (29.5 mL, 200 mmol) was added and the reaction was heated at reflux for 16 hours under N_2. To drive the reaction forward, 1 equivalent of K_2CO_3 (6.9 g, 50 mmol) and 3 equivalents of 1-iodohexane (22.2 mL, 150 mmol) were added. Volatiles were evaporated in vacuo and the remaining solid was washed with H_2O and dried under high vacuum yielding **22** as a light brown solid

(15.965 g, 48.6 mmol, 97%). M.f.: $C_{22}H_{32}O_2$. MW: 328.50 g/mol. M.p.: 51 °C. IR (neat) ν_{max}: 3051, 2924, 2857, 1626, 1599, 1508, 1462, 1404, 1250 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$, ppm) δ 7.68 – 7.63 (dd, *J* = 6.1, 3.3 Hz, 2 H), 7.33 – 7.27 (dd, *J* = 6.1, 3.3 Hz, 2 H), 7.11 (s, 2 H), 4.11 (t, *J* = 6.7 Hz, 4 H), 1.95 – 1.85 (m, 4 H), 1.54 – 1.48 (m, 4 H), 1.40 – 1.33 (m, 8 H), 0.92 (t, *J* = 7.1 Hz, 6 H). ^{13}C NMR (75 MHz, $CDCl_3$, ppm) δ 149.52, 129.33, 126.33, 124.04, 107.84, 68.93, 31.76, 29.19, 25.89, 22.77, 14.19. HRMS (ES+) calcd. for $C_{22}H_{33}O_2$ $[M + H]^+$ 329.2481, found 329.2487 (error: 1.8 ppm).

6-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolane)-2,3-*bis* (hexyloxy) naphthalene (23)

To a flame-dried thick-walled microwave tube was added 2,3-bis(hexyloxy)naphthalene **22** (1 g, 3 mmol) under N_2. 4,4′-di-*tert*-butyl-2,2′-dipyridyl (dtbbpy) (21 mg, 0.078 mmol), pinacolborane (2.7 mL, 18.8 mmol) and dry THF (2.1 mL) were added. The reaction was degassed by bubbling N_2 for 30 min and (1,5-cyclooctadiene)(methoxy) Iridium (I) dimer $[Ir(COD)OMe]_2$ (21.9 mg, 0.033 mmol) was added. The reaction was heated under microwave irradiation at 120 °C for 40 hours. The suspension was filtered through Celite and washed with CH_2Cl_2. Purification by silica gel chromatography (CH_2Cl_2/PE 1 : 1 to 3 : 1) afforded **23** as a brown oil (0.257 g, 0.57 mmol, 19%). M.f.: $C_{28}H_{43}BO_4$. MW: 454.46 g/mol. M.p.: Oil. IR (neat) ν_{max}: 2980, 2955, 2930, 2359, 1624, 1489, 1466, 1379, 1340, 1082 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$, ppm) δ 8.20 (s, 1 H), 7.74 – 7.60 (m, 2 H), 7.16 (s, 1 H), 7.10 (s, 1 H), 4.14 – 4.05 (m, 4 H), 1.95 – 1.82 (m, 4 H), 1.55 – 1.47 (m, 4 H), 1.47 – 1.32 (m, 20 H), 0.92 (t, *J* = 6.5 Hz, 6 H). ^{13}C NMR (75 MHz, $CDCl_3$, ppm) δ 150.46, 149.20, 134.56, 131.23, 128.86, 128.56, 125.42, 108.41, 107.37, 83.77, 68.83, 68.78, 31.68, 31.65, 29.78, 29.04, 25.81 (2C), 24.98, 22.70 (2C), 14.12 (2C) (1 aromatic carbon signals missing, probably due to coupling with boron; 2 aliphatic carbon signals missing, probably due to overlapping). HRMS (ES^+) calcd. For $C_{28}H_{44}O_4B$ $[M + H]^+$ 454.3369, found 455.3343 (error: 0.2 ppm).

