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Olefin Cross-Metathesis: a Versatile Synthetic Reaction for the Design of *Janus* Liquid Crystals

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Dedicated to Professor Georg Süss-Fink on the occasion of his 65th birthday

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The olefin cross-metathesis reaction using the second-generation Grubbs catalyst was employed to prepare non-symmetrical thermotropic liquid crystals from various mesomorphic or nonmesomorphic type I and type II olefinic constructs, including linear, chiral, dendritic and ferrocenyl olefins. Smectic C, smectic A and nematic phases, as well as chiral smectic A and chiral nematic phases were observed in agreement with the structure and nature of the mesogens. The olefin cross-metathesis proved to be a valuable chemical reaction in designing dimeric and *Janus*-like thermotropic liquid crystals built from two different molecular entities.

Introduction

Olefin cross-metathesis is an effective and elegant reaction which is widely used in synthetic chemistry and materials science.[1,2] Its tolerance towards a wide range of functional groups, and the mild reaction conditions that it requires, have made olefin cross-metathesis a popular reaction in many academic and industrial laboratories. Based on this metal-catalyzed transformation, a great variety of chemicals has been engineered, such as polymers,[3] functionalized dendrimers,[4] water-soluble dendrimers,[4c,5] functionalized gold nanoparticles,[4c,6] modified proteins,[7] glycopeptoids[8] and naturally occurring products.[9]

With the goal of designing new and functional thermotropic *Janus*-type liquid crystals, i.e. liquid crystals made of two different molecular parts, which favor the formation or the induction of different types of supramolecular organizations and therefore expand the diversity of liquid-crystalline phases,[10] we applied the olefin cross-metathesis reaction by connecting type I (terminal olefins) and type II (α,β-unsaturated carbonyl olefins) olefins carrying mesomorphic or nonmesomorphic moieties. This combination of olefins was chosen according to the guiding rules described by Grubbs, who emphasized that the cross-metathesis between olefins of types I and II yields products with high chemo- and stereoselectivity, leading predominantly to the (*E*)-configured cross-metathesis products.[11] Furthermore, in order to explore the scope of the olefin cross-metathesis for the preparation of the title compounds, olefins with various structures were chosen rather than focusing on a particular family of chemicals. Our study includes linear (**5** and **7**), chiral (**8**), and dendritic (**6**) olefins as well as a nonmesomorphic ferrocene derivative (**9**). The successful achievements described herein open avenues for the design of nonsymmetrical molecular structures, in particular *Janus*-like oligomers[10,12] and dendrimers,[13] with, in addition, the facile incorporation of various active molecular units such as redox-active units, dyes, drugs, radicals or metallic fragments. This synthetic strategy can be generalized and applied to a wide choice of mesomorphic archetypes which are of relevance for the investigation of either bulk or solution self-assembling behavior. Finally, it is noteworthy that ring-opening metathesis polymerization (ROMP)[14] of norbornene and cyclobutene derivatives and acyclic diene metathesis (ADMET)[15] of aliphatic and aromatic α,ω-dienes, have been used to synthesize side-chain and main-chain liquid-crystalline polymers. Nematic,[14a,14b,14e,15c] smectic A,[14b] columnar hexagonal,[14c] and chiral smectic C[15a,15d] phases were observed for those materials. Thus, the olefin

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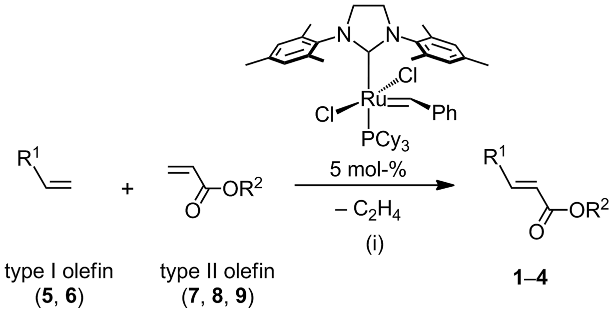
cross-metathesis reported here enriches the available synthetic tools for the synthesis of novel liquid crystals from olefinic building blocks.

