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Graphical Abstract

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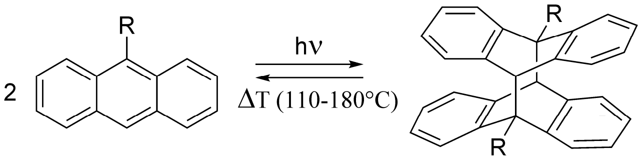

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Synthesis and evaluation of 9-substituted anthracenes with potential in reversible polymer systems

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ABSTRACT

A large series of functional 9-substituted anthracenes was synthesized and evaluated for the ability to undergo [4+4]-cycloadditions, forming dimers upon irradiation with UVA, and for their dimers to dissociate thermally. This scission of the dimers was shown to proceed in a clean and efficient way at temperatures between 90°C and 200°C. It was shown that the dissociation temperature is significantly influenced by the substituent. The Arrhenius parameters of the scission reactions were determined by fluorescence spectroscopy and correlated to the type of substituent. The absorption and emission maxima of the prepared monomeric anthracenes red-shift with increasing electron-donating power of the 9-substituent. Those results will be applied in a forthcoming study addressing tailor-made reversible polymer systems.

1. Introduction

The dimerization of anthracene under the influence of near-UV radiation (UVA) was first reported by Fritzsche in 1867 when he exposed an anthracene solution to direct sunlight (Figure 1).[1] A crystalline product with very low solubility was formed, which upon heating formed the starting product anthracene. This insoluble substance was identified as the dimer of anthracene[2] and as both [4+4]-cycloaddition and cycloreversion are only photochemically allowed,[3] the thermal scission must follow a radical mechanism.

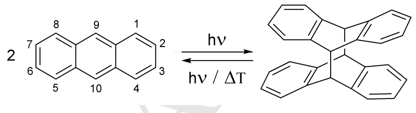

Figure 1. Reversible dimerization of anthracene.

Thus far, many anthracene derivatives have been shown to share the dimer forming properties with their parent compound anthracene,[4] provided that there is no significant steric hindrance that could interfere with the formation of a dimer, such as bulky substituents on the 9- and 10-position of the central ring. For example, introduction of two phenyl moieties on both the 9- and 10-position of anthracene leads to a complete loss of the dimerization ability.[5] However, this substitution pattern also blocks non-radiative decay of the excited state of anthracene, leading to very efficient fluorescence and to fluorescence quantum yields approximating unity.[6] Throughout the years, anthracene and other reversible [4+4]-cycloaddition systems have been studied extensively and several good reviews are available.[7]

The dimerization of anthracene has been used for (reversible) polymerization[8] and reversible crosslinking in various fields ranging from self-healing polymer materials[9] to surface patterning[10] and controlled drug release.[11] The dimerizable anthracene moieties provide control over polymerization or crosslinking degree by the application of UV-light to form dimers, while heat or UVC are applied to breakup dimers into the original anthracene derivatives.

In order to quantify and predict the behavior of anthracene derivatives and their corresponding dimer species with regard to UV-exposure and thermal stability, both as bare building blocks and in crosslinked networks, quantitative data regarding the scission of anthracene dimers is required. Unfortunately such data are currently only available for a small selection of anthracene derivatives.[12] Moreover, thermodynamic data are mostly limited to the dimer dissociation enthalpy of a few non-functional 9-substituted anthracene dimers that cannot be used for the synthesis of linear or crosslinked polymer systems.[13]

In this paper, the synthesis of a series of anthracene derivatives and their corresponding dimers, substituted at the 9-position with moieties having a different degree of

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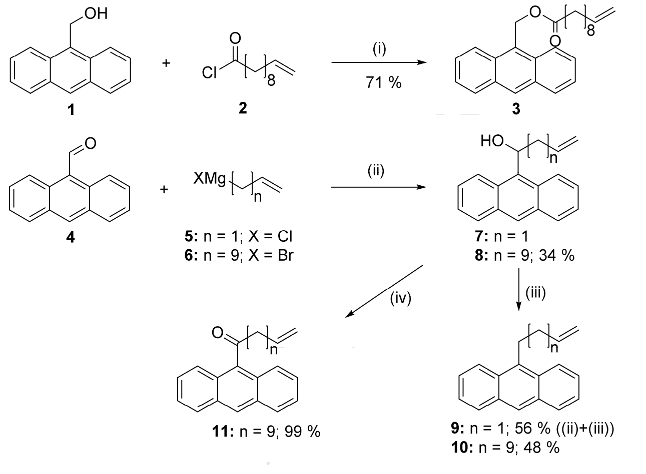
electronegativity, is described with the aim to understand the relationship between the (photo)chemical properties of these structures and their chemical structure. Each derivative is subsequently spectroscopically characterized with regard to absorption and fluorescence emission in chloroform, acetonitrile and ethanol. The kinetic parameters determining the thermal reversion are then obtained in order to be able to predict the behavior of the prepared derivatives for their potential application in functional crosslinked polymer materials.

2. Results and discussion

2.1. Synthesis of anthracene derivatives

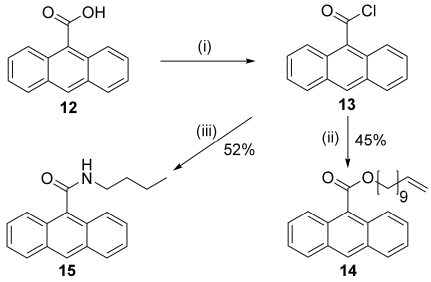
As explained in the introductory section, the aim of this study is to create a toolbox of well-characterized functional anthracene derivatives that can be used in a forthcoming study to construct polymer materials with reversible crosslinks. For this reason, synthetic efforts and commercial accessibility played a major role in the selection of the type of anthracene derivative. Since the 9-position is the most reactive position towards electrophilic aromatic substitution,[14] the synthesis of 9-substituted anthracene compounds is typically more upscalable than for other substituted anthracenes, making material applications more viable. Examples of available low-cost anthracene derivatives and precursors include anthracene methanol **1**, anthrylcarboxylic acid **12**, 9-anthraldehyde **4**, which can be prepared using the Vilsmeier reaction[15] and anthrone, which can be prepared by partial reduction of anthraquinone.[16]

The first series, consisting of '9-CH_2' anthracene derivatives, i.e. compounds with a methylene unit attached to the anthracene structure, was synthesized either by esterification of anthracene methanol **1** with freshly distilled undecenoyl chloride **2** in pyridine to form ester **3** or by a Grignard reaction of 9-anthraldehyde **4** with allylmagnesium chloride **5** or undecen-10-en-1-ylmagnesium bromide **6**, followed by reduction of the formed benzylic alcohol with triethyl silane and trifluoroacetic acid (Scheme 1) with formation of **9** and **10**, respectively.



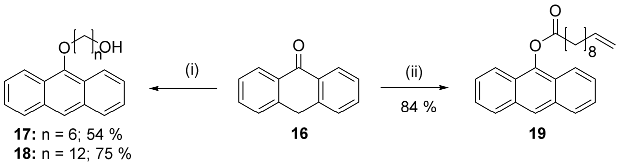
Scheme 1. (i) C_5H_5N, 5 min, 0 °C; overnight, rt, (ii) (1) THF, 5 min, 0 °C; 1 h, rt, (2) NH_4Cl, (iii) CH_2Cl_2, Et_3SiH, CF_3COOH, overnight, rt, (iv) (1) CH_2Cl_2, $C_2O_2Cl_2$, DMSO, 30 min, -78 °C, (2) Et_3N

In a second series, consisting of electron-poor 9-carbonyl anthracene derivatives, an aromatic ketone **11** was synthesized in high yield (99%) by Swern oxidation of the intermediate **8** produced by the Grignard reaction of anthraldehyde **4** with undecen-10-en-1-ylmagnesium bromide **6** (Scheme 1). Starting from 9-anthrylcarboxylic acid, aromatic amides and esters could be synthesized. First, 9-anthrylcarboxylic acid **12** was converted to the corresponding acid chloride **13** by reaction with thionylchloride as previously reported.[17] Reaction of **13** with 10-undecen-1-ol yielded the aromatic ester **14** with end-standing double bond (Scheme 2). Bases such as triethylamine or pyridine could not be used, since steric hindrance of the carbonyl position by the anthracene moiety leads to the formation of stable quaternary acylammonium salts that are hardly reactive towards alcohols, severely lowering the yield when tertiary amines are added.[18] Similarly, the non-functional aromatic amide **15** was synthesized by adding two equivalents of butylamine to **13** in dichloromethane.



Scheme 2. (i) $SOCl_2$, 2 h, reflux, (ii) 10-undecen-1-ol, CH_2Cl_2, overnight, rt, (iii) n-butyl amine, CH_2Cl_2, overnight, rt.

A third type of derivative, consisting of anthracenes with an oxygen at the 9-position, was synthesized starting from anthrone **16**. 9-Alkoxyanthracenes were synthesized by acid catalyzed etherification of alcohols with **16** as described in literature (Scheme 3).[19] By using an excess of either 1,6-hexanediol or 1,12-dodecanediol, a functionalized anthracene derivative with either a short **17** or a long spacer **18** was synthesized. Upon dimerization of **17** or **18**, diols are created that can be used as such as building blocks in polyurethanes. Alternatively, 9-alkoxyanthracenes such as **17** can be synthesized via base mediated proton abstraction at the methylene bridge, followed by alkylation of the formed anion with alkyl halides.[20] By adding undecenoyl chloride instead of alkyl halides to anthrone **16**, after addition of a (strong) base and allowing enol rearrangement, ester **19** was synthesized in good yield (84%).