2,3-*Bis*(hexyloxy)naphthalen-6-ol (24)

A solution of 6-(4,4,5,5-tetramethyl-1,3,2-dioxaborolane)-2,3-bishexyloxynaphthalene **23** (257 mg, 0.57 mmol) in THF (15.5 mL) was cooled to 0 °C. H_2O_2 (0.6 mL, 26 mmol) and 1 M NaOH (0.6 mL) were added to the mixture. The reaction was stirred for 20 min at 0 °C and quenched with Et_2O (20 mL). The suspension was washed with H_2O (3 × 20 mL) and with brine (25 mL), dried over $MgSO_4$, filtered and dried in vacuo. Purification by silica gel chromatography (CH_2Cl_2/PE 1 : 1 to 1 : 0) afforded **24** as a pale brown solid (131 mg, 0.38 mmol, 67%). M.f.: $C_{22}H_{32}O_3$. MW: 344.50 g/mol. M.p.: 90 °C. IR (neat) ν_{max}: 3310, 2951, 2924, 2857, 2361, 1636, 1614, 1585, 1508, 1357, 1209 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$, ppm) δ 7.55 (d, *J* = 8.7 Hz, 1 H), 7.09 (s, 1 H), 7.01 (d, *J* = 2.0 Hz, 1 H), 6.96 – 6.93 (m, 2 H), 5.30 (s, 1 H), 4.10 – 4.04 (m, 4 H), 1.92 – 1.83 (m, 4 H), 1.52 – 1.47 (m, 4 H), 1.34 (d, *J* = 3.5 Hz, 8 H), 0.91 (t, *J* = 6.7 Hz, 6 H). ^{13}C NMR (75 MHz, $CDCl_3$, ppm) δ 152.50, 150.05, 147.56, 130.55, 128.05, 124.22, 115.49, 108.94, 108.44, 106.66, 69.17, 68.91, 31.71 (2C), 29.15, 29.09, 25.86 (2C), 22.73 (2C), 14.16 (2C) (4 aliphatic carbon signals missing, probably due to overlapping). HRMS (ES^+) calcd. for $C_{22}H_{33}O_3$ $[M + H]^+$ 345.2430, found 345.2437 (error: 2.0 ppm).

1,2,7,8-Tetrakis(hexyloxy)xantheno[2,1,9,8-*klmna*] xanthene (4)

A suspension of 2,3-bis(hexyloxy)naphthalen-6-ol **24** (34.4 mg, 0.10 mmol) and CuO (80 mg, 1.0 mmol) in $PhNO_2$ (1 mL) was stirred under reflux for 4 h. The reaction was cooled and purified by silica gel chromatography (CH_2Cl_2/PE 1 : 3 to 1 : 1) affording **4** as a bright yellow solid (12.9 mg, 0.019 mmol, 38%). M.f.: $C_{44}H_{58}O_6$. MW: 682.94 g/mol. M.p.: 181 °C. IR (neat) ν_{max}: 2953, 2926, 2857, 2350, 1636, 1684, 1717, 1506, 1231 cm^{-1}. ^1H NMR (300 MHz, CD_2Cl_2, ppm) δ 7.21 (d, *J* = 9.0 Hz, 2 H), 6.92 (d, *J* = 9.0 Hz, 2 H), 6.56 (s, 2 H), 4.05 – 3.99 (m, 8 H), 1.88 – 1.82 (m, 4 H), 1.81 – 1.75 (m, 4 H), 1.39 – 1.35 (br m, 12 H), 1.29 – 1.26 (br m, 12 H), 0.92 (t, *J* = 6.6 Hz, 12 H). $^{13}CNMR$ (75 MHz, CD_2Cl_2) δ 154.46, 144.74, 143.32, 134.31, 127.62, 125.54, 117.55, 116.92, 111.11, 100.78, 74.09, 69.25, 32.31, 32.17, 30.76, 29.76, 26.42, 26.32, 23.30, 23.21, 14.45, 14.38. HRMS (AP^+) calcd. for $C_{44}H_{59}0_6$ $[M + H]^+$ 683.4312, found 683.4304 (error −1.2 ppm).

