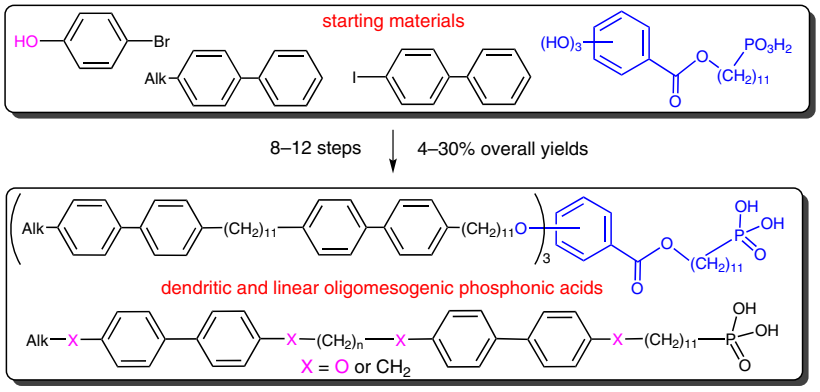
Synlett M. F. Prodanov et al. Letter

Towards New Oligomesogenic Phosphonic Acids as Stabilizers of Nanoparticles Colloids in Nematic Liquid Crystals

Maksym F. Prodanov*
Maksym Y. Diakov
Ganna S. Vlasenko
Valerii V. Vashchenko

State Scientific Institution 'Institute for Single Crystals', NAS of Ukraine, 60 Lenin Ave., Kharkiv, Ukraine
prodanov@isc.kharkov.com



Received: 10.04.2015
Accepted after revision: 04.05.2015
Published online: 07.07.2015
DOI: 10.1055/s-0034-1379930; Art ID: st-2015-d0261-l

Abstract Several synthetic strategies for the construction of linear and branched oligomesogenic phosphonic acids are examined, which differ in the method of building the key bimesogen unit. An efficient synthetic approach to the most promising compounds employs regioselective Kumada cross-coupling between [11-(4′-pentylbiphenyl-4-yl)undecyl]magnesium bromide and 4-(11-bromoundecyl)-4′-iodobiphenyl as the key step. Preliminary studies on the ability of the new ligands to stabilize nanoparticles colloids in nematic liquid crystals are undertaken for the example of quantum dots.

Key words acylation, cross-coupling, phosphonic acids, total synthesis, ligands

Colloids of inorganic nanoparticles (NPs) in liquid crystals (LCs) are very promising materials for application in displays, photonics, and metamaterials.[1–6] However, the application of these materials is hampered by a strong tendency of NPs to aggregate in the LC even if the surface of the NP is modified with ligands comprising promesogenic units (PMUs).[7–15] Recently, progress in the stabilization of colloids of small Au nanospheres and quantum dots (QDs) in LC was achieved by using mainly mixtures of promesogenic ligands with aliphatic co-surfactants.[5,7,8,10,12,14,16–19] In particular, we have studied extensively the stabilizing ability of ligands with different molecular shape in combination with variable amounts of aliphatic co-surfactants of different length in a nematic LC host[10] and found that dendritic ligands (of general structure **B**, Figure 1) are more efficient than linear analogues (**A**). This approach was successfully extended for the stabilization of spherical ferromagnetic NPs in nematic LC[20] and QDs in polymers.[21] However, the proposed ligands, apparently, have limited applicability for LC-colloids of elongated NPs.[11,22,23] Dendritic oligomesogenic ligands are also reported to induce mesomorphic properties in inorganic NPs,[24–28] although the colloidal stability of these composite materials in LC host has not been studied.

Clearly, an enhancement in the stabilizing ability of promesogenic ligands could be achieved by increasing the number of PMUs in the ligand molecule. However, it should be performed along the long molecular axis to retain the elongated flexible shape of the ligand favoring the efficient interaction with the LC environment.[5,10,14,15] Thus, a promising modification of the known ligands to the target structures can be schematically represented as a pass from structures **A** and **B** to **C** and **D** (compounds **1** and **2**; Figure 1). As a starting point for increasing the number of PMUs, we opted for a doubling of the 4,4′-disubstituted biphenylene groups. The linkage of biphenyl units through the alkoxy spacers (X = O; Figure 1) appeared to be synthetically more straightforward, therefore compounds **1a** and **2a** were initially considered.