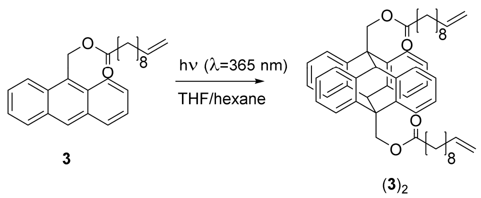


Scheme 3. (i) C_7H_8, diol, H_2SO_4 (cat.), overnight, reflux, (ii) (1) Et_3N, 1 h, reflux, (2) 10-undecenoyl chloride **2**, 2 h, reflux.

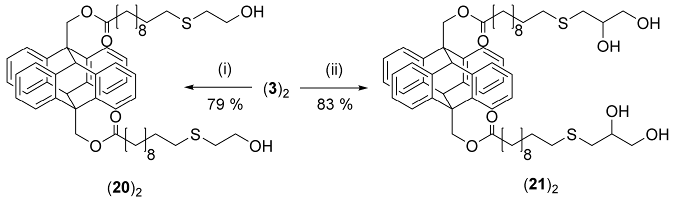
2.2. Functional group modification

In order to implement the synthesized anthracene derivatives as building blocks for stepgrowth polymers (e.g. polyurethane synthesis), alcohol groups are desired. Terminal double bonds, present in many derivatives, can be hydrothiolated with alcohol-containing thiols to form monofunctional or multifunctional alcohols. However, as thiols can also undesirably react with the central anthracene ring,[21] derivatives were first dimerized under UVA irradiation prior to reaction. Derivative **3** was dissolved in THF/hexane and irradiated (using mercury lamps with primary emission at 365 nm) to form dimer $(\mathbf{3})_2$, which precipitated during reaction (Scheme 4). After recrystallization in hexane, $(\mathbf{3})_2$ was dissolved in THF and radically reacted with 2-

mercaptoethanol or thioglycerol using DMPA as a photoinitiator to form diol $(\mathbf{20})_2$ and tetraol $(\mathbf{21})_2$, respectively (Scheme 5).



Scheme 4. Dimerization of **3**.



Scheme 5. (i) 2-mercaptoethanol, THF, DMPA, 1 h, rt, hν, (ii) 1-thioglycerol, THF, DMPA, 1 h, rt, hν.

2.3. UV-vis absorption and fluorescence behavior

The UV-vis and fluorescence properties of anthracenes may vary depending on the surrounding solvent or (polymer) matrix. Therefore, the absorption wavelengths, λ_{max}, and Stokes shifts of the anthracene derivatives were determined in three different solvents, respectively chloroform (aprotic), acetonitrile (aprotic) and ethanol (protic), as shown in Table 1 and Table S1 (Supporting Information). In general, the λ_{max} of the anthracene chromophore (e.g. at 359 nm in chloroform) shifts to higher wavelengths (e.g. 365 to 372 nm in chloroform) by the presence of a substituent, which lowers the HOMO—LUMO gap. This shift of λ_{max} increases as the electron donating power of the substituent increases. The highest shift is therefore found for the strongest electron donating substituents such as the 9-alkoxyethers **17** and **18**.[22]

The absorption red-shift encountered for 9-carbonyl anthracenes such as ester **14**, amide **15** and ketone **11** is not due to intramolecular charge displacement stabilization by an electron withdrawing carbonyl (mesomeric effect), as steric hindrance inhibits the carbonyl to be in plane with the anthracene ring.[23] Instead, the absorption shift should only be ascribed to the inductive effect of the substituents, lowering the energy gap.

Absorption spectra in acetonitrile and ethanol had lower wavelength maxima (2 to 3 nm difference) compared to chloroform (Table 1). This change in absorption wavelength is attributed to a different stabilization of the excited and ground state by the solvents.

The relative order in energy gap size is confirmed by DFT calculations (basis set 6.311G*) on several anthracenes (Table 2). In order to limit the amount of conformers, the alkyl chain length was shortened for calculation. This is done by assuming that the influence of the chain length on the anthracene rings is negligible. This assumption is supported by the observation that variation in the absorption wavelengths of similar anthracenes is within the range of experimental uncertainty.

Molar attenuation coefficients (ε) in chloroform at λ_{max} vary between ~6.85 x 10^3 (**18** and **19**) and 10.3 x 10^3 L mol^{-1} cm^{-1} (**3**), while that for unsubstituted anthracene was 8.3 x 10^3 L mol^{-1} cm^{-1}. In acetonitrile, the molar attenuation coefficients varied between 2.95 x 10^3 (**8**) and 12 x 10^3 L mol^{-1} cm^{-1} (**9**). Both absorption wavelength maxima and molar attenuation are important factors in polymer applications when considering the penetration depth of light upon irradiation and the choice of the UV source.

The absorption spectra of several anthracene dimers were also measured (Figure S2, Supporting Information). Compared to the reported UV-absorption spectrum of the virtually insoluble unsubstituted dianthracene,[3] no significant absorption wavelength shifts were found. This may be due to the inability of resonance, rendering the aromatic systems less electron rich.

Aside from dimerizing (in concentrated solution) upon irradiation, excited anthracene molecules are also known to decay via fluorescence. As is shown in Table 1 (and Table S1, Supporting Information), the formed derivatives have medium (0.49) to low (0.01) fluorescence quantum yield Φ_f in dilute solutions of chloroform, acetonitrile or ethanol. The very low values of 0.01-0.03 are found for the aromatic ketone **11**. This lack of fluorescence at room temperature for 9-anthryl alkyl ketones has been previously observed by Lai and Lim[24] and Hirayama[25], and has been ascribed to a very efficient non-radiative decay. The highest fluorescence quantum yield is found for aromatic ester **14**, having a similar quantity of radiative and non-radiative decay. Additionally, **14** has exceptional high Stokes shifts (97- 106 nm) in comparison to the other derivatives (44-52 nm), along with high broadening of the vibrational bands, leading to a diffuse emission. Werner and Hercules[26] ascribed this effect for 9-anthroic esters (and 9-anthrylcarboxylic acid **12**) to rotation of the carbonyl to a coplanar excited-state configuration with intramolecular hydrogen bonding. Ghoneim et al.[27] contradict this conclusion and ascribed this effect to twisted intramolecular charge transfer.

2.4. Dimerization

The kinetics of dimerization (Figure 2) were tested by irradiation of solutions of 10 mM anthracene monomer in hexane under inert atmosphere. The samples were irradiated with twelve 9 W standard UVA-lamps with an emission maximum at 365 nm and were analyzed using ^{1}H-NMR.

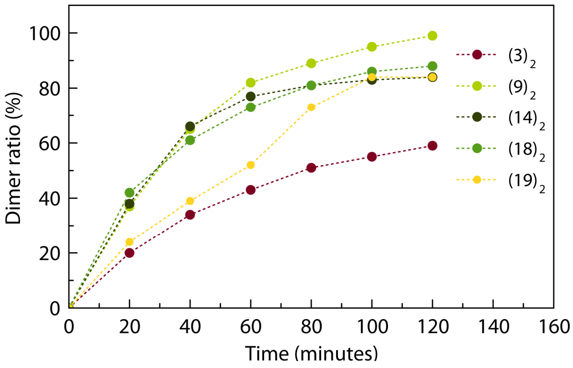


Figure 2. Dimerization of anthracenes (10 mM in hexane).

Amide **15** did not properly dissolve in hexane and could therefore not be tested. Upon irradiation, the aromatic ketone **11** formed more byproducts than dimers. This formation of side products limits the reversibility of dimerization, and therefore anthryl ketones are not deemed useful for the envisioned applications.

Table 1. Spectroscopic data of anthracene derivatives (ordered from low to high λ_{max}) in chloroform and acetonitrile.

	Chloroform					Acetonitrile				
Derivative	λ_{max} (nm)	ε_{max} (10^3 M^{-1} cm^{-1})	Φ_f	Stokes shift[a] (nm)	Stokes shift[a] (10^3 cm^{-1})	λ_{max} (nm)	ε_{max} (10^3 M^{-1} cm^{-1})	Φ_f	Stokes shift[a] (nm)	Stokes shift[a] (10^3 cm^{-1})
Anthracene	359	8.31	0.11	45	3.1	357	8.17	0.19	44	3.1
14	365	7.09	0.49	97	5.8	363	8.2	0.36	100	5.9
15	365	7.10	0.13	52	3.4	362	7.2	0.12	45	3.0
11	366	7.00	0.02	51	3.4	364	5.61	0.01	44	3.0
19	367	6.86	0.21	45	3.0	364	10.6	0.20	46	3.1
3	368	10.3	0.27	48	3.1	365	8.91	0.24	46	3.1
8	369	7.21	0.25	49	3.2	366	2.95	0.15	49	3.2
9	370	8.72	0.39	48	3.1	368	12	0.40	46	3.0
10	371	7.36	0.40	47	3.0	368	7.97	0.40	46	3.0
17	372	7.08	0.33	51	3.2	369	6.68	0.17	51	3.3
18	372	6.85	0.39	52	3.3	369	8.34	0.15	52	3.3

[a] The Stokes shift is taken as the difference of wavelength or wavenumber between the absorption and fluorescence maxima.

As can be seen in Figure 2, 59 to 99% dimerization was acquired after 2 hours of UVA irradiation (~5 mW cm^{-2}). These dimerization rates are in the same order of those previously reported in literature for anthracenes in solution[3] or in polymers having high chain mobility.[4c, 9-11]

As expected, the dimerization rate can be increased by using higher concentrations and light intensity. This is shown by the dimerization of **3** in the melt, using a photo-DSC equipment with a high intensity UV lamp having 12 W cm^{-2} intensity. After 25 minutes, 72% conversion was confirmed by ^{1}H-NMR (Figure S3, Supporting Information).

Table 2. HOMO, LUMO and energy gap E calculations.