6,7-Dibromonaphthalene-2,3-diol (25)

To a solution of 2,3-dihydroxynaphthalene **21** (12.82 g, 80.0 mmol) in glacial AcOH (200 mL) was added bromine (16.8 mL, 320 mmol). The reaction was stirred at reflux for 1 h (till a solid was formed). The reaction mixture was cooled down to r.t. and H_2O (400 mL) was added resulting in a yellow precipitate. The solid was filtrated and dissolved in Et_2O (120 mL). The organic phase was washed with H_2O (2 × 120 mL) and the aqueous phase washed with Et_2O (2 × 120 mL). The organic layers were combined, dried over $MgSO_4$, filtered and evaporated in vacuo. Recrystallisation from hot AcOH afforded 1,4,6,7-tetrabromonaphthalene-2,3-diol as a yellow solid (27.5 g, 57.8 mmol, 79%). 1,4,6,7-Tetrabromonaphthalene-2,3-diol (25.0 g, 52.5 mmol) was dissolved in glacial AcOH (500 mL) and $SnCl_2$ (79.98 g, 422 mmol) and H_2O (53 mL) were added. The reaction was heated near reflux and concentrated HCl (150 mL) was added, resulting in evolution of HBr gas. The mixture was heated at reflux for 2 h after which HBr formation appeared to have ceased. The solution was cooled to r.t. and H_2O (1 L) and concentrated HCl (120 mL) were added. Solvents were partially removed in vacuo and the resulting precipitate was filtered to afford a white solid (9.368 g, 29.46 mmol, 37% over two steps). M.f.: $C_{10}H_6Br_2O_2$. MW: 454.46 g/mol. M.p.: 212 °C. IR (neat) ν_{max}: 3649, 2922, 2310, 1496, 1489,

1252, 1232, 1150, 1105, 1024, 941, 887, 727, 692, 457 cm^{-1}. ^1H NMR (300 MHz, Acetone-d_6) δ 8.86 (s, 2 H), 8.01 (s, 2 H), 7.21 (s, 2 H). ^{13}C NMR (75 MHz, Acetone-d_6) δ 148.66, 131.10, 130.50, 118.68, 109.51. HRMS: molecular peak not found with available techniques.

3-(Benzyloxy)-6,7-dibromonaphthalen-2-ol (26)

To a solution of 6,7-dibromonaphthalene-2,3-diol **25** (5.80 g, 18.2 mmol) in anhydrous DMF (36 mL), $NaHCO_3$ (1.53 g, 18.2 mmol) was added under Ar. The resulting mixture was heated at 100 °C for 1 h. Benzyl bromide (2,16 mL, 18.2 mmol) was added and heated at 100 °C for 16 h. After cooling to r.t., the mixture was diluted with CH_2Cl_2 (50 mL) and extracted with H_2O (3 × 30 mL). The aqueous layer was washed with CH_2Cl_2 (3 × 30 mL). The combined organic phases were dried over $MgSO_4$, filtered and evaporated in vacuo. Purification by silica gel column chromatography (CyHex/CH_2Cl_2 1 : 1) afforded **26** as a white solid (2.870 g, 7.03 mmol, 39%). M.f.: $C_{17}H_{12}Br_2O_2$. MW: 408.09 g/mol. M.p.: 165 °C. IR (neat) ν_{max}: 3515, 1498, 1453, 1304, 1352, 1292, 1251, 1151, 1104, 1024, 942, 887, 736, 695, 539 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 7.93 (s, 2 H), 7.48 – 7.38 (m, 5 H), 7.15 (s, 1 H), 7.07 (s, 1 H), 6.04 (s, 1 H), 5.22 (s, 2 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 147.53, 146.95, 135.43, 130.86, 30.65, 129.79, 129.05, 128.95, 128.18, 120.17, 119.51, 108.66, 105.97, 71.32 (1 carbon signal missing, probably due to overlap). HRMS (ES^+) cacld. for $C_{17}H_{13}Br_2O_2$ $[M + H]^+$ 406.9277, found 406.9272 (error −1.2 ppm).