We describe, herein, the synthesis, characterization and mesomorphic properties of three selected representatives *Janus*-like liquid crystals, **2**–**4**, a liquid-crystalline dimer, **1**, which is used for comparative purposes, and type I (**5** and **6**) and type II (**7**–**9**) precursory olefins. Structural models of the mesophases obtained for compounds **2**–**4** are provided based on X-ray diffraction studies.

Results and Discussion

Synthesis

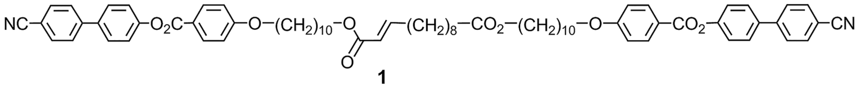
Compounds **1**–**4** (Figure 1) were prepared by following the general reaction shown in Scheme 1. In a typical procedure, a mixture of type I (1 equiv.) and type II (1.2–1.6 equiv.) olefins was stirred in CH_2Cl_2 for 16 hours at 40 °C in the presence of 5 mol-% of the second-generation Grubbs catalyst (under Ar). An excess of type II olefin was chosen to favor the formation of the cross-metathesis products versus the dimerization of type I olefins. The final compounds were purified by column chromatography on silica gel (eluent: CH_2Cl_2/AcOEt = 100:2) and precipitation in AcOEt. For the synthesis of compounds **1**–**3**, the yield of the olefin cross-metathesis was found to be around 65% after purification. A lower yield was obtained in the case of **4** (46% after purification), which is, most likely, the result of steric hindrance due to the size of dendron **6**.



Scheme 1. Synthesis of compounds **1**–**4** via olefin cross-metathesis and structure of second-generation Grubbs catalyst. Conditions: (i) CH_2Cl_2, 40 °C, 16 h, 46–67%.

Olefins **5** and **6** (Figure 2) were prepared by EDC-mediated esterification of the appropriate alcohol or phenol derivatives with 10-undecenoic acid (Scheme S1 in the Supporting Information). Olefins **7** and **8** were synthesized from acryloyl chloride and the corresponding alcohol derivatives (Scheme S1 in the Supporting Information). Finally, esterification of ferrocenecarboxylic acid with 2-hydroxyethyl acrylate under EDC reaction conditions gave compound **9** (Scheme S1 in the Supporting Information).

The formation, stereochemistry and purity of the cross-metathesis compounds **1**–**4** were clearly established by ^{1}H NMR spectroscopy. The reaction of **5** with **8** to furnish **2** is discussed as an illustrative example (Figure 3): first, the formation of compound **2** was revealed by (i) the disappearance of the signals which correspond to the two terminal olefinic protons at δ = 5.00 and 4.94 ppm for **5** and at δ =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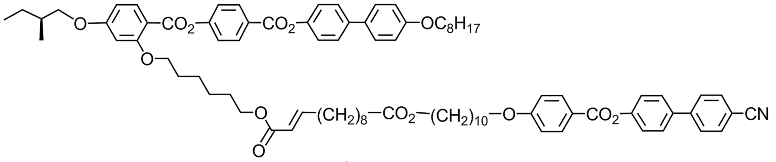
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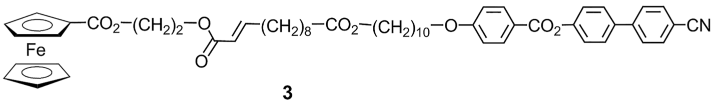
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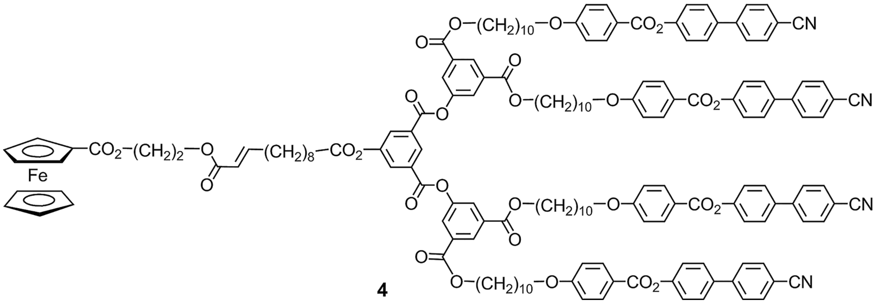
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Figure 1. Structures of target compounds **1**–**4**.