It is seen that target compound **1a** comprises two asymmetrically substituted 4,4′-dihydroxybiphenylyl moieties (Scheme 1). To avoid any statistical reactions, related to functionalization of commercially available 4,4′-dihydroxybiphenyl, we employed a direct method to assemble the biphenylyl unit by Suzuki cross-coupling reaction of phenols that already contain suitable protective groups (reaction **4**→**5**; Scheme 1). Further, asymmetrically functionalized biphenyl building blocks **7** and **8** were proposed, which can be useful not only in the synthesis of bimesogens (e.g., **9**, **10**, and **1a**) but also for subsequent multiplication of PMUs.

On the way to the target compound **1a**, we encountered low reactivity of some intermediates. In particular, the hydrogenation of **6** (**6**→**8**) did not proceed under the typical reaction conditions, which was clearly due to its limited solubility. We succeeded in obtaining **8** only after heating the reaction mixture at elevated temperature (55–60 °C) for five days with multiple additions of catalyst. Most of the

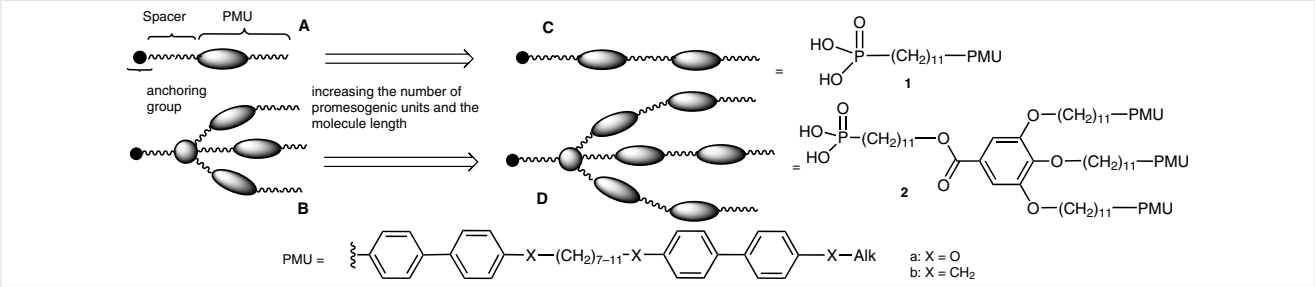


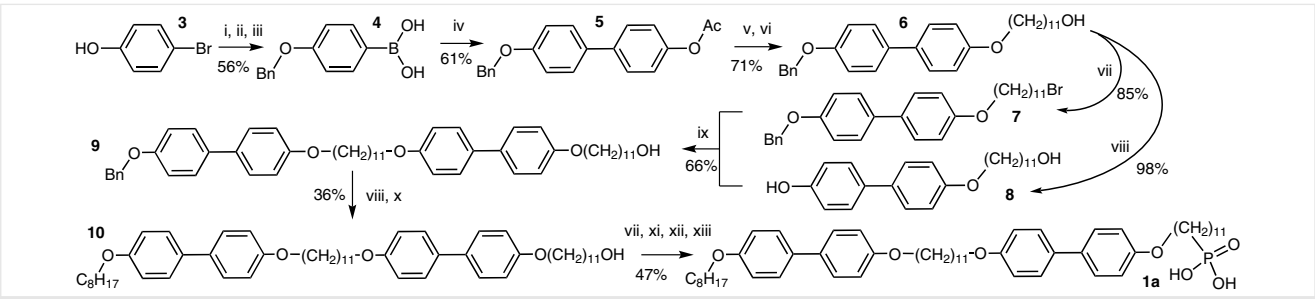
Figure 1 Schematic representation of described (A, B) and proposed (C, D) promesogenic ligands; structures of proposed ligands **1** and **2**

subsequent transformations (**7**→**1a**) also required unusually high temperatures (see the Supporting Information). Ultimately, the obtained target compound **1a** appeared to have a melting point (255 °C) that was higher than expected and the compound had an extremely low solubility in most organic solvents. These properties seriously hamper their use as ligands for NPs because it affects both the completeness of surface modification and the compatibility of the organic shell of the NP with the surrounding LC. A lowered melting point and increased solubility could be expected for non-oxygen analogues of **1a**; therefore, we focused further on the synthesis of compounds **1b** and **2b** (Figure 1).