2-(Benzyloxy)-6,7-dibromo-3-(hexyloxy)naphthalene (27)

To a flame-dried Schlenk flask was added K_2CO_3 (3.32 g, 24.0 mmol), 3-(benzyloxy)-6,7-dibromonaphthalen-2-ol **26** (1.224 g, 3.0 mmol) and dry DMF (5 mL). The reaction was heated at 110 °C for 3 h before adding hexyl iodide (1.77 mL, 12.0 mmol). After 14 h at 110 °C, the reaction was cooled to r.t. and poured into 200 mL of ice cooled H_2O and stirred for 1 h at r.t. Purification by filtration afforded **27** as an off-white solid (1.372 g, 2.79 mmol, 93%). M.f.: $C_{23}H_{24}Br_2O_2$. MW: 492.25 g/mol. M.p.: 92 °C. IR (neat) ν_{max}: 2924, 2857, 1624, 1501, 1447, 1247, 1163, 1024, 993, 889, 727, 692, 580 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 7.92 (s, 1 H), 7.88 (s, 1 H), 7.49 (d, J = 7.4 Hz, 2 H), 7.42 – 7.32 (m, 3 H), 7.01 (s, 1 H), 6.98 (s, 1 H), 5.22 (s, 2 H), 4.11 (t, J = 6.5 Hz, 2 H), 1.95 – 1.88 (m, 2 H), 1.60 – 1.51 (m, 2 H), 1.42 – 1.35 (m, 4 H), 0.96 – 0.89 (m, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.67, 149.98, 136.70, 130.58, 130.47, 129.56, 129.05, 128.67, 128.03, 127.12, 119.67, 119.38, 107.63, 106.44, 70.72, 69.01, 31.67, 29.08, 25.85 22.72, 14.13. HRMS (ES+) calcd. For $C_{23}H_{25}O_2Br_2$ $[M + H]^+$ 491.0221, found 491.0219 (error −0.4 ppm).

General Procedure for the Ullman Ether Synthesis of 28 – 30

To a flame-dried Schlenk flask was added 2-(benzyloxy)-6,7-dibromo-3-(hexyloxy)naphthalene **27** (496.2 mg, 1.008 mmol), CuI (61.4 mg, 0.33 mmol), Cs_2CO_3 (1.146 g, 3.5 mmol) and 3,4,7,8-tetramethyl-1,10-phenanthroline (164.4 mg, 0.69 mmol). The system was dried under vacuum for 20 min before being back-filled with N_2. Anhydrous 1-hexanol (2 mL) was added and the suspension was heated at 130 °C for 60 h. The reaction was filtered on silica pad (CH_2Cl_2) before being purified by silica gel chromatography (PE to PE/CH_2Cl_2 6 : 4) to afford first an inseparable mixture of 2-(benzyloxy)-3,6-bis(hexyloxy)naphthalene **28** and 2-(benzyloxy)-3,7-bis(hexyloxy)naphthalene **29** (146.5 mg, 0.337 mmol, 34%), and 2-(benzyloxy)-3,6,7-tris(hexyloxy)-naphthalene **30** (216.5 mg, 0.405 mmol, 40%) as white solids.

2-(Benzyloxy)-3,6-bis(hexyloxy)naphthalene (28) and 2-(Benzyloxy)-3,7-bis(hexyloxy)naphthalene (29)