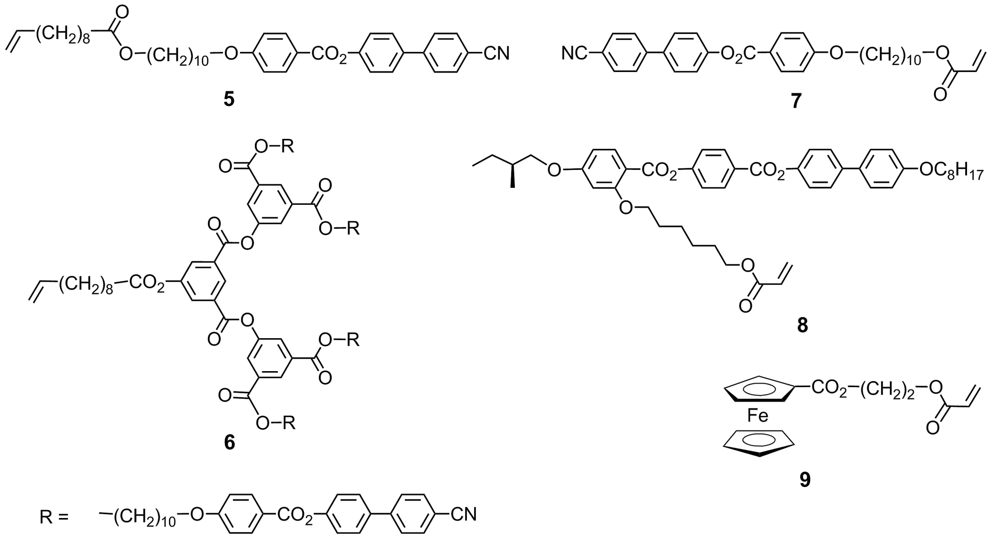

Figure 2. Structures of type I olefins (**5** and **6**) and type II olefins (**7**–**9**).

6.35 and 5.79 ppm for **8**, and (ii) the appearance of two doublets of triplets at $\delta = 6.92$ and 5.78 ppm, which correspond to the internal olefinic protons in **2**; second, the 15.6 Hz value for the coupling constant between the olefinic protons indicates the (*E*)-configuration of the newly formed carbon–carbon double bond; and third, no other olefinic signals were detected in the ^{1}H NMR spectrum. Similar data were obtained for compounds **1**, **3** and **4**.

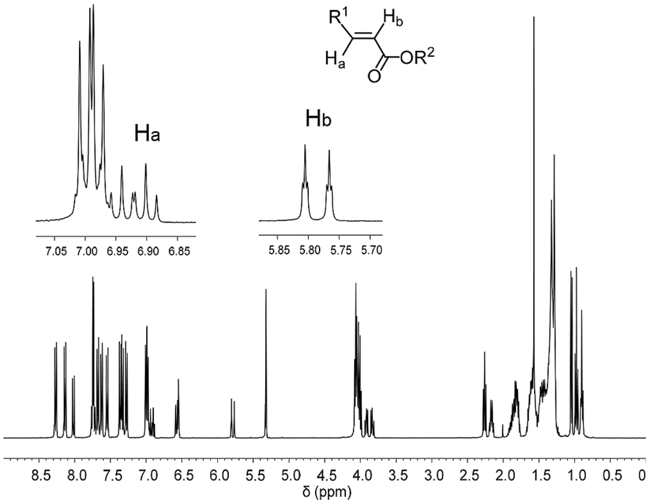

Figure 3. ^{1}H NMR spectra of **2** in CD_2Cl_2 (insets show the internal olefinic protons H_a and H_b as doublets of triplets at $\delta = 6.92$ and 5.78 ppm, respectively).