	HOMO[a] (eV)	LUMO[a] (eV)	E_{calc}[b] (eV)	$E_{chloroform}$[c] (eV)	$E_{ethanol}$[c] (eV)
14	-5.73	-2.22	3.51	3.40	3.42
3	-5.61	-2.11	3.50	3.37	3.40
10	-5.35	-1.86	3.49	3.35	3.37
18	-5.34	-1.86	3.48	3.33	3.36

[a] HOMO and LUMO are calculated for the derivatives having shorter chain lengths (3 to 5 carbons), using 6.311G* as a basis set.

[b] Calculated as E = LUMO – HOMO.

[c] Calculated as E = hc / λ_{max}.

2.5. Thermal dissociation of dianthracene derivatives

The dissociation of dianthracene to anthracene can occur either photochemically by using UVC or thermally by heating.[28] Photochemical dissociation may give rise to an equilibrium between anthracene and dianthracene, as anthracene also absorbs UVC wavelengths. Additionally, UV irradiation may cause side reactions, limiting the use of this reversible system when many cycles are desirable. The thermal dissociation, however, does not result in an equilibrium between anthracene and its dimer and occurs in a clean and complete way.

The purified anthracene dimers were heated at a constant rate (10 K/min) and kept isothermal at different temperatures for 10 minutes under inert atmosphere in a thermogravimetrical analysis (TGA) equipment. Afterwards, the ^{1}H-NMR spectra of the samples were measured if no mass loss was observed, ensuring quantitative analysis (Supporting Information, Figure S4). Dissociation occurred without any side reactions for most derivatives.

As observed in Figure 3, the thermal dissociation of the derivatives greatly depends on the substituent and can thus happen over a broad temperature window (from around 110 to 180°C). The thermal dissociation results for the dimers $(\mathbf{3})_2$ and $(\mathbf{20})_2$ are very similar, which indicates that the further extension of the chain length and change of the end functionality does not influence the thermal dimer dissociation in a significant way. However, the thermal dissociation of the short dimer $(\mathbf{9})_2$ greatly differs from that of the longer $(\mathbf{10})_2$. Indeed, dimer $(\mathbf{10})_2$ shows a gradual dissociation occurring over a large temperature range (110 – 160 °C), while $(\mathbf{9})_2$ remains stable up to 150 °C and is completely dissociated after 10 minutes at 180 °C. It should also be noted that $(\mathbf{9})_2$, unlike $(\mathbf{10})_2$, becomes liquid around 182 °C and differential scanning calorimetry shows an endothermic peak at 193 °C immediately followed by an exothermic signal due to scission of the dimer. Either some dissociation occurred first, forming liquid monomer which dissolves the remaining dimer, or true melting occurs followed by fast dissociation as a result of better thermal contact or lower stability as a liquid. This is in contrast with $(\mathbf{10})_2$, which is liquid at 115 °C, before a significant amount of dissociation occurs.

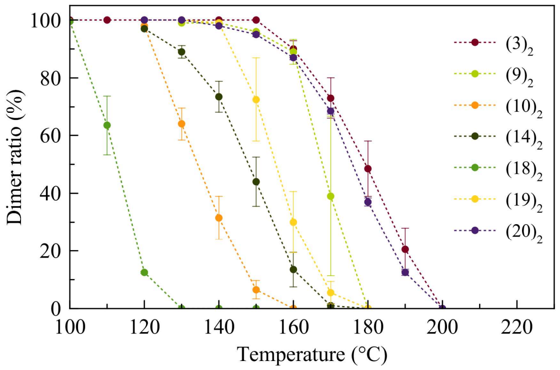


Figure 3. Thermal dissociation of anthracene dimers in bulk after 10 minutes, measured by ^{1}H-NMR.

To eliminate the possibly stabilizing effect of crystallinity, the thermal dissociation was also studied in a high boiling solvent solution (tributyrin). The anthracenes generated upon scission were detected by fluorescence spectroscopy of the diluted samples in dichloromethane. As an overnight reaction leads to full scission at the measured temperatures, conversions were normalized to the last (overnight) sample. The rate constants (k) of **(3)**$_2$, **(9)**$_2$, **(10)**$_2$, **(14)**$_2$, **(18)**$_2$ and **(19)**$_2$ were calculated from the slopes of ln(D_0/D) versus time, in which D is the calculated and D_0 is the original dimer concentration. The ln k values at different temperatures are depicted in the Arrhenius plot in Figure 4. The reaction rates found for **(9)**$_2$ and **(10)**$_2$ were identical, confirming that their difference in bulk thermal stability can be ascribed to **(9)**$_2$ being crystalline and **(10)**$_2$ being liquid upon scission.

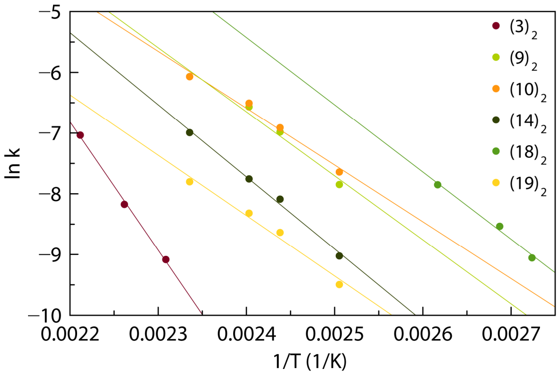


Figure 4. Arrhenius plot for the thermal dissociation of **(3)**$_2$, **(9)**$_2$, **(10)**$_2$, **(14)**$_2$, **(18)**$_2$ and **(19)**$_2$ in tributyrin.

From the slopes in the Arrhenius plot (Figure 4), the activation energies E_a for thermal dissociation were calculated, along with the corresponding pre-exponential factor A (Table 3). Activation energies ranged between ~78 and 176 kJ/mol. However, the variation in lnA is very high (15.5 to 39.7), which we assumed would be similar for all derivatives as A depends on the frequency of collision and the proper orientation of the molecules upon collision. Therefore, and as the uncertainties on the measurements are relatively high, the activation energies should be interpreted with care.

Table 3. Activation energies E_a and lnA-values of thermal scission of anthracene dimers.

	9-substituent	E_a (kJ/mol)	lnA
(3)$_2$	-CH_2OCOR	176±8	39.7±2.2
(9)$_2$	-CH_2R	87.7±9.0	18.7±2.6
(10)$_2$	-CH_2R	77.8±7.6	15.9±2.2
(14)$_2$	-COOR	98.7±5.1	20.8±1.5
(18)$_2$	-OCH_2R	92.0±9.5	21.1±3.1
(19)$_2$	-OCOR	82.6±8.3	15.5±2.4

Using the Arrhenius parameters E_a and A from the thermal scission in solution, the results from the bulk scission were simulated and are shown in Figure 5. The calculated theoretical bulk conversions showed good similarity to the actual experimental bulk dissociation. The only exception is for **(9)**$_2$, which is the only derivate having its melting point above the dissociation temperature (as determined using DSC, Figures S5 to S10, Supporting Information). It can therefore be assumed that the thermal dissociation of anthracenes is not influenced by concentration, as long as there is no crystallization occurring.

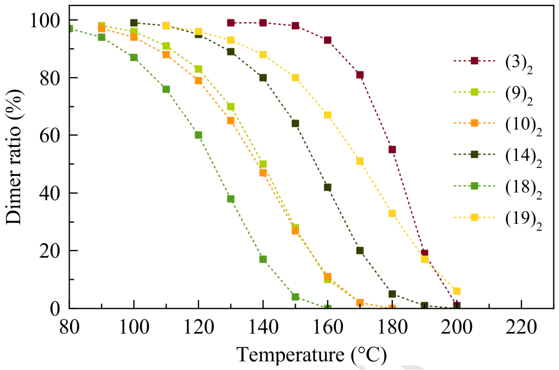


Figure 5. Bulk thermal dissociation simulation with calculated ratios using the experimentally determined Arrhenius parameters.

3. Conclusion

A range of novel 9-substituted functional anthracene compounds, with direct applications in polymer science as reversible bonds or crosslinks, was successfully synthesized in several reaction steps from inexpensive, readily available precursors. Synthesis of derivatives with different substituents (methylene, ether, carbonyl, ester, amide) at the 9-position resulted in a variation in absorption and thus dimerization wavelengths. The (modest) increase in λ_{max} after substitution ranged from 6 to 13 nm. Additionally, the absorption wavelength varies several nanometers when changing the polarity of the surrounding media. While the influence of the type of substituent on the dimerization kinetics is modest, the thermal dissociation rates of the dimers in bulk and solution changed significantly. By different substitution at the 9-position only, thermal dissociation temperatures could be varied up to 70°C. This difference in thermal stability of anthracene dimers enables the development of polymer materials having reversible bonds, which are formed by UVA irradiation, and break at a tunable temperature. This research will be presented in a forthcoming paper.