M.f.: $C_{29}H_{38}O_3$. MW: 434.62 g/mol. M.p.: 68 °C. IR (neat) ν_{max}: 2927, 1629, 1604, 1510, 1406, 1250, 1215, 1118, 862 cm^{-1}. ^1H NMR (400 MHz, CD_2Cl_2) δ 7.66 – 7.56 (m, 3 H), 7.50 – 7.40 (m, 3 H), 7.23 – 7.03 (m, 4 H), 5.25 – 5.20 (m, 2 H), 4.17 – 4.07 (m, 4 H), 1.97 – 1.87 (m, 4 H), 1.60 – 1.59 (m, 4 H), 1.53 – 1.32 (m, 8 H), 1.04 – 1.01 (m, 6 H). ^{13}C NMR (100 MHz, CD_2Cl_2) δ 156.46, 156.28, 150.27, 150.24, 149.62, 149.58, 147.90, 147.86, 147.28, 137.54, 137.40, 130.91, 130.87, 130.30, 130.26, 128.56, 128.54, 128.52, 127.88, 127.86, 127.78, 127.74, 127.68, 127.65, 127.51, 127.49, 127.45, 127.43, 124.54, 124.50, 123.99, 123.95, 116.60, 116.35, 109.53, 108.36, 108.25, 107.19, 106.36, 106.33, 106.29, 70.88, 70.63, 68.94, 68.79, 68.10, 31.80, 31.76, 29.46, 29.43, 29.35, 29.31, 29.27, 25.94, 25.90, 25.75, 22.79, 22.75, 14.00, 13.98, 13.95. HRMS (ES^+) calcd. for $C_{29}H_{39}O_3$ $(M + H)^+$ 435.2899, found 435.2910 (error 2.5 ppm).

2-(Benzyloxy)-3,6,7-tris(hexyloxy)naphthalene (30)

M.f.: $C_{35}H_{50}O_4$. MW: 534.78 g/mol. M.p.: 89 °C. IR (neat) ν_{max}: 2928, 2359, 1605, 1508, 1420, 1248, 1179, 870, 696, 617, 401 cm^{-1}. ^1H NMR (400 MHz, CD_2Cl_2) δ 7.58 (d, J = 1.4 Hz, 1 H), 7.57 – 7.55 (m, 1 H), 7.48 – 7.44 (m, 2 H), 7.40 (ddd, J = 7.3, 3.7, 1.4 Hz, 1 H), 7.17 (s, 1 H), 7.13 (s, 1 H), 7.11 (s, 1 H), 7.08 (s, 1 H), 5.22 (s, 2 H), 4.16 – 4.08 (m, 6 H), 1.98 – 1.89 (m, 6 H), 1.62 – 1.56 (m, 6 H), 1.47 – 1.41 (m, 12 H), 1.04 – 0.94 (m, 9 H). ^{13}C NMR (100 MHz, CD_2Cl_2) δ 148.46, 148.33, 148.28, 147.66, 137.62, 128.49, 127.81, 127.45, 124.94, 124.30, 108.92, 107.83, 107.75, 107.72, 70.92, 68.99 (2C), 68.94, 31.76 (3C), 29.39 (2C), 29.37, 25.92 (2C), 25.91, 22.76 (3C), 13.94 (3C). HRMS (ES^+) calcd. for $C_{35}H_{51}O_4$ $[M + H]^+$ 535.3787, found 535.3785 (error −0.4 ppm).

3,7-Bis(hexyloxy)naphthalene-2-ol (31)