Liquid-Crystalline Properties

The mesomorphic and thermal properties of all compounds were investigated by polarized optical microscopy (POM) and differential scanning calorimetry (DSC). Small-angle X-ray scattering (SAXS) investigations were performed for compounds **2**–**4**. The liquid-crystalline phases were primarily identified from the observation of typical textures by POM, i.e., smectic A/smectic A* phases: focal-conic fan texture and homeotropic areas; smectic C phase: focal-conic fan and *schlieren* textures; nematic phase: *schlieren* texture; chiral nematic phase: Grandjean-plane and fingerprint textures. Illustrative examples are shown in Figure 4 and in Figures S19–21 in the Supporting Information. The phase-transition temperatures and enthalpies of compounds **1**–**8** are collected in Table 1.

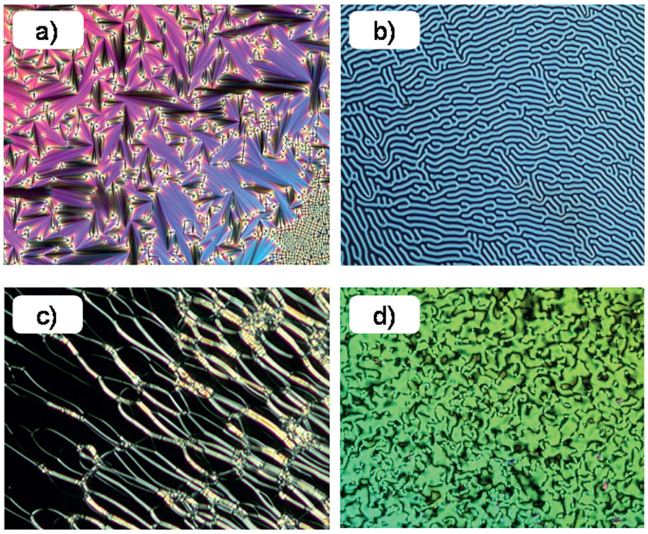

Figure 4. Thermal-polarized optical micrographs of a) the focal-conic fan texture displayed by **1** in the smectic A phase at 188 °C; b) the fingerprint texture displayed by **2** in the chiral nematic phase at 112 °C; c) small focal-conic and myelinic textures and homeotropic area displayed by **4** in the smectic A phase at 140 °C; d) the *schlieren* texture displayed by **4** in the nematic phase at 164 °C.

Olefinic precursors. With the exception of ferrocene derivative **9**, which is characterized by a nonmesomorphic structure, all other olefinic derivatives **5**–**8** showed liquid-crystalline behavior. A smectic A (SmA) phase was observed for **5**–**7**, which is explained by the strong tendency

Table 1. Phase transitions and enthalpy changes of **1**–**8**.[a]

Compd.	T_g [°C]	Transitions	T [°C]	ΔH [kJ mol^{-1}]
1	–	Cr→SmA	106	117.7
		SmA→N[b]	196	–
		N→I	197	4.6 [c]
2	–	Cr→SmA*	36	3.6
		SmA*→N*	107	0.3
		N*→I	150	2.0
3	–	Cr→SmA	51	42.8
		(SmC→SmA)[b],[d]	35	–
		SmA→I	75	1.8
4	40	SmA→N	163	
		N→I	168	8.4[c]
5	–	Cr→SmA	74	75.3
		SmA→I	152	3.5
6	40	SmA→I	198	12.0
7	–	Cr→SmA[e]	110	66
		Polymerization[f]	–	–
8	–	Cr→N*	92	44.8
		N*→I	115	0.7

[a] T_g: glass transition temperature, Cr: crystalline or semi-crystalline solid, SmA: smectic A phase, SmC: smectic C phase, N: nematic phase, SmA*: chiral smectic A phase, N*: chiral nematic phase, I: isotropic liquid. [b] Observed by polarized optical microscopy. [c] Overall enthalpy. [d] Monotropic transition. [e] Obtained from the first heating run. [f] See text for details. Transition temperatures are given as the onset of the peaks obtained during the second heating run.

of the cyanobiphenyl units to align parallel to each other, leading to the formation of layers,[16] and a chiral nematic (N*) phase was observed for **8** due to the presence of the chiral fragment in the laterally-branched molecule[17]. The thermal properties of compound **7** could not be fully examined because it polymerized when heated on the microscope hot stage. Nevertheless, fluidity of the SmA phase was observed at least up to 180 °C.