4. Experimental section

4.1. Materials and instruments

All chemicals were purchased from either Sigma-Aldrich, TCI Europe or Acros Organics and were used as such. IR spectra were recorded with a Perkin Elmer FTIR SPECTRUM 1000 and a PIKE Miracle ATR unit. NMR spectra were recorded with a Bruker AVANCE 300 (300 MHz), Bruker Avance-III (400 MHz) or Bruker DRX500 (500 MHz) NMR spectrometers. LC-MS analyses were performed on an Agilent Technologies 1100 series LC/MSD system with a diode array detector (DAD) and single quad MS. Analytical reversed phase HPLC-analyses were performed with a Phenomenex Luna C18 (2) column (5 µm, 250 mm × 4.6 mm) and a solvent gradient (75 - 100% acetonitrile in H_2O in 15 minutes), the eluted compounds were analyzed via UV detection (214 nm). A Mettler-Toledo TGA/SDTA 851e under nitrogen atmosphere was used as an oven for the thermal dissociation of bulk dimers. The uncertainties on the results were calculated as the differences between both results divided by $2\sqrt{2}$.UV dimerization occurred under inert atmosphere in a Metalight Classic from Primotec, with 12 double 365 nm UV lamps of 9 W each (intensity measured in the middle ~ 5mW cm^{-2}). Higher intensity irradiation occurred in a TA Instruments Q9000 DSC apparatus, equipped with a PCA Novacure 2100 EXFO. The irradiation source was a 100W mercury lamp, and a 300-500 nm bandpass filter was used. UV-vis absorption was measured with a Specord 200 from AnalitykJena from 200 nm to

600 nm with a speed of 5 nm s^{-1}, a slit of 2 nm and $\Delta\lambda$= 0.1 nm. Melting points were determined using the IA9000 melting point apparatus from Electrothermal at a heating rate of 1 °C/min. Differential scanning calorimetry (DSC) was performed using a DSC1/700 Mettler-Toledo apparatus. The used heating rate was 10 K/min and all measurements were done under nitrogen flow. For fluorescence analysis, a Cary Eclipse Fluorescence Specrophotometer from Agilent with a Xenon flash lamp was used. Excitation occurred at the absorption peak maxima (in choroform and acetonitrile) or at 372 nm (in ethanol) and the fluorescence spectrum was measured between 380 nm and 600 nm with a 2.5 nm slit and a scan rate of 600 nm min^{-1}. The concentration of the samples were chosen to ensure a transmission of 95 to 99% at the emission wavelength. 9,10-Diphenylanthracene in ethanol (Φ_f = 0.95) was used as standard[29] in the quantum yield calculations using following equation,

$$\Phi = \Phi_R \frac{Int}{Int_R} \frac{1-10^{-A_R}}{1-10^{-A}} \frac{\eta^2}{\eta_R^2}$$

where "*Int*" is the integrated area under the fluorescence curve, A the absorption, η the refractive index of the medium and Φ the fluorescence quantum yield. Subscript "R" is used when referring to the standard. The uncertainties on the activation energies and pre-exponential factors were determined using Excel's LINEST function.

*4.2. Anthracen-9-ylmethyl-undec-10-enoate (**3**)*

A solution of 32.3 g 9-anthracene methanol (0.155 mmol, 1 eq) in dry pyridine (300 mL) under inert atmosphere was cooled in an ice bath, while adding 50 mL of distilled undecenoyl chloride (0.23 mmol, 1.5 eq). After a night of stirring at room temperature, the reaction mixture was washed with water (100 mL) and brine (100 mL). The combined aqueous phases were extracted with diethyl ether (3 x 50 mL). The combined organic phases were dried over magnesium sulfate and concentrated *in vacuo*. Chromatography over silica, eluting with a gradient from heptane to chloroform, resulted in anthracen-9-ylmethyl-undec-10-enoate **3** as a yellow solid (41.9 g, 71 %); Mp = 49-50.5 °C; R_f (25% $CHCl_3$/hexane) 0.42; ^{1}H-NMR (400 MHz, $CDCl_3$)**:** δ (ppm) = 1.15-1.40 (m, 10H, $CH_2C\underline{H}_2CH_2$), 1.62 (quin, *J*=7.2 Hz, 2H, $COCH_2C\underline{H}_2$), 2.02 (q, *J*=7.3 Hz, 2H, $C\underline{H}_2CHCH_2$), 2.34 (t, *J*=7.5 Hz, 2H, $COC\underline{H}_2CH_2$), 4.90-5.03 (m, 2H, $CH_2CHC\underline{H}_2$), 5.73-5.88 (m, 1H, $CH_2C\underline{H}CH_2$), 6.17 (s, 2H, $CC\underline{H}_2O$), 7.47-7.54 (m, 2H, $CH_2CCCHCH\underline{H}CH$), 7.56-7.61 (m, 2H, $CH_2CCCHCHC\underline{H}$), 8.05 (d, *J*=8.4 Hz, 2H, $CHCC\underline{H}CH$), 8.35 (dd, *J*=8.9 Hz, *J*=0.8 Hz, 2H, $CCC\underline{H}CH$), 8.52 (s, 1H, $CC\underline{H}C$); ^{13}C-NMR (100 MHz, $CDCl_3$): δ (ppm) = 25.0 (CH_2), 28.9 (CH_2), 29.0 (CH_2), 29.1 (CH_2), 29.2 (CH_2), 29.3 (CH_2), 33.8 (CH_2), 34.3 (CH_2), 58. 7 (CH_2), 114.1 (CH_2), 124.0 (CH), 125.1 (CH), 126.4 (C), 126.6 (CH), 129.1 (CH), 131.1 (C), 131.4 (C), 139.2 (CH), 174.2 (C); IR ν_{max} cm^{-1}: 2922, 2848, 1726, 1386, 1318, 1278, 1244, 1210, 1158, 1060; LC-MS (m/z) 191.1 $[C_{15}H_{11}]^+$; GC-MS (m/z) 191.1 $[C_{15}H_{11}]^+$, 374.2 $[M]^+$; HRMS (m/z for $[MH]^+$): calcd.: 375.232; found: 375.231; *only traces of the molecular ion were found in LC-MS and HRMS, probably due to very efficient fragmentation forming* $[C_{15}H_{11}]^+$. *In GC-MS both the molecular ion and fragment product were found. (Supporting Information, Figures S11 and S12)*

*4.3. 1-(Anthracene-9-yl)dodec-11-en-1-ol (**8**)*

In a 250 mL flask under inert atmosphere, bromine (3.3 mL, 0.064 mol, 0.6 eq) was added to magnesium flakes (5.4 g, 0.22 mol, 2 eq). The mixture was heated to reflux for 30 minutes, after which the flask was cooled in an ice bath. Dry diethyl ether (25 mL) was quickly added, followed by 11-bromo-undec-1-ene (25 mL, 0.11 mol, 1 eq). The reaction mixture was heated to reflux for one hour until the magnesium flakes had disappeared. To the grignard reagent (0.11 mol, 1.2 eq) a solution of anthraldehyde (19 g, 0.092 mol, 1 eq) in dry diethyl ether (50 mL) was added until the reaction stopped. The reaction mixture was washed with a saturated ammonium chloride solution (50 mL), after which it was extracted with ether. The collected organic phases were dried with sodium sulfate and concentrated *in vacuo*. Purification by chromatography over silica (eluent: chloroform) was required to obtain the pure 1-(anthracene-9-yl)dodec-11-en-1-ol **8** as a yellow oil (11.3 g, 31 mmol, 34%); R_f ($CHCl_3$) 0.5; ^{1}H-NMR (300 MHz, $CDCl_3$): δ (ppm) = 1.22-1.76 (m, 14H, $CH_2C\underline{H}_2CH_2$), 1.54-1.73 (m, 2H, $CH_2C\underline{H}_2CH_2$), 2.03 (q, *J*=7.3 Hz, 2H, $CH_2C\underline{H}_2CH$), 4.90-5.04 (m, 2H, $CHC\underline{H}_2$), 5.75-5.87 (m, 1H, $CH_2C\underline{H}CH_2$), 6.27 (dd, *J*=8.3 Hz, *J*=6.1 Hz, 1H, $CH_2C\underline{H}OH$), 7.43-7.52 (m, 4H, $CHC\underline{H}C\underline{H}CH$), 7.97-8.04 (m, 2H, $CC\underline{H}CH$), 8.38 (s, 1H, $CC\underline{H}C$), 8.53-8.83 (m, 2H, $CCC\underline{H}CH$); IR ν_{max} cm^{-1}: 2924, 2852, 1722, 1454, 1382, 1344, 1292, 1156, 1054; LC-MS (m/z) 343.2 $[M\text{-}OH]^+$; HRMS (m/z for $[M\text{-}OH]^+$): calcd.: 343.2426; found: 343.2427

*4.4. 9-(But-3-en-1-yl)anthracene (**9**)*

9-Anthraldehyde (10.8 g, 52.4 mmol, 1 eq) was dissolved in dry tetrahydrofuran (60 mL), put under inert atmosphere and cooled with an ice bath. Allylmagnesium chloride solution was slowly added (26.4 mL, 2 M in THF, 52.8 mmol, 1.01 eq). The reaction mixture stirred at room temperature for one hour. Ammonium chloride was added and the reaction mixture was dried using sodium sulfate. The crude 1-(anthracen-9-yl)but-3-en-1-ol **7** was obtained after concentration *in vacuo*.

The crude 1-(anthracen-9-yl)but-3-en-1-ol (13 g, 52 mmol, 1 eq), was dissolved in dichloromethane (60 mL). To the solution, triethylsilane (9.75 mL, 61 mmol, 1.15 eq) was added. The reaction mixture was cooled with an ice bath and trifluoroacetic acid (6.5 mL, 83 mmol, 1.6 eq) was added. The reaction mixture was stirred overnight at room temperature and concentrated *in vacuo*. The crude product was purified using chromatography over silica (gradient: heptane; heptane:chloroform 3:2) to give **9** as a yellow solid. Mp = 67-68 °C; R_f. ($CHCl_3$) 0.62; ^{1}H-NMR (500 MHz, $CDCl_3$): δ (ppm) = 2.55-2.61 (m, 2H, $CCH_2C\underline{H}_2CH$), 3.70-3.75 (m, 2H, $CC\underline{H}_2CH_2CH$), 5.10 (dd, *J*=10.1 Hz, *J*=1.6 Hz, 1H, $CH_2CHC\underline{H}_2$), 5.22 (dq, *J*= 17.1 Hz, *J*=1.7 Hz, 1H, $CH_2CHC\underline{H}_2$), 6.08 (ddt, *J*=17 Hz, *J*=10.3 Hz, *J*=6.6 Hz, 1H, $CH_2C\underline{H}CH_2$), 7.47-7.50 (m, 2H, $CH_2CCCHC\underline{H}$), 7.50-7.55 (m, 2H, $CH_2CCCHCHC\underline{H}$), 8.02 (d, *J*=8.2 Hz, 2H, $CHCC\underline{H}CH$), 8.27 (d, *J*=8.7 Hz, 2H, $CH_2CCC\underline{H}CH$), 8.36 (s, 1H, $CC\underline{H}C$);^{13}C-NMR (125 MHz, $CDCl_3$): δ (ppm) = 27.4 (CH_2), 35.1 (CH_2), 115.0 (CH_2), 124.4 (CH), 124.8 (CH), 125.5 (CH), 125.8 (CH), 129.2 (CH), 129. 6 (C), 131.7 (C), 134.2 (C), 138.3 (CH); IR ν_{max} cm^{-1}: 3054, 2896, 1622, 1436, 1350, 1318, 1242, 1154, 1006; GC-MS (m/z) 232 $[M]^+$