A suspension of the mixture of regioisomers **28** and **29** (141.5 mg, 0.325 mmol), NH_4HCO_2 (1.00 g, 15.9 mmol) and Pd/C (10% w/w, 200.0 mg) in a mixture THF/MeOH (1 : 1 3.0 mL/3.0 mL) was refluxed for 3 h. The reaction was filtered over silica and Celite and washed with CH_2Cl_2. Purification by silica gel chromatography (PE to PE/CH_2Cl_2 9 : 1) afforded of **31** as a white solid (50.4 mg, 0.146 mmol, 45%) and an impure brownish oil (50.1 mg, 0.145 mmol, 44%) that corresponded to 3,6-bis(hexyloxy)naphthalene-2-ol. M.f.: $C_{22}H_{32}O_3$. MW: 344.50 g/mol. M.p.: 86 °C. IR (neat) ν_{max}: 3539, 2936, 2857, 2363, 1612, 1514, 1275, 1215, 1117, 1030, 869, 810, 621, 419 cm^{-1}. ^1H NMR (400 MHz, CD_2Cl_2) δ 7.56 (d, *J* = 8.8 Hz, 1 H), 7.12 (s, 1 H), 7.08 (s, 1 H), 6.99 (d, *J* = 2.4 Hz, 1 H), 6.96 (dd, *J* = 8.8, 2.5 Hz, 1 H), 6.02 (s, 1 H), 4.13 (t, *J* = 6.6 Hz, 2 H), 4.02 (t, *J* = 6.6 Hz, 2 H), 1.91 – 1.85 (m, 2 H), 1.84 – 1.78 (m, 2 H), 1.57 – 1.46 (m, 4 H), 1.41 – 1.32 (m, 8 H), 0.94 – 0.91 (m, 6 H). 13C NMR (100 MHz, CD_2Cl_2) δ 156.78, 146.94, 145.57, 131.12, 128.32, 124.44, 116.79, 108.69, 107.14, 106.38, 69.53, 68.54, 32.21, 32.14, 29.85, 29.63, 26.34, 26.28, 23.21, 23.18, 14.40, 14.38. HRMS (ES^+) calcd. for $C_{22}H_{33}O_3$ $[M + H]^+$ 345.2430, found 345.2433 (error 0.9 ppm).

3,3′,6,6′-Tetrakis(hexyloxy)-[1,1′-binaphthalene]-2,2′-diol (32)

A solution of 3,7-*bis*(hexyloxy)naphthalene-2-ol **31** (42.0 mg, 0.122 mol) and Cu-TMEDA (1.2 mg, 2.6 µmol) in CH_2Cl_2 (15 mL) was stirred at r.t. for 3 h under open air conditions. The reaction was filtered through a pad of silica and volatiles were removed in vacuo. Purification by silica gel chromatography (PE/CH_2Cl_2 1 : 1) afforded **32** as a yellowish oil (32.5 mg, 0.047 mol, 77%). M.f.: $C_{44}H_{62}O_6$. MW: 686.97 g/mol. M.p.: 92 °C. IR (neat) ν_{max}: 2926, 2361, 1611, 1508, 1456, 1275, 1260, 1211, 1115, 895, 843, 621, 459 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$) δ 7.66 (d, *J* = 8.8 Hz, 2 H), 7.22 (s, 2 H), 7.00 (dd, *J* = 8.8, 2.5 Hz, 2 H), 6.53 (d, *J* = 2.5 Hz, 2 H), 5.99 (s, 2 H), 4.29 – 4.16 (m, 4 H), 3.78 – 3.63 (m, 4 H), 1.96 – 1.87 (m, 4 H), 1.65 – 1.48 (m, 8 H), 1.45 – 1.14 (m, 20H), 0.95 – 0.84 (m, 12 H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 156.38, 144.96, 144.30, 130.15, 128.30, 124.17, 115.86, 113.93, 107.13, 105.81, 69.05, 67.91, 31.71, 31.68, 29.28, 29.18, 25.89, 25.79, 22.72, 22.68, 14.13. HRMS (ES^+) calcd. for $C_{44}H_{63}O_6$ $[M + H]^+$ 687.4625, found 687.4643 (error 2.6 ppm).

2,5,8,11-Tetrakis(hexyloxy)xantheno[2,1,9,8-*klmna*]xanthene (5)