Cross-metathesis products. All the cross-metathesis compounds **1**–**4** showed liquid-crystalline behavior. They all displayed a SmA (or SmA* for **2**) phase. In addition, a nematic (N) phase for **1** and **4**, a chiral nematic (N*) phase for **2** and a monotropic smectic C (SmC) phase for **3** were also observed. The connection of the two smectogens **5** and **7** preserved the nature of the SmA phase in **1** with the induction of a very narrow N phase (1 °C). In compound **2**, the chiral rod (derived from **8**) was laterally branched with the cyanobiphenyl unit (derived from **5**). Interestingly, compound **2** displayed mesomorphic properties arising from both mesogens **5** (SmA) and **8** (N*). During the first heating run, compound **3** gave only a crystal-to-isotropic liquid transition, i.e. a melting point. However, its mesomorphic behavior was fully established after the first cooling run, and was found to be reversible for the successive heating-cooling cycles (Figure S22 in the Supporting Information). Finally, the SmA phase of dendrimer **4** was strongly stabilized with respect to **3** as a consequence of the larger number of peripheral mesogenic units (four cyanobiphenyl units in **4** versus one cyanobiphenyl unit in **3**). Such a behavior has already been observed for analogous dendrimers.[13b] This compound also yielded an N phase which was not displayed by dendron **6**.

X-ray Analysis

The X-ray diffractograms of chiral compound **2** recorded between 60 and 105 °C showed a sharp and intense reflection at low Bragg angles and a diffuse halo at high Bragg angles (Figure 5). The intense reflection in the small-angle region corresponds to a *d*-layer spacing of 40 Å, and is invariant with temperature. This behavior corresponds to a SmA/SmA* phase, and is in agreement with the POM observations. The diffuse halo in the high-angle region (d = 4.6 Å) is characteristic of the liquid-like order of the alkyl chains and mesogens (h_{ch} + h_{mes}). Alongside the weak d_{002} reflection, another weak feature could also be observed. The latter signal was actually due to the presence of some impurity resulting from some partial degradation of the sample upon heating and X-ray beam exposure. At 120 °C, in the N* phase, the X-ray diffractograms showed two diffuse halos at 35 and 4.5 Å (Figure S23 in the Supporting Information) which correspond to the formation of cybotactic groups and molten alkyl chains and mesogens, respectively. The SmA* and N* phases were reversibly observed when the sample was cooled from the isotropic liquid. The layer spacing was less than half of the sum of all molecular segments' lengths; and the ratio of the molecular volume V_{Mol} over the *d*-layer spacing (ca. 58 Å^2) was more than twice the natural section of segments (ca. 20–22 Å^2). The side-on substitution, which is unfavorable for generating efficient nanosegregation, plays a role, but the main discrepancy arises from the presence of two aliphatic chains and two rigid segments: the exchange of similar types of sublayers within smectic domains indeed reduces the spacing to a single hard segment alternation, i.e. to the half-molecule periodicity.[18]

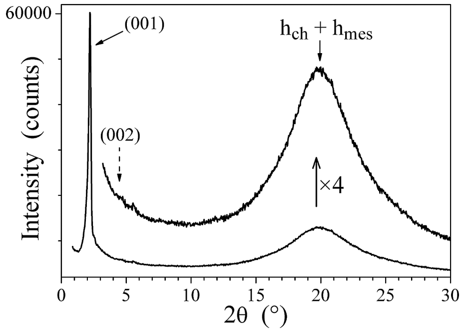

Figure 5. X-ray diffractograms of compound **2** recorded at 80 °C in the chiral smectic A phase.