*4.5. 9-(Dodec-11-en-1-yl)anthracene (**10**)*

Crude **8** (9.24 g, 75% pure, 19.2 mmol, 1 eq) was dissolved in 30 mL dichloromethane. To the solution, triethylsilane (4.75 mL, 29.4 mmol, 1.5 eq) was added. The reaction mixture was cooled in an ice bath and trifluoroacetic acid (3.2 mL, 42 mmol, 2.2 eq) was slowly added. The reaction mixture was stirred overnight at room temperature and concentrated *in vacuo*. The crude product was purified using chromatography over silica (eluent dichloromethane:hexane). 4.64 g pure **10** was obtained as a yellow oil (53%). ^{1}H-NMR (500 MHz, $CDCl_3$): δ (ppm) = 1.27-1.47 (12H, $CH_2C\underline{H}_2CH_2$), 1.6 (quin, *J*=15.2 Hz, *J*=7.4 Hz, 2H, $CH_2C\underline{H}_2CH_2$), 1.83 (quin, *J*=15.8 Hz, *J*=7.9 Hz, 2H, $CCH_2C\underline{H}_2CH_2$), 2.06 (q, *J*=7.9 Hz, 2H, $CH_2C\underline{H}_2CH$), 3.61 (t,

J=8.2 Hz, 2H, $CC\underline{H}_2CH_2$), 4.95 (ddt, J=10.2 Hz, J=2.2 Hz, J=1.1 Hz, 1H, $CH_2CHC\underline{H}_2$), 5.02 (dq, J=17.1 Hz, J=1.8 Hz, 1H, $CH_2CHC\underline{H}_2$), 5.84 (ddt, J=17 Hz, J=10.2 Hz, J=6.7 Hz, 1H, $CH_2C\underline{H}CH_2$), 7.45-7.54 (m, 4H, $CCHC\underline{H}C\underline{H}CHC$), 8.02 (d, J=7.8 Hz, 2H, $CHCC\underline{H}CH$), 8.28 (d, J=8.9 Hz, 2H, $CH_2CCC\underline{H}CH$), 8.34 (s, 1H, $CC\underline{H}C$);^{13}C-NMR (125 MHz, $CDCl_3$): δ (ppm) = 28.1 (CH_2), 29.0 (CH_2), 29.2 (CH_2), 29.5 (CH_2), 29.6 (CH_2), 29. 7 (CH_2), 30.4 (CH_2), 31.4 (CH_2), 33.8 (CH_2), 114.1 (CH_2), 124.5 (CH), 124.8 (CH), 125.3 (CH), 125.5 (CH), 129.2 (CH), 129.5 (C), 131.7 (C), 135.5 (C), 139.3 (CH); IR ν_{max} cm^{-1}: 2920, 2850; GC-MS (m/z) 191 $[C_{15}H_{11}]^+$, 344 $[M]^+$

*4.6. 1-(Anthracen-9-yl)dodec-11-en-1-one (**11**)*

Oxalylchloride (0.30 mL, 3 mmol, 1.1 eq) in dry dichloromethane (5 mL) in a 50 mL flask, was cooled to -78°C, after which a solution of dimethylsulfoxide (0.50 mL, 6.1 mmol, 2.2 eq) in dry dichloromethane (5 mL) was added. After 2 minutes of stirring, a solution of 1-(anthracene-9-yl)dodec-11-en-1-ol **8** (1.0 g, 2.8 mmol, 1 eq) in dry dichloromethane (10 mL) was added dropwise over 5 minutes. The reaction mixture was stirred for 15 minutes, and an excess of triethyl amine (2 mL) was added. The mixture was stirred for another 5 minutes and was warmed up to room temperature. Water (50 mL) was added, and the mixture was extracted with dichloromethane (3 x 50 mL). The combined organic phases were washed respectively with brine (20 mL), water (20 mL), 5% bicarbonate solution (20 mL) and water (20 mL). The combined organic phases were dried on magnesium sulphate and concentrated *in vacuo* to a red oil (5.8 g, 2.8 mmol, >99%); ^{1}H-NMR (500 MHz, $CDCl_3$): δ (ppm) = 1.17-1.70 (m, 12H, $CH_2C\underline{H}_2CH_2$), 1.89 (quin, J=7.5 Hz, 2H, $C\underline{H}_2CH_2CO$), 2.04 (q, J=6.8 Hz, 2H, $C\underline{H}_2CHCH_2$), 3.07 (t, J=7.5 Hz, 2H, $C\underline{H}_2CO$), 4.92-4.96 (m, 1H, $CHC\underline{H}_2$), 4.97-5.04 (m, 1H, $CHC\underline{H}_2$), 5.82 (ddt, J=17 Hz, J=10.3 Hz, J=6.7 Hz, 1H, $C\underline{H}CH_2$), 7.47-7.54 (m, 4H, $CHC\underline{H}C\underline{H}CH$), 7.77-7.83 (m, 2H, $CHC\underline{H}C\underline{H}CH$), 8.02-8.06 (m, 2H, $CCC\underline{H}CH$), 8.49 (s, 1H, $CC\underline{H}C$); ^{13}C-NMR (125 MHz, $CDCl_3$): δ (ppm) = 23.9 (CH_2), 29.0 (CH_2), 29.1 (CH_2), 29.3 (CH_2), 29.5 (CH_2), 33.8 (CH_2), 46.5 (CH_2), 114.2 (CH_2), 124.4 (CH), 125.5, (CH), 126.7 (CH), 127.0 (C), 127.2 (CH), 128.1 (CH), 128.8 (CH), 131.1 (C), 134.1, (CH), 136.9 (C), 139.2 (CH), 210.6 (C); IR ν_{max} cm^{-1}: 2924, 2852, 1696, 1444, 1160;LC-MS (m/z) 359.2 $[MH]^+$; HRMS (m/z for $[MH]^+$): calcd.: 359.2371; found: 359.2363

*4.7. Undec-10-en-1-yl anthracene-9-carboxylate (**14**)*

9-Anthracenecarboxylic acid (1.50 g, 6.75 mmol, 1 eq) was dissolved in thionyl chloride (20 mL). A drop of dimethylformamide was added and the solution was heated to reflux for 2 hours according to literature.[17] The excess thionyl chloride was removed from **13** *in vacuo* after cooling to room temperature.

Dry dichloromethane (20 mL) and 10-undecen-1-ol (1.5 ml, 7.5 mmol, 1.1 eq) were added to **13** and the reaction mixture was stirred for 1 hour in an ice bath. The ice bath was then removed and the reaction mixture was stirred overnight at room temperature. Potassium carbonate (1.00 g, 17.5 mmol, 1.1 eq) was added and the reaction was stirred for another 3 hours. The solution was filtered over a silica plug and concentrated *in vacuo*. After column chromatography over silica (eluent: chloroform), the pure undec-10-en-1-yl anthracene-9-carboxylate **14** was acquired as a yellow oil (1.13 g, 3.02 mmol, 45 %); R_f ($CHCl_3$) 0.66; ^{1}H-NMR (500 MHz, $CDCl_3$): δ (ppm) = 1.24-1.44 (m, 10H, $CH_2C\underline{H}_2CH_2$), 1.50 (quin, J=7.8 Hz, 2H, $OCH_2CH_2C\underline{H}_2$), 1.89 (quin, J=7.5 Hz, 2H, $OCH_2C\underline{H}_2$), 2.04 (q, J=6.9 Hz, 2H, $C\underline{H}_2CHCH_2$), 4.63 (t, J=6.8 Hz, 2H, $OC\underline{H}_2CH_2$), 4.94 (dt, J=10.2 Hz, J=1 Hz, 1H, $CH_2CHC\underline{H}_2$), 5.00 (dq, J=17.1 Hz, J=1.7 Hz, 1H, $CH_2CHC\underline{H}_2$), 5.84 (ddt, J=17 Hz, J=10.3 Hz, J=6.7 Hz, 1H, $CH_2C\underline{H}CH_2$), 7.48-7.52 (m, 2H, $CHC\underline{H}CH$), 7.53-7.57 (m, 2H, $CHC\underline{H}CH$), 8.05 (t, J=9.9 Hz, 4H, $CCC\underline{H}CH$), 8.54 (s, 1H, $CC\underline{H}C$); ^{13}C-NMR (125 MHz, $CDCl_3$): δ (ppm) = 26.1 (CH_2), 28.8 (CH_2), 28.9 (CH_2), 29.1 (CH_2), 29.2 (CH_2), 29.4 (CH_2), 29.5 (CH_2), 33.8 (CH_2), 66.0 (CH_2), 114.2 (CH_2), 125.1 (CH), 125.5 (CH), 126.9 (CH), 128.2 (C), 128.4 (C), 128.6 (CH), 129.2 (CH), 131.0 (C), 139.3 (CH), 169.8 (C); IR ν_{max} cm^{-1}: 2922, 2850, 1718, 1446, 1288, 1200; LC-MS (m/z) 375.3 $[MH]^+$; HRMS (m/z for $[MH]^+$) calcd.: 375.2324; found: 375.2335

*4.8. N-Butylanthracene-9-carboxamide (**15**)*

9-Anthracenecarboxylic acid (1.50 g, 6.75 mmol, 1 eq) was dissolved in thionyl chloride (20 mL). A drop of dimethylformamide was added and the solution was heated to reflux for 2 hours according to literature.[17] The excess thionyl chloride was removed from **13** *in vacuo* after cooling to room temperature.