A solution of 3,3′,6,6′-tetrakis(hexyloxy)-[1,1′-binaphthalene]-2,2′-diol **32** (25.0 mg, 36.4 µmol) and Cu-TMEDA (8.32 mg, 17.9 µmol) in m-xylene (1.4 mL) was degassed and then stirred at 140 °C for 1 h under N_2. The solution was quenched by filtration over a pad of silica and washed with CH_2Cl_2. Purification by silica gel chromatography (PE/CH_2Cl_2 1 : 1 to 3 : 7) afforded **5** as a yellow solid (14.0 mg, 20.5 µmol, 56%). M.f.: $C_{44}H_{58}O_6$. MW: 682.94 g/mol. M.p.: 167 °C. IR (neat) ν_{max}: 2927, 2361, 1321, 1217, 1161, 1096, 409 cm^{-1}. ^1H NMR (500 MHz, THF-d_8) δ 6.92 (d, J = 8.9 Hz, 4 H), 6.75 (s, 2 H), 4.11 (t, J = 4.04 Hz, 4 H), 4.04 (t, J = 4.04 Hz, 4 H), 1.88 – 1.82 (m, 4 H), 1.80 – 1.75 (m, 4 H), 1.59 – 1.51 (m, 8 H), 1.41 – 1.36 (m, 16 H), 0.95 – 0.92 (m, 12 H). ^{13}C NMR (126 MHz, THF-d_8) δ 148.24, 141.96, 141.42, 137.35, 128.57, 121.86, 119.92, 118.31, 112.42, 107.10, 72.06, 69.64, 32.92, 32.84, 31.12, 30.42, 26.90, 26.88, 23.77, 23.76, 14.64 (2C) (1 aliphatic carbon signal missing probably due to overlap). HRMS (AP+) calcd. for $C_{44}H_{59}O_6$ $[M + H]^+$ 683.4312, found 683.4310 (error −0.3 ppm).

3,6,7-Tris(hexyloxy)naphthalene-2-ol (33)

A suspension of 2-(benzyloxy)-3,6,7-tris(hexyloxy)naphthalene **30** (206.0 mg, 0.385 mmol), NH_4HCO_2 (639.0 mg, 10.1 mmol), and Pd/C (10% w/w, 220.0 mg) in a mixture THF/MeOH (1 : 1 3.2 mL/3.2 mL) was refluxed for 3.5 h. The reaction was filtered over a pad of silica/Celite and washed with CH_2Cl_2. Purification by silica gel chromatography (PE to PE/CH_2Cl_2 2 : 1) afforded **33** as a white solid (159.2 mg, 0.358 mmol, 93%). M.f.: $C_{28}H_{44}O_4$. MW: 444.66 g/mol. M.p.: 82 °C. IR (neat) ν_{max}: 2922, 2855, 1616, 1508, 1431, 1396, 1329, 1251, 1180, 1070, 1049, 864, 750, 621, 472 cm^{-1}. ^1H NMR (400 MHz, CD_2Cl_2) δ 7.15 (s, 1 H), 7.07 (s, 1 H), 7.05 (s, 1 H), 7.02 (s, 1 H), 5.99 (s, 1 H), 4.13 – 4.07 (m, 6 H), 2.19 – 1.72 (m, 6 H), 1.56 – 1.49 (m, 6 H), 1.48 – 1.34 (m, 12 H), 1.18 – 0.84 (m, 9 H). ^{13}C NMR (100 MHz, CD_2Cl_2) δ 149.02, 148.63, 146.08, 145.15, 125.40, 124.78, 108.94, 108.59, 107.98, 106.51, 69.59, 69.54, 69.46, 32.34 (2C), 32.28, 29.96, 29.94, 29.78, 26.48 (2C), 26.41, 23.33 (2C), 23.29, 14.50 (3C) (9 aliphatic carbon signals missing, probably due to overlap). HRMS (ES^+) calcd. for $C_{28}H_{45}O_4$ $[M + H]^+$ 445.3318, found 445.3303 (error −3.4 ppm).

3,3′,6,6′,7,7′-Hexakis(hexyloxy)-[1,1′-binaphthalene]-2,2′-diol (34)

Procedure A: A solution of 3,6,7-tris(hexyloxy)naphthalene-2-ol **33** (41.9 mg, 94.2 µmol) and CuO (86 mg, 1.08 mmol) in $PhNO_2$ (2 mL) was refluxed for 1.5 h. The reaction was filtered through a pad of silica and Celite (CH_2Cl_2). Purification by silica gel chromatography (PE to PE/CH_2Cl_2 1 : 1) afforded **34** as a brownish oil (21.1 mg, 23.8 µmol, 50.5%).