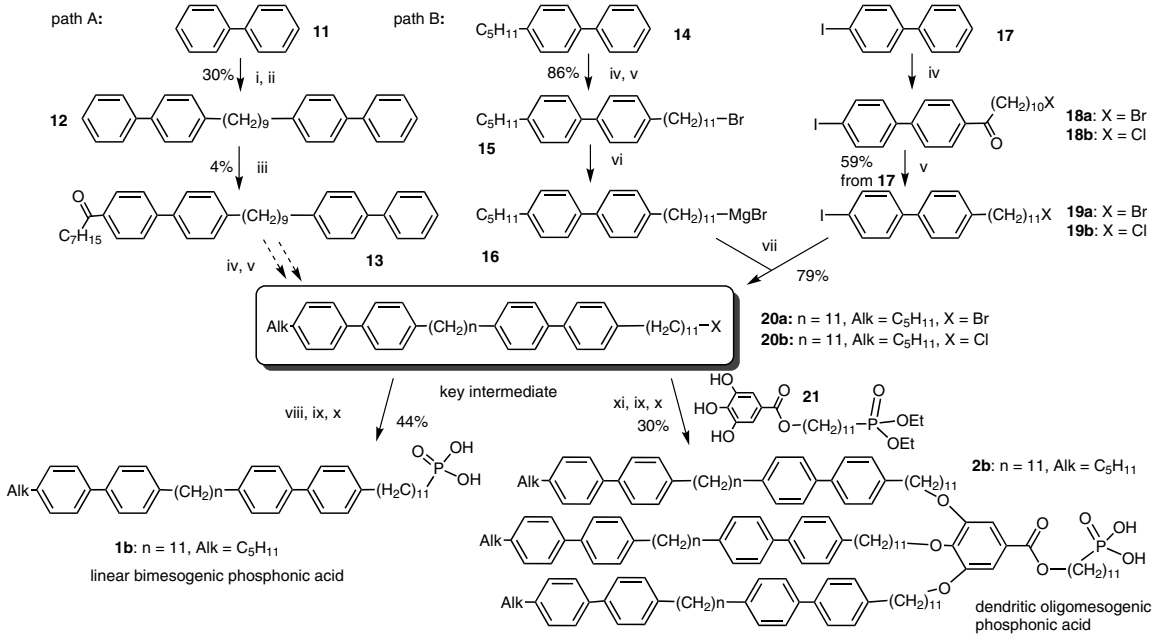
The synthetic approaches toward target compounds **1b** and **2b** are shown in Scheme 2. To construct the key intermediate bromide **20a**, two alternative synthetic pathways were proposed. Path A is based on a combination of Friedel–Crafts acylation and reduction of the obtained ketones; this route has only a few distant analogous reported examples: synthesis of symmetrical ω-bis(biphenylyl)alkanes[29–31] and an isolated example of the synthesis of an asymmetrically substituted analogue of **13**[32] comprising, however, terminal phenyl groups instead of biphenylyl groups. The drawback is that one of the acylation steps in path A (**12**→**13**) is a statistical reaction due to presence of two equivalent reaction centers in substrate **12**.

The alternative synthetic approach (Path **B**) employs Kumada–Corriu cross-coupling of Grignard reagent **16** with dihalo-derivative **19** as the key step. We did not find examples of Kumada–Corriu reactions that occur selectively at the aromatic ring in the presence of a halogenated sp^3-carbon. Nevertheless, selective coupling at the sp^2-carbon can be expected, because it is known that alkylhalides react slower in oxidative addition to the palladium catalysts than aryl halides.[33] Therefore, the rate of the main reaction (**19**→**20**) is expected to be considerably greater than that of the side processes. To further enhance the selectivity, we employed iodoarene as the most reactive halide (**19**; Scheme 2).

Initially, the more documented path A (Scheme 2) was examined. Acylation of biphenyl with nonanedioyl dichloride followed by reduction by using the Huang Minlon method gave 1,9-di([1,1′-biphenyl]-4-yl)nonane (**12**) in 30% overall yield. However, attempts to acylate this compound with octanoyl chloride under typical reaction conditions ($AlCl_3$, CH_2Cl_2, r.t.) led to the formation of a complex mixture of products (according to HPLC), from which the desired monoacyl derivative **13** was isolated in poor yield (4%). We attempted to optimize the acylation of **12** by varying the temperature and the catalyst for this reaction in CH_2Cl_2 or 1,2-dichlorobenzene (DCB; Table 1).