Dry dichloromethane (30 mL) and butyl amine (1.08 g, 14.9 mmol, 2.2 eq) are added to **7** and the reaction mixture was stirred for 1 hour in an ice bath. The reaction mixture was then stirred at room temperature for 3 days. The reaction mixture was concentrated *in vacuo*. The product was purified by chromatography over silica (eluent: chloroform with 1% methanol), giving product **15** (0.97 g, 3.5 mmol, 52%) as a white solid; Mp > 250°C *(solid became dark brown, signifying decomposition before melting)*; ^{1}H-NMR (500 MHz, $CDCl_3$): δ (ppm) = 1.03 (t, J=7.3 Hz, 3H, $C\underline{H}_3$), 1.51 (sxt, J=7.5, 2H, $C\underline{H}_2CH_3$), 1.74 (quin, J=7.5 Hz, 2H, $C\underline{H}_2CH_2CH_3$), 3.72 (td, J=7.2 Hz, J=6 Hz, 2H, $NHC\underline{H}_2$), 6.03 (1H, $CON\underline{H}CH_2$), 7.47-7.57 (m, 4H, $CCHC\underline{H}$), 8.02 (d, J=8.4 Hz, 2H, $CC\underline{H}CH$), 8.09 (d, J=8.2 Hz, 2H, $CC\underline{H}CH$), 8.49 (s, 1H, $CC\underline{H}C$); ^{13}C-NMR (125 MHz, $CDCl_3$): δ (ppm) = 13.8 (CH_3), 20.3 (CH_2), 31.8 (CH_2), 40.0 (CH_2), 125.1 (CH), 125.5 (CH), 126.7 (CH), 128.0 (C), 128.2 (CH), 128.5 (CH), 131.1 (C), 132.2 (C), 169.5 (C); IR ν_{max} cm^{-1}: 3212, 3044, 2954, 2930, 2872, 2368, 2160, 2024, 1978, 1612, 1568, 1470, 1376, 1292, 1254, 1226, 1156, 1080, 1012; LC-MS (m/z) 278.2 $[MH]^+$; HRMS (m/z for $[MH]^+$) calcd.: 278.1545; found: 278.1552

*4.9. 6-(Anthracen-9-yloxy) hexan-1-ol (**17**)*

In a 500 mL flask equipped with a Dean-Stark water separator, 10.0 g anthrone (51.5 mmol, 1 eq) was dissolved in 250 mL toluene. 1,6-hexanediol (60.3 g, 515 mmol, 10 eq) and 2 mL sulfuric acid (≥ 95 %) were added and the solution was heated to reflux. The reaction mixture was stirred overnight and the reaction was monitored by thin layer chromatography. After cooling, the precipitated excess 1,6-hexanediol was removed by filtration and the filtrate was washed with a saturated aqueous sodium bicarbonate solution (300 mL) and water (300 mL). The combined aqueous phases were extracted with diethyl ether, the combined organic phases were dried over magnesium sulfate and concentrated *in vacuo*. To obtain pure 6-(anthracen-9-yloxy) hexan-1-ol **17** (8.2 g, 54 %) as a yellow-orange oil, the dried mixture was purified via chromatography on silica (eluent: dichloromethane/hexane); R_f (CH_2Cl_2/hexane) 0.16; ^{1}H-NMR (400 MHz, $CDCl_3$): δ (ppm) = 1.50-1.60 (m, 2H, $CH_2C\underline{H}_2CH_2$), 1.65-1.77 (m, 4H, $CH_2C\underline{H}_2CH_2$), 2.08 (quin, J=7.5 Hz, 2H, $C\underline{H}_2CH_2O$), 3.65 (t, J=6.5 Hz, 2H, $C\underline{H}_2OH$), 4.14 (t, J=6.7 Hz, 2H, $AnthrOC\underline{H}_2$), 7.46-7.53 (m, 4H, $CHC\underline{H}C\underline{H}CH$), 7.98-8.02 (m, 2H, $CHCC\underline{H}CH$), 8.12 (s, 1H, $CC\underline{H}C$), 8.28-8.32 (m, 2H, $CCC\underline{H}CH$); ^{13}C-NMR (100 MHz, $CDCl_3$): δ (ppm) = 25.8 (CH_2), 26.1 (CH_2), 30.7 (CH_2), 32.8 (CH_2), 63.0 (CH_2), 76.0 (CH_2), 122.0 (CH), 122.4 (CH), 124.8 (C), 125.1 (CH), 125.5 (CH), 128.5 (CH), 132.5 (C), 151.5 (C); IR ν_{max} cm^{-1}: 3315, 2934, 2854, 1676, 1590, 1442, 1416, 1338, 1282, 1170, 1084, 1008; LC-MS (m/z): 295.1 [MH]$^+$; HRMS (m/z for [MH]$^+$): calcd.: 295.1693; found: 295.1691

*4.10. 12-(Anthracen-9-yloxy) dodecan-1-ol (**18**)*

In a 2 L flask equipped with a Dean-Stark water separator, 12.0 g anthrone (61.7 mmol, 1 eq) was dissolved in 1 L toluene. 1,12-dodecanediol (125 g, 617 mmol, 10 eq) and 2.5 mL sulfuric acid (≥ 95 %) were added and the solution was heated to reflux. The reaction mixture was stirred overnight and the reaction was monitored by thin layer chromatography. After cooling, the precipitated excess of 1,12-dodecanediol was removed by filtration and the filtrate was washed with a saturated aqueous sodium bicarbonate solution (300 mL) and water (300 mL). The combined aqueous phases were extracted with diethyl ether, the combined organic phases were dried over magnesium sulfate and concentrated *in vacuo*. To obtain purified 12-(anthracen-9-yloxy) dodecan-1-ol **18** (17.7 g, 75.3 %) as a yellow-orange oil, the dried mixture was purified via chromatography on silica (eluent: CH_2Cl_2); R_f (CH_2Cl_2) 0.13; ^{1}H-NMR (400 MHz, $CDCl_3$): δ (ppm) = 1.26-1.51 (m, 14H, $CH_2C\underline{H}_2CH_2$), 1.54-1.62 (m, 2H, $CH_2C\underline{H}_2CH_2$), 1.68 (quin, *J*=7.5 Hz, 2H, $CH_2C\underline{H}_2CH_2$), 2.07 (quin, *J*=7.4 Hz, 2H, $C\underline{H}_2CH_2OH$), 3.65 (t, *J*=6.7 Hz, 2H, $C\underline{H}_2OH$), 4.21 (t, J=6.7 Hz, 2H, AnthrO$C\underline{H}_2$), 7.45-7.52 (m, 4H, $CHC\underline{H}C\underline{H}CH$), 7.98-8.03 (m, 2H, $CHCC\underline{H}CH$), 8.22 (s, 1H, $CC\underline{H}C$), 8.29-8.34 (m, 2H, $CCC\underline{H}CH$); ^{13}C-NMR (100 MHz, $CDCl_3$): δ (ppm) = 25.8 (CH_2), 26.3 (CH_2), 29.5 (CH_2), 29.6 (CH_2), 29.7 (CH_2), 30.7 (CH_2), 32.8 (CH_2), 63.1 (CH_2), 76.2 (CH_2), 122.0 (CH), 122.5 (CH), 124.8 (C), 125.0 (CH), 125.5 (CH), 128.4 (CH), 132.5 (C), 151.6 (C); LC-MS (m/z) 379.20 [MH]$^+$; HRMS (m/z for [MH]$^+$) calcd.: 379.2633; found: 379.2633

*4.11. Anthracen-9-yl undec-10-enoate (**19**)*

1.0 g of anthrone (3.4 mmol, 1 eq) was dissolved in 20 mL toluene and 0.86 mL of triethyl amine (4.1 mmol, 1.2 eq). The solution was heated to reflux for one hour. After cooling to room temperature, 0.87 mL undecenoyl chloride was added (4.1 mmol, 1.2 eq) and the reaction was heated to reflux for two hours. The solvent was removed *in vacuo*, and the crude product was purified by column chromatography (eluent: $CHCl_3$/hexane) to a light yellow oil that crystalized to a white powder (1.32 g, 2.85 mmol, 84%). Mp = 58-60 °C; ^{1}H-NMR (500 MHz, $CDCl_3$): δ (ppm) = 1.24-1.49 (m, 10H, $CH_2C\underline{H}_2CH_2$), 1.59 (quin, *J*=7.4 Hz, 2H, $CH_2C\underline{H}_2CH_2$), 2.00 (quin, *J*=7.6 Hz, 2H, $COCH_2C\underline{H}_2$), 2.09 (q, *J*=7.2 Hz, 2H, $C\underline{H}_2CHCH_2$), 2.95 (t, *J*=7.6 Hz, 2H, $COC\underline{H}_2CH_2$), 4.96 (ddt, *J*=10.1 Hz, *J*=2.1 Hz, *J*=1.2 Hz, 1H, $CH_2CHC\underline{H}_2$), 5.03 (dq, *J*=17.1 Hz, *J*=1.8 Hz, 1H, $CH_2CHC\underline{H}_2$), 5.85 (ddt, *J*=17 Hz, *J*=10.3 Hz, *J*=6.7 Hz, 1H, $CH_2C\underline{H}CH_2$), 7.47-7.54 (m, 4H, $CCHC\underline{H}$) 7.94 (d, *J*=8.2 Hz, 2H, $CHCC\underline{H}CH$), 8.03 (d, *J*=8.1 Hz, 2H, $CCC\underline{H}CH$), 8.38 (s, 1H, $CC\underline{H}C$); ^{13}C-NMR (125 MHz, $CDCl_3$): δ (ppm) = 25.3 (CH_2), 28.9 (CH_2), 29.1 (CH_2), 29.3 (CH_2), 29.4 (CH_2), 29.4 (CH_2) 33.8 (CH_2), 34.3 (CH_2), 114.2 (CH_2), 121.4 (CH), 124.0 (C), 124.7 (CH), 125.6 (CH), 126.2 (CH), 128.5 (CH), 131.9 (C), 139.2 (CH), 142.1 (C), 172.4 (C); IR ν_{max} cm^{-1}: 3326, 2926, 2854, 1454, 1338, 1292, 1254, 1226, 1164, 1118, 1052; LC-MS (m/z) 378.3 [MNH_4]$^+$; HRMS (m/z for [MNH_4]$^+$): calcd.: 378.2433; found: 378.2428