Although the mesomorphic behavior of compounds **3** and **4** was clearly identified by POM from the observation of typical textures, the X-ray measurements gave little satisfaction. For compound **3**, a weak reflection at small Bragg angle (d spacing: 42.2 Å) was detected beside the diffuse halo at 4.6 Å only when the sample was cooled to 40 °C from the isotropic liquid. Long-range order of the structure within the SmA phase was then suggested as follows: the central chains and calamitic end groups of molecules **3** nanosegregated in alternating sublayers. Although the ferrocene and cyanobiphenyl units were incompatible and formed distinct sublayers, both sublayers exchanged within smectic domains in a head-to-tail fashion, leading to a monolayer periodicity (V_{Mol}/d about 37 Å^2).[18]

For compound **4**, no reflection was detected within the whole temperature range, which indicated more disorder compared to **2** and **3**. The reason for the nondetectable structure by X-ray diffraction for **4** within the SmA phase was thought to be the diffuse interface between the smectic layers, resulting from the difference in bulkiness between molecular halves bearing the cyanobiphenyl tails and the ferrocene group. Analogous behavior has been reported for thermotropic liquid-crystalline materials constructed from similar cyanobiphenyl-based dendrons.[19]

Conclusions

New *Janus* liquid-crystalline materials were synthesized via olefin cross-metathesis. Liquid-crystalline properties in agreement with the structure and nature of the mesogens were observed. Our study demonstrates that olefin cross-metathesis is of general interest for the design of liquid crystals. For example, it can be used to connect two olefinic mesogens with antagonist properties (chiral-achiral, polar-apolar, hydrophilic-hydrophobic) or to introduce an additional functionality within the molecular architecture (redox-active units, drugs, radicals or metallic fragments). Unique supramolecular organizations within the liquid-crystalline state could be obtained from such materials.

Experimental Section

General Procedure for the Olefin Cross-Metathesis: To a solution of type I olefin (1 equiv.) and type II olefin (1.2 to 1.6 equiv.) in CH_2Cl_2, was added second-generation Grubbs catalyst (0.05 equiv.). The reaction mixture was heated under reflux for 16 h (under Ar), and evaporated under reduced pressure. Purification of the solid residue by column chromatography [SiO_2, CH_2Cl_2/AcOEt (100:2)] and precipitation from AcOEt gave compounds **1**–**4**.

Compound 1: Compounds **5** (128 mg, 0.20 mmol) and **7** (126 mg, 0.24 mmol) in CH_2Cl_2 (8 mL) yielded 153 mg (67%) of product **1**. ^{1}H NMR ($CDCl_3$): δ = 8.16 (d, 4 H, arom. H), 7.74 (d, 4 H, arom. H), 7.69 (d, 4 H, arom. H), 7.64 (d, 4 H, arom. H), 7.33 (d, 4 H, arom. H), 7.00 (d, 4 H, arom. H), 6.93 (dt, J = 15.6, 7.0 Hz, 1 H, $C\mathit{H}=CHCO_2$), 5.81 (dt, J = 15.7, 1.6 Hz, 1 H, $CH=C\mathit{H}CO_2$), 4.12 (t, 2 H, $C\mathit{H}_2O_2CCH=CH$), 4.06 and 4.05 (2t, 6 H, CO_2CH_2 and 2× CH_2OAr), 2.29 (t, 2 H, CH_2CO_2), 2.24–2.13 (m, 2 H, $=CHC\mathit{H}_2$), 1.88–1.78 (m, 4 H, 2× $C\mathit{H}_2CH_2OAr$), 1.68–1.33 (m, 40 H, aliph. H) ppm. ^{13}C NMR ($CDCl_3$): δ = 173.73, 167.02, 164.81, 163.88, 151.80, 144.80, 139.38, 136.80, 132.76, 132.28, 128.39, 127.76, 122.66, 121.38, 118.98, 114.45, 113.92, 111.14, 68.56, 64.30, 54.06, 53.79, 53.72, 53.52, 53.25, 52.98, 34.38, 33.87, 29.56, 29.55, 29.42, 29.40, 29.32, 29.21, 29.19, 29.17, 29.03, 28.78, 26.03, 25.11 ppm. MS (ESI): 1157.90 [M + Na]$^+$. $C_{72}H_{82}N_2O_{10}$ (1135.45): calcd. C 76.16, H 7.28, N 2.47; found C 76.05, H 7.37, N 2.48.