Scheme 1 Synthesis of oligomesogenic phosphonic acids with O-linkages **1a**. *Reagents and conditions*: (i) BnCl, K_2CO_3, MEK, reflux; (ii) Mg, THF, reflux; (iii) $B(OMe)_3$, THF then HCl (conc.); (iv) $Pd(dppf)_2$, $NaHCO_3$, SDS, toluene, H_2O; (v) NaOH, H_2O; (vi) 11-bromo-1-undecanol, K_2CO_3, MEK; (vii) PBr_3, DMF; (viii) H_2, Pd/C, EtOAc, 65 °C; (ix) K_2CO_3, DMF, 120 °C; (x) $C_8H_{17}Br$, K_2CO_3, DMF, 130 °C; (xi) $P(OEt)_3$, reflux; (xii) TMSBr, CH_2Cl_2, reflux; (xiii) MeOH, THF, reflux.



Scheme 2 Synthesis of phosphonic acids with simple bond linkages **1b** and **2b**. *Reagents and conditions*: (i) nonanedioyl dichloride, $AlCl_3$, CH_2Cl_2; (ii) N_2H_4, KOH, DEG, 130 °C; (iii) octanoyl chloride, $AlCl_3$, CH_2Cl_2; (iv) 11-bromoundecanoyl chloride, $AlCl_3$, CH_2Cl_2; (v) $(C_2H_5)_3SiH$, $AlCl_3$, CH_2Cl_2; (vi) Mg, THF, reflux; (vii) $PdCl_2$(dppf), THF; (viii) $P(OEt)_3$, 150 °C; (ix) TMSBr, CH_2Cl_2; (x) MeOH, THF; (xi) K_2CO_3, MEK.

Table 1 Content of **13** and Byproducts in the Reaction Mixture upon Acylation of **12** with Octanoyl Chloride

Lewis acid	Temp (°C)	Solvent	Quantity after 90 min (%)[a]	
			13	Byproducts (total)
$AlCl_3$	0	CH_2Cl_2	21	47
	20	CH_2Cl_2	29 (4[b])	70
$FeCl_3$	0	CH_2Cl_2	11	4
	20	CH_2Cl_2	15	7
	70	DCB	25 (4[b])	53
$ZnCl_2$	0	CH_2Cl_2	0	0
	90	DCB	0	0
	100	DCB	trace	trace

[a] As estimated by internal standardized HPLC analyses.
[b] Yield of isolated product.

The results suggest that the use of both weaker Lewis acids and lower temperature increases the selectivity of reaction, however at the cost of low conversion (Table 1), and we did not succeed in obtaining the desired monoacylated product **13** with satisfactory yield. The large number of side products can be caused by skeletal rearrangements of alkylaromatic groups in substrate **12** and **13** in the presence of strong Lewis acids, as is often observed in Friedel–Crafts alkylation.[34] HPLC analysis revealed that treatment of **12** with $AlCl_3$ in DCB at 0–5 °C even for 30 minutes results in the formation of several products at more than 50% conversion of starting material **12**. Thus, we can conclude that the presence of a labile alkylaromatic moiety in the reaction product **13** leads to the formation of a large amount of byproducts, and path A does not appear to be effective for obtaining of the key intermediate **20**.

In path B (Scheme 2), for the synthesis of 4-(11-bromoundecyl)-4′-iodo-1,1′-biphenyl (**19**), starting 4-iodobiphenyl **17** was acylated with 11-bromoundecanoyl chloride followed by one-pot reduction with triethylsilane.[35] In this reaction sequence, exchange of the 11-bromine atom with chlorine unexpectedly occurred and the mixture of desired 11-bromo (**19a**) and 11-chloro (**19b**) undecyldiphenyl derivatives (ca. 65:35 according to HPLC, GCMS analysis and NMR spectroscopy, see the Supporting Information) was formed. We found that prolonged stirring (ca. 24 h) of 11-bromoundecanoyl chloride in the presence of $AlCl_3$ in CH_2Cl_2 followed by quenching with methanol led to the formation of only the corresponding methyl 11-bromoundecanoate. However, in the presence of 4-iododiphenyl **17** at 0 °C, a mixture of 11-bromo and 11-chloro acylated products (**18a** and **18b**) formed immediately, and their ratio remained constant during the reaction. Although we failed to avoid the formation of chlorinated product **19b**, we used this mixture without separation because both halides **19a** and **19b** should yield the same products in the subsequent transformations. The reason for halogen exchange is not clear; moreover, in the case of acylation of 4-pentyldiphenyl **14** (**14**→**15**), the chlorinated byproduct formed only in trace amounts.