*4.12. 5,12:6,11-Bis([1,2]benzeno)dibenzo[a,e][8]annulene-5,11(6H,12H)-diylbis(methylene) bis(11-((2-hydroxyethyl) thio) undecanoate) ((**20**)$_2$)*

A dimer of anthracen-9-ylmethyl undec-10-enoate (**3**)$_2$ (3.41 g, 4.5 mmol, 1 eq) was dissolved in a minimal amount of tetrahydrofuran (15 mL). 3.14 mL mercaptoethanol (45 mmol, 5 eq) and 229 mg DMPA (0.9 mmol, 0.1 eq) was added. The mixture was irradiated (*λ* = 365 nm) for 1 h under nitrogen gas atmosphere and the reaction was monitored with TLC. The reaction mixture was washed with water (10 mL), after which the aqueous phases were extracted with diethyl ether (3 x 10 mL). The combined organic phases were dried over magnesium sulfate and the filtrate was concentrated *in vacuo*. Recrystallization in THF/water was required to obtain (**20**)$_2$ as a white solid (3.2 g, 79 %); Mp = 121-125 °C; R_f ($CHCl_3$) 0.1; ^{1}H-NMR (400 MHz, $CDCl_3$): δ (ppm) = 1.13-1.62 (m, 28H, $CH_2C\underline{H}_2CH_2$), 1.71-2.04 (m, 4H, $CH_2C\underline{H}_2CH_2$), 2.13-2.26 (m, 3H, $COC\underline{H}_2CH_2$), 2.51 (t, *J*=7.3 Hz, 4H, $CH_2C\underline{H}_2S$), 2.73 (t, *J*=5.9 Hz, 4H, $SC\underline{H}_2CH_2OH$), 3.72 (t, *J*=5.9 Hz, 4H, $SCH_2C\underline{H}_2OH$), 3.71+4.4 (s, 2H, $CC\underline{H}C$), 5.12-5.28 (m, 4H, $CC\underline{H}_2O$), 6.81-7.14 (m, 16H, $CC\underline{H}C\underline{H}C\underline{H}C\underline{H}C$); ^{13}C-NMR (100 MHz, $CDCl_3$): δ (ppm) = 24.9 (CH_2), 25.1 (CH_2), 28.1 (CH_2), 29.0 (CH_2), 29.1 (CH_2), 29.3 (CH_2), 29.4 (CH_2), 29.7 (CH_2), 31.6 (CH_2), 34.2 (CH_2), 35.4 (CH_2), 55.1 (CH_2), 59.0 (CH), 60.2 (C), 63.5 (CH_2), 68.9 (CH_2), 124.7 (CH), 125.8 (CH), 127.7 (CH), 128.0 (CH), 142.1 (C), 174.5 (C); IR ν_{max} cm^{-1}: 3518, 2922, 2852, 2160, 2028, 1978, 1722, 1454, 1384, 1342, 1246, 1210, 1168, 1060, 1008; LC-MS (m/z) 887.4 [M-OH]$^+$, 922.4 [MNH_4]$^+$; HRMS (m/z for [M+OAc]$^-$) calcd.: 963.4903; found: 963.4907

*4.13. 5,12:6,11-Bis([1,2]benzeno)dibenzo[a,e][8]annulene-5,11 (6H,12H) - diylbis(methylene) bis(11-((2,3 -dihydroxypropyl) thio) undecanoate ((**21**)$_2$)*

A dimer of anthracen-9-ylmethyl undec-10-enoate (**3**)$_2$ (7.25 g, 9.5 mmol, 1 eq) was dissolved in a minimal amount of tetrahydrofuran (20 mL). 8.2 mL thioglycerol (95 mmol, 5 eq) and 487 mg DMPA (0.9 mmol, 0.1 eq) was added. The mixture was irradiated (*λ*=365 nm) for 1 h under nitrogen gas atmosphere and the reaction was monitored with TLC. The reaction mixture was washed with water (10 mL), after which the aqueous phase was extracted with diethyl ether (3 x 10 mL). The combined organic phases were dried over magnesium sulfate and the filtrate was concentrated *in vacuo*. Recrystallization in THF/water was required to obtain (**21**)$_2$ as a white solid (7.88 g, 83 %); Mp = 129.5 – 134.5 °C; R_f ($CHCl_3$) 0; ^{1}H-NMR (400 MHz, $CDCl_3$): δ (ppm) = 1.13-1.95 (m, 32H, $CH_2C\underline{H}_2CH_2$), 2.18 (m, 3H, $C\underline{H}_2CH_2CO$(*ht*)), 2.53-2.89 (m, 9H, $C\underline{H}_2SC\underline{H}_2$+$C\underline{H}_2CH_2CO$(*hh*)), 3.57-3.83 (m, 7.5H, $C\underline{H}C\underline{H}_2OH$+ $CC\underline{H}C$(*ht*)), 4.48 (s, 0.5H, $CC\underline{H}C$(*hh*)), 5.12-5.27 (m, 4H, $CC\underline{H}_2O$), 6.81-7.12 (m, 16H, $CC\underline{H}C\underline{H}C\underline{H}C\underline{H}C$); ^{13}C-NMR (100 MHz, $CDCl_3$): δ (ppm) = 24.9 (CH_2), 28.8 (CH_2), 29.0 (CH_2), 29.1 (CH_2), 29.3 (CH_2), 29.7 (CH_2), 32.3 (CH_2), 34.2 (CH_2), 35.9 (CH_2), 55.1 (CH_2), 59.0 (CH), 63.5 (CH_2), 65.5 (CH_2), 69.7 (CH), 124.7 (CH), 125.8 (CH), 127.7 (CH), 128.0 (CH), 142.1 (C), 174.5 (C); IR ν_{max} cm^{-1}: 3378, 2924, 2852, 1726, 1454, 1384, 1344, 1172, 1068, 1026; LC-MS (m/z) 947.4 [M-OH]$^+$, 982.4 [MNH_4]$^+$; HRMS (m/z for [M-H]$^-$) calcd.: 963.4903; found: 963.4890; HRMS (m/z for [M-OH]$^+$) calcd.: 947.495424; found: 947.4955

4.14. General dimerization method

Anthracene derivatives are dissolved in a minimal amount of hexane and/or THF. The solution is irradiated using UVC lamps for several hours under inert atmosphere. Dimers were separated from the mixture, either by filtration and recrystallization or column chromatography. All were white to slightly yellow powders. Determined melting points of dimers are either by true melting or liquefaction due to thermal dissociation, possibly followed by dimers dissolving in formed monomers.

*4.15. (**3**)$_2$ (head-head (hh) and head-tail (ht) dimer)*

Mp = 154.5-157.5 °C; ^{1}H-NMR (400 MHz, $CDCl_3$): δ (ppm) = 0.12-1.64 (m, 23H, $CH_2C\underline{H_2}CH_2$), 1.87-1.95 (m, 1H, $C\underline{H_2}CH_2CO$, *hh*), 1.98-2.09 (m, 4H, $C\underline{H_2}CHCH_2$), 2.15-2.25 (m, 3H, $C\underline{H_2}CO$, *ht*), 2.74 (t, *J*=7 Hz, 1H, $C\underline{H_2}CO$, *hh*), 3.78 (s, 1.5H, $CC\underline{H}C$, *ht*), 4.48 (s, 0.5H, $CC\underline{H}C$, *hh*), 4.90-5.04 (m, 4H, $CH_2CHC\underline{H_2}$), 5.12-5.27 (m, 4H, $CC\underline{H_2}O$), 5.74-5.87 (m, 2H, $CH_2C\underline{H}CH_2$), 6.81-7.15 (m, 16H, $CC\underline{H}C\underline{H}C\underline{H}C\underline{H}C$); ^{13}C-NMR (100 MHz, $CDCl_3$): δ (ppm) = 24.9 (CH_2), 28.9 (CH_2), 29.0 (CH_2), 29.0 (CH_2), 29.1 (CH_2), 29.2 (CH_2), 29.4 (CH_2), 33.8 (CH_2), 34.3 (CH_2), 59.0 (CH), 63.4 (CH_2), 68.9 (CH_2), 114.2 (CH_2), 124.7 (CH), 125.8 (CH), 127.7 (CH), 128.0 (CH), 139.2 (CH), 142.1 (C), 143.9 (C), 174.5 (C); IR ν_{max} cm^{-1}: 2926, 2852, 1724, 1640, 1454, 1382, 1344, 1292, 1242, 1176, 1116, 1070