Compound 2: Compounds **5** (96 mg, 0.15 mmol) and **8** (140 mg, 0.18 mmol) in CH_2Cl_2 (10 mL) yielded 130 mg (62%) of product **2**. ^{1}H NMR (CD_2Cl_2): δ = 8.27 (d, 2 H, arom. H), 8.14 (d, 2 H, arom. H), 8.02 (d, 1 H, arom. H), 7.76 (d, 2 H, arom. H), 7.72 (d, 2 H, arom. H), 7.68 (d, 2 H, arom. H), 7.62 (d, 2 H, arom. H), 7.55 (d, 2 H, arom. H), 7.36 (d, 2 H, arom. H), 7.33 (d, 2 H, arom. H), 7.28 (d, 2 H, arom. H), 7.01 (d, 2 H, arom. H), 6.99 (d, 2 H, arom. H), 6.92 (dt, J = 15.6, 7.0 Hz, 1 H, $C\mathit{H}=CHCO_2$), 6.57 (dd, 1 H, arom. H), 6.54 (d, 1 H, arom. H), 5.78 (dt, J = 15.6, 1.6 Hz, 1 H, $CH=C\mathit{H}CO_2$), 4.11–3.79 (m, 10 H, 3× CH_2OAr, $CH_2CO_2C\mathit{H}_2$ and $C\mathit{H}_2O_2CCH=$), 3.92 [dd, J = 9.0, 6.0 Hz, 1 H, 1 diastereotopic H of $OC\mathit{H}_2CH(CH_3)$] and 3.83 [dd, J = 9.0, 6.6 Hz, 1 H, 1 diastereotopic H of $OC\mathit{H}_2CH(CH_3)$], 2.26 (t, 2 H, $C\mathit{H}_2CO_2CH_2$), 2.22–2.12 (m, 2 H, $=CHC\mathit{H}_2$), 1.92–1.77 (m, 7 H, 3× $C\mathit{H}_2CH_2OAr$ and $C\mathit{H}CH_3$), 1.67–1.33 (m, 44 H, aliph. H), 1.04 (d, 3 H, $CHC\mathit{H}_3$), 0.97 and 0.89 (2t, 6 H, CH_3) ppm. ^{13}C NMR (CD_2Cl_2): δ = 174.01, 166.90, 165.37, 165.10, 164.95, 164.14, 163.62, 162.13, 159.33, 156.07, 152.05, 150.34, 149.72, 145.06, 139.02, 137.07, 134.74, 133.04, 132.80, 132.56, 131.96, 128.67, 128.39, 128.04, 127.92, 127.06, 122.94, 122.64, 122.38, 121.63, 121.49, 119.19, 115.16, 114.72, 111.39, 110.88, 105.99, 100.37, 73.57, 69.13, 68.82, 68.52, 64.60, 64.41, 35.09, 34.63, 32.52, 32.22, 29.84, 29.76, 29.70, 29.67, 29.65, 29.61, 29.58, 29.54, 29.49, 29.46, 29.41, 29.05, 29.01, 28.40, 26.42, 26.32, 26.30, 26.05, 26.02, 25.36, 23.06, 16.60, 14.26, 11.47 ppm. MS (ESI): 1410.90 [M + Na]$^+$. $C_{87}H_{105}NO_{14}$ (1388.78): calcd. C 75.24, H 7.62, N 1.01; found C 75.01, H 7.56, N 1.08.