The cross-coupling of dihalides **19a**,**b** with Grignard reagents was initially studied by using a model reaction with hexylmagnesium bromide. As we expected, the reaction occurred selectively at the aromatic ring in high yield and it was further successfully applied for cross-coupling of **19** with **16** to furnish the key intermediate **20a**,**b** in 79% yield.[36] The target oligomesogenic phosphonic acids **1b** and **2b** were obtained by phosphorylation (in case of **1b**) and by alkylation of phosphonate **21**[37] (in case of **2b**) followed by mild hydrolysis of the intermediate diethyl phosphonates. Overall yields of the desired compounds **1b**, **2b** based on 4-pentylbiphenyl **14** were 30 and 20%, respectively (Scheme 2).

Compounds **1b** and **2b** did not possess any liquid crystal properties, as was revealed by differential scanning calorimetry and polarized optical microscopy. Notably, both phosphonic acids **1b** and **2b** have substantially lower melting points (158 and 121 °C, respectively) than their oxygen-bridged analogue **1a**. Moreover, phosphonic acids **1b** and **2b** are considerably more soluble in toluene under heating than **1a**, which is almost insoluble. At ambient temperature, dendritic phosphonic acid **2b** is prone to gelatinize the solution even in quite low concentration (5–6 mg/mL).

The stabilizing effect of new oligomesogenic ligands in nematic LC colloids was examined by using spherical luminescent CdSe/ZnS nanoparticles (quantum dots, λ_{max} = 530 nm, $\eta_{em} \approx 30\%$, d = 3.6 nm) in LC hosts: 4-pentyl-4′-cyanobiphenyl (5CB) and a commercially available nematic LC mixture E7 (Merck). The surface modification of NPs with new ligands was performed similarly to the method described by Prodanov et al.[10] and, as starting point, we used the same molar ratios of promesogenic ligands and short-chain cosurfactant (hexylphosphonic acid, HPA): 1:2 in the case of linear **1b** and 1:4 for dendritic **2b** (samples QD-**1b**-HPA and QD-**2b**-HPA). Feed concentrations of modified QDs in 5CB and E7 were approximately 0.25 wt%. All samples were subjected to polythermal fluorescence microscopy (FM) at excitation wavelength 405 nm. Under heating–cooling cycles, all colloids reproducibly change from a homogeneously emitting sample in their isotropic state (above 60 °C) to inhomogeneous field with various amounts of aggregates (as bright-green points) in the LC phase (see Figure 2).

It is clear that in QD-**1b**-HPA colloids (Figure 2, a, c, e), the aggregates are larger, with almost non-luminescent background. This result indicates a negligibly small concentration of QDs in fine-dispersed state in the sample, similar to what was observed for colloids of QDs coated with inappropriate ligand combinations or native surfactant.[10] Conversely, the colloids containing QD-**2b**-HPA nanoparticles reveal much more uniform emission between the small bright-green spots (Figure 2, b, d), thereby suggesting a significant amount of QDs was homogeneously distributed in the samples. We also did not observe any significant differences between dispersions in 5CB and E7 for modified NPs.

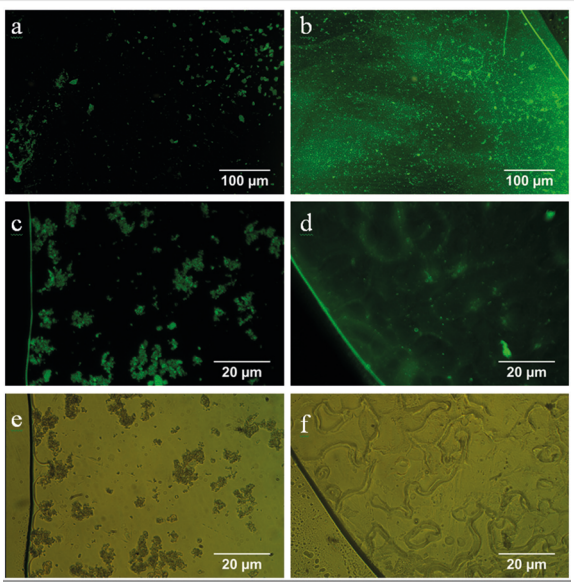


Figure 2 FM images of 0.25 wt% dispersions of (a) QD-**1b**-HPA in 5CB; (b) QD-**2b**-HPA in 5CB; (c) QD-**1b**-HPA in E7; (d) QD-**2b**-HPA in E7; (e,f) The same areas as in (c,d) additionally illuminated with a halogen lamp. The microphotographs were taken in nematic phase (at 25 °C) with the same shooting parameters.