*4.16. (**9**)$_2$*

Mp = 182-183 °C; ^{1}H-NMR (500 MHz, $CDCl_3$): δ (ppm) = 2.13 (q, *J*=7.3 Hz, 4H, $CCH_2C\underline{H_2}CH$), 2.76-2.82 (m, 4H, $CC\underline{H_2}CH_2CH$), 3.88 (s, 2H, $CC\underline{H}C$), 5.10 (d, *J*=10.2 Hz, 2H, $CH_2CHC\underline{H_2}$), 5.15 (d, *J*=17.1 Hz, 2H, $CH_2CHC\underline{H_2}$), 6.04 (ddt, *J*=16.9 Hz, *J*=10.3 Hz, *J*=6.5 Hz, 2H, $CH_2C\underline{H}CH_2$), 6.79-6.93 (m, 12H, $CCHC\underline{H}C\underline{H}C\underline{H}C$), 6.99 (d, J=7.5 Hz, 4H, $CC\underline{H}CH$); ^{13}C-NMR (125 MHz, $CDCl_3$): δ (ppm) = 29.3 (CH_2), 36.2 (CH_2), 56.5 (C), 64.8 (CH), 114.5 (CH_2), 125.2 (CH), 125.3 (CH), 126.2 (CH), 127.5 (CH), 138.6 (CH), 142.7 (C), 143.7 (C); IR ν_{max} cm^{-1}: 3066, 3018, 2930, 2862, 2160, 2032, 1976, 1640, 1472, 1448, 1122, 1046; GC-MS (m/z) 232 $[M/2]^+$

*4.17. (**10**)$_2$*

Mp = 111.5-114 °C; ^{1}H-NMR (500 MHz, $CDCl_3$): δ (ppm) = 1.23-1.43 (m, 28H, $CH_2C\underline{H_2}CH_2$), 1.47-1.59 (m, 4H, $CCH_2C\underline{H_2}$), 2.05 (q, *J*=7.1 Hz, 4H, $C\underline{H_2}CHCH_2$), 2.65 (t, *J*=7.9 Hz, 4H, $CC\underline{H_2}CH_2$), 3.84 (s, 2H, $CC\underline{H}C$), 4.94 (d, *J*=10.2 Hz, 2H, $CH_2CHC\underline{H_2}$), 5.00 (d, *J*=17.1 Hz, 2H, $CH_2CHC\underline{H_2}$), 5.83 (ddt, *J*=17.1 Hz, *J*=10.3 Hz, *J*=6.7 Hz, 2H, $CH_2C\underline{H}CH_2$), 6.77-6.89 (m, 12H, $CCHC\underline{H}C\underline{H}C\underline{H}C$), 6.96 (d, *J*=7.5 Hz, 4H, $CC\underline{H}CH$); ^{13}C-NMR (125 MHz, $CDCl_3$): δ (ppm) = 24.9 (CH_2), 29.0 (CH_2), 29.2 (CH_2), 29.5 (CH_2), 29.5 (CH_2), 29.6 (CH_2), 29.6 (CH_2), 30.7 (CH_2), 33.8 (CH_2), 37.8 (CH_2), 56.6 (C), 65.0 (CH), 114.1 (CH_2), 125.1 (CH), 126.2 (CH), 127.4 (CH), 139.3 (CH), 143.0 (C), 143.9 (C); IR ν_{max} cm^{-1}: 2924, 2852, 2530, 2478, 2160, 2028, 1978, 1734, 1450, 1364, 1328, 1252, 1166, 1096

*4.18. (**14**)$_2$*

Mp = 83.5-85 °C; ^{1}H-NMR (500 MHz, $CDCl_3$): δ (ppm) = 1.18-1.39 (m, 20H, $CH_2C\underline{H_2}CH_2$), 1.67 (quin, *J*=6.7 Hz, 4H, $OCH_2C\underline{H_2}$), 2.02 (q, *J*=7.1 Hz, 4H, $C\underline{H_2}CHCH_2$), 4.31 (t, 4H, $OC\underline{H_2}CH_2$) , 4.93 (dt, *J*=10.1 Hz, *J*=1.1 Hz, 2H, $CH_2CHC\underline{H_2}$), 4.93 (dq, *J*=17.1 Hz, *J*=1.8 Hz, 2H, $CH_2CHC\underline{H_2}$), 5.74 (s, 2H, $CC\underline{H}C$), 5.74 (ddt, *J*=17.1 Hz, *J*=10.3 Hz, *J*=6.7 Hz, 2H, $CH_2C\underline{H}CH_2$), 6.65 (dd, *J*=7.5 Hz, *J*=1.4 Hz, 2H, $CC\underline{H}CH$), 6.79-6.86 (m, 4H, $CCHC\underline{H}$), 7.00 (dd, *J*=7.1 Hz, *J*=1.6 Hz, 2H, $CC\underline{H}CH$); ^{13}C-NMR (125 MHz, $CDCl_3$): δ (ppm) = 26.1 (CH_2), 28.4 (CH_2), 28.9 (CH_2), 29.1 (CH_2), 29.1 (CH_2), 29.3 (CH_2), 29.4 (CH_2), 33.8 (CH_2), 55.0 (CH), 66.2 (C), 114.1 (CH_2), 125.5 (CH), 126.1 (CH), 126.5 (CH), 128.2 (CH), 139.2 (CH), 141.9 (C), 142.7 (C), 174.5 (C); IR ν_{max} cm^{-1}: 3072, 3024, 2922, 2852, 2160, 2030, 1978, 1722, 1640, 1454, 1198, 1104, 1006; LC-MS (m/z) 766.4 $[MNH_4]^+$; HRMS (m/z for $[MNH_4]^+$) calcd.: 766.4835; found: 766.4830

*4.19. (**17**)$_2$*

Mp = 117-119 °C; ^{1}H-NMR (400 MHz, $CDCl_3$): δ (ppm) = 1.42-1.55 (m, 10H, $CH_2C\underline{H_2}CH_2$), 1.65 (quin, *J*=6.8 Hz, 4H, $COCH_2C\underline{H_2}$), 1.87 (quin, *J*=7 Hz, 4H, $C\underline{H_2}CH_2OH$), 3.53 (t, *J*=7 Hz, 4H, $COC\underline{H_2}$), 3.69 (t, *J*=6.5 Hz, 4H, $C\underline{H_2}OH$), 4.46 (s, 2H, $CC\underline{H}C$), 6.82-6.90 (m, 8H, $CCHC\underline{H}$), 7.00-7.06 (m, 8H, $CC\underline{H}CH$); ^{13}C-NMR (100 MHz, $CDCl_3$): δ (ppm) = 25.8 (CH_2), 26.0 (CH_2), 30.5 (CH_2), 32.8 (CH_2), 63.0 (CH_2), 64.0 (CH), 65.0 (CH_2), 89.3 (C), 125.1 (CH), 125.6 (CH), 125.8 (CH), 127.6 (CH), 141.0 (C), 142.1 (C); IR ν_{max} cm^{-1}: 3341, 2934, 2858, 1452, 1292, 1254, 1202, 1154, 1118, 1052; HRMS (m/z for $[MNH_4]^+$) calcd.: 606.3583; found: 606.3574

*4.20. (**18**)$_2$*

Mp = 118-118.5 °C; ^{1}H-NMR (500 MHz, $CDCl_3$): δ (ppm) = 1.24-1.47 (m, 36H), 1.54-1.62 (m, 4H, $COCH_2C\underline{H_2}$), 1.85 (quin, *J*=7.2 Hz, 4H, $C\underline{H_2}CH_2OH$) 3.53 (t, *J*=7.1 Hz, 4H, $COC\underline{H_2}$), 3.65 (t, *J*=6.7 Hz, 4H, $C\underline{H_2}OH$), 4.46 (s, 2H, $CC\underline{H}C$), 6.82-6.89 (m, 8H, $CCHC\underline{H}$), 7.00-7.07 (m, 8H, $CC\underline{H}CH$); ^{13}C-NMR (125 MHz, $CDCl_3$): δ (ppm) = 25.3 (CH_2), 25.8 (CH_2), 26.2 (CH_2), 29.5 (CH_2), 29.6 (CH_2), 32.8 (CH_2), 63.1 (CH_2), 65.1 (CH_2), 89.2 (C), 125.1 (CH), 125.8 (CH), 127.5 (CH), 141.0 (C), 142.2 (C)); IR ν_{max} cm^{-1}: 3324, 2920, 2850, 1452, 1290, 1256, 1202, 1154, 1118, 1056; HRMS (m/z for $[MH]^+$) calcd.: 757.5196; found: 757.5181

*4.21. (**19**)$_2$*

Mp = 150-151 °C; ^{1}H-NMR (400 MHz, $CDCl_3$): δ (ppm) = 1.27-1.62 (20H), 1.78-2.00 (m, 4H, $COCH_2C\underline{H_2}$), 2.07 (q, *J*=6.9 Hz, 4H, $C\underline{H_2}CHCH_2$), 2.70-2.80 (m, 4H, $COC\underline{H_2}CH_2$), 4.57-4.74 (1.35H, $CC\underline{H}C$), 4.95 (dt, *J*=10.2 Hz, *J*=1 Hz, 2H, $CH_2CHC\underline{H_2}$), 5.02 (dq, *J*=17.1 Hz, *J*=1.7 Hz, 2H, $CH_2CHC\underline{H_2}$), 5.09-5.22 (0.65H, $CC\underline{H}C$), 5.84 (ddt, *J*=17 Hz, *J*=10.3 Hz, *J*=6.6 Hz, 2H, $CH_2C\underline{H}CH_2$), 6.66-7.33 (16H, $CC\underline{H}C\underline{H}C\underline{H}C\underline{H}C$); ^{13}C-NMR (100 MHz, $CDCl_3$): δ (ppm) = 25.2 (CH_2), 29.0 (CH_2), 29.1 (CH_2), 29.4 (CH_2), 29.4 (CH_2), 33.8 (CH_2), 114.2 (CH_2), 125.6 (CH), 126.2 (CH), 139.2 (CH); IR ν_{max} cm^{-1}: 3066, 3032, 2924, 2850, 2160, 2020, 1978, 1744, 1640, 1452, 1376, 1294, 1210, 1154, 1118, 1010; HRMS (m/z for $[MNH_4]^+$) calcd.: 738.4522; found: 738.4537

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