Procedure B: A solution of 3,6,7-tris(hexyloxy)naphthalene-2-ol **33** (202.0 mg, 0.454 mol) and Cu-TMEDA (2.8 mg, 6.0 µmol) in CH_2Cl_2 (15 mL) was stirred at r.t. for 1 h under open air conditions. The reaction was filtered through a pad of silica and were volatiles removed in vacuo. Purification by silica gel chromatography (PE/CH_2Cl_2 1 : 1) afforded **34** as a yellowish oil (162.4 mg, 0.183 mol, 81%). M.f.: $C_{56}H_{86}O_8$. MW: 887.30 g/mol. M.p.: Oil. IR (neat) ν_{max}: 2924, 1611, 1504, 1464, 1423, 1292, 1244, 1173, 926, 853, 662, 621,

415 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$) δ 7.14 (s, 2 H), 7.10 (s, 2 H), 6.50 (s, 2 H), 5.79 (s, 2 H), 4.26–4.14 (m, 4 H), 4.14–4.05 (m, J = 6.7 Hz, 4 H), 3.74–3.58 (m, 4 H), 1.95–1.82 (m, 8 H), 1.68–1.09 (m, 40H), 0.96–0.81 (m, 18 H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 148.36, 148.21, 145.38, 142.38, 124.35, 124.18, 114.27, 108.52, 107.18, 106.45, 69.14, 69.05, 68.99, 31.77, 31.72, 31.64, 29.34, 29.31, 28.97, 25.92, 25.90, 25.72, 22.77, 22.73, 22.70, 14.17, 14.15, 14.11. HRMS (ES^+) calcd. for $C_{56}H_{87}O_8$ $[M + H]^+$ 887.6401, found 887.6390 (error −1.2 ppm).

1,2,5,7,10,11-Hexakis(hexyloxy)xantheno[2,1,9,8-*klmna*]xanthene (6)

Procedure A: A degassed suspension of 3,6,7-tris(hexyloxy)naphthalene-2-ol **33** (20.0 mg, 45.0 µmol), K_2CO_3 (36.2 mg, 262 µmol), CuCl (10.7 mg, 108 µmol) and NMI (0.1 mL, 103 mg, 1.25 mmol) in PhMe (1.5 mL) was refluxed for 24 h under N_2. The reaction was diluted with CH_2Cl_2, filtered over a Celite/Silica pad and volatiles removed in vacuo. Purification by silica gel chromatography (PE to PE/CH_2Cl_2 1 : 1) afforded **6** as a yellow solid (4.4 mg, 5.0 mmol, 22%).

Procedure B: A solution of 3,3′,6,6′,7,7′-hexakis(hexyloxy)-[1,1′-naphthalene]-2,2′-diol **34** (14.6 mg, 16.5 µmol) and Cu-TMEDA (8.32 mg, 17.9 µmol) in m-xylene (1.4 mL) was degassed and then was refluxed for 1 h under N_2. Purification by silica gel chromatography (PE/CH_2Cl_2 1 : 1 to 3 : 7) of the crude reaction afforded **6** as a yellow solid (10.0 mg, 11.3 mmol, 69%).

M.f.: $C_{56}H_{82}O_8$. MW: 883.26 g/mol. M.p.: 162 °C. IR (neat) ν^{max}: 2954, 2923, 2855, 2354, 1638, 1680, 1715, 1642 1505, 1231 cm^{-1}. ^1H NMR (400 MHz, CD_2Cl_2) δ 6.66 (s, 2 H), 6.48 (s, 2 H), 4.07–3.98 (m, 12 H), 1.93–1.74 (m, 12 H), 1.59–1.44 (m, 12 H), 1.44–1.28 (m, 24 H), 0.98–0.85 (m, 18 H). ^{13}C NMR (500 MHz, $CDCl_3$) was not conclusive due to degradation of the material in solution. HRMS (ES^+) calcd. for $C_{56}H_{83}O_8$ $[M + H]^+$ 883.6088, found 883.6086 (error −0.2 ppm).

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Supporting Information

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Conflict of Interest

The authors declare no conflict of interest.

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