Compound 3: Compounds **5** (191 mg, 0.30 mmol) and **9** (118 mg, 0.36 mmol) in CH_2Cl_2 (10 mL) yielded 178 mg (63%) of product **3**. ^{1}H NMR ($CDCl_3$): δ = 8.15 (d, 2 H, arom. H), 7.72 (d, 2 H, arom. H), 7.69 (d, 2 H, arom. H), 7.64 (d, 2 H, arom. H), 7.33 (d, 2 H, arom. H), 7.05 (dt, J = 15.6, 7.0 Hz, 1 H, $C\mathit{H}=CHCO_2$), 6.98 (d, 2 H, arom. H), 5.86 (dt, J = 15.6, 1.6 Hz, 1 H, $CH=C\mathit{H}CO_2$), 4.81 (t, 2 H, $FcCO_2CH_2$), 4.44 (s, 4 H, $C_5H_4CO_2$), 4.40 (t, 2 H, $FcCO_2CH_2C\mathit{H}_2$), 4.19 (s, 5 H, C_5H_5), 4.06 and 4.05 (2t, 4 H, CH_2OAr and $CH_2CO_2C\mathit{H}_2$), 2.28 (t, 2 H, $C\mathit{H}_2CO_2CH_2$), 2.24–2.15 (m, 2 H, $=CHC\mathit{H}_2$), 1.89–1.77 (m, 2 H, $C\mathit{H}_2CH_2OAr$), 1.69–1.21 (m, 26 H, aliph. H) ppm. ^{13}C NMR ($CDCl_3$): δ = 174.07, 171.66, 166.55, 164.96, 163.84, 151.74, 150.59, 145.02, 136.84, 132.79, 132.49, 128.48, 127.83, 122.70, 121.38, 120.83, 114.51, 111.15, 71.57, 70.80, 70.37, 69.95, 68.49, 64.50, 62.28, 62.17, 34.50, 32.28, 29.59, 29.58, 29.46, 29.36, 29.32, 29.26, 29.24, 29.20, 28.79, 28.07, 26.12, 26.05, 25.11 ppm. MS (ESI): 960.70 [M + Na]$^+$. $C_{55}H_{63}FeNO_9$ (937.95): calcd. C 70.43, H 6.77, N 1.49; found C 70.35, H 6.84, N 1.49.

Compound 4: Compounds **6** (150 mg, 0.06 mmol) and **9** (33 mg, 0.10 mmol) in CH_2Cl_2 (6 mL) yielded 77 mg (46%) of product **4**. ^{1}H NMR (CD_2Cl_2): δ = 8.89 (t, 1 H, arom. H), 8.60 (t, 2 H, arom. H), 8.22 (d, 2 H, arom. H), 8.12 (d, 8 H, arom. H), 8.11 (d, 4 H, arom. H), 7.74 (d, 8 H, arom. H), 7.73 (d, 8 H, arom. H), 7.67 (d, 8 H, arom. H), 7.32 (d, 8 H, arom. H), 7.03 (dt, J = 15.6, 7.0 Hz, 1 H, $C\mathit{H}=CHCO_2$), 6.98 (d, 8 H, arom. H), 5.86 (dt, J = 15.6, 1.6 Hz, 1 H, $CH=C\mathit{H}CO_2$), 4.78 (t, 2 H, $FcCO_2CH_2$), 4.40 (s, 4 H, $C_5H_4CO_2$), 4.38 (t, 2 H, $FcCO_2CH_2C\mathit{H}_2$), 4.35 (t, 8 H, Ar-CO_2CH_2), 4.19 (s, 5 H, C_5H_5), 4.04 (t, 8 H, CH_2OAr), 2.63 (t, 2 H, CH_2CO_2Ar), 2.29–2.14 (m, 2 H, $=CHC\mathit{H}_2$), 1.82–1.32 (m, 76 H, aliph. H) ppm. ^{13}C NMR (CD_2Cl_2): δ = 171.87, 166.28, 164.84, 164.78, 163.85, 163.20, 151.77, 151.48, 150.75, 150.38, 144.76, 136.77, 132.84, 132.75, 132.26, 131.28, 128.81, 128.37, 128.16, 127.74, 126.90, 122.64, 121.36, 120.78, 118.88, 114.43, 111.12, 71.53, 70.94, 70.21, 69.90, 68.53, 65.95, 62.21, 62.08, 34.22, 32.27, 29.55, 29.52, 29.40, 29.32, 29.25, 29.19, 29.17, 29.15, 29.12, 28.71 ppm. MS (MALDI-TOF): 2813.11 [M + Na]$^+$. $C_{169}H_{168}FeN_4O_{30}$ (2791.04): calcd. C 72.73, H 6.07, N 2.01; found C 72.49, H 6.34, N 2.00.

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