Thus, our preliminary studies show a higher stabilizing ability in nematic LC nanocomposites for dendritic oligomesogenic ligand **2b** combined with hexylphosphonic acid. To finally establish the potential of the new ligands, additional experiments are required; these include an adjustment of the ratio and the length of the aliphatic co-surfactants and a determination of the real composition of organic shells of modified NPs. This work is in progress and the results will be published elsewhere.

In conclusion, we have developed an efficient synthetic pathway to new oligomesogenic phosphonic acids of both linear and branched molecular shape. The key bimesogenic intermediate, 4-{11-[4′-(11-haloundecyl)biphenyl-4-yl]undecyl}-4′-pentylbiphenyl (**20**) was formed by cross-coupling reaction. We demonstrated that Pd-catalyzed sp^3–sp^2 cross-coupling reactions of alkyl Grignard reagents with iodoarenes occur selectively at the aromatic ring in the presence of an alkyl halide moiety in the substrate. An alternative route to the target compounds was found to be ineffective because of the instability of intermediate 1,ω-bis(biphenylyl)alkanes in the presence of Lewis acids. Preliminary results reveal a higher stabilizing effect of dendritic ligand compared with the linear analogues in nematic LC colloids of quantum dots, albeit for unoptimized ligand shell compositions. Studies on their influence on the colloidal stability of other types of NPs both in nematic and smectic LCs is in progress and will be published along with details of the physical properties of the new materials separately.

Acknowledgment

Financial support from the National Academy of Science of Ukraine (projects # 0112U004502, #0115U003044, and #0112U002186) is gratefully acknowledged. We also thank Dr. N. Gorobets for valued discussions and Dr. Olga V. Vashchenko for providing the DSC measurements.

Supporting Information

Supporting information for this article is available online at http://dx.doi.org/10.1055/s-0034-1379930.

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(35) To a suspension of $AlCl_3$ (7.86 g, 59 mmol) in CH_2Cl_2 (250 mL), a solution of iodobiphenyl **17** (15.0 g, 53 mmol) was added at 0 °C. To this mixture, a solution of 11-bromoundecanoyl chloride (16.7 g, 59 mmol) was added dropwise during 20 min at 0 °C. After stirring at 0°C for 2 h and at r.t. for 7 h, a solution of triethylsilane (13.7 g, 0.12 mol) in CH_2Cl_2 (20 mL) was added dropwise at r.t. during 45 min. The reaction mixture was stirred overnight and then evaporated to dryness; the residue was dissolved in hexane (400 mL) and subjected to flash chromatography through a short pad of silica (hexane). The solution was evaporated to dryness and the residue was recrystallized from *i*-PrOH (300 mL). The washed precipitate was transferred to a modified Soxhlet extractor and washed with hot CCl_4 (500 mL) for 12 h. The solvent was evaporated and the residue was recrystallized from *i*-PrOH. The colorless solid product was dried in vacuo at 80–100 °C to give **19a** and **19b** as a mixture of compounds. Yield: 16.3 g (59%). According to GCMS, HPLC and NMR spectroscopy (Figure 2) the obtained mixture contained about 35% of chloro derivative **19b**. Mp 61–64 °C. IR (KBr): 2918, 2848, 1678, 1461, 1387, 1131, 1069, 1000, 857, 810, 792, 723, 686, 646, 472 cm^{-1}. ^1H NMR (200 MHz, $CDCl_3$): δ = 1.29 (m, 14 H, 3-CH_2, 4-CH_2, 5-CH_2, 6-CH_2, 7-CH_2, 8-CH_2, 9-CH_2), 1.56–1.73 (m, 2 H, 10-CH_2), 1.73–1.94 (m, 2 H, 2-CH_2), 2.64 (t, *J* = 8.3 Hz, 2 H, 11-CH_2), 3.41 (t, *J* = 6.9 Hz, 1.36 H, 1-CH_2Br), 3.53 (t, *J* = 6.7 Hz, 0.64 H, 1-CH_2Cl), 7.25 (d, *J* = 7.8 Hz, 2 H, ArH), 7.32 (d, *J* = 8.4 Hz, 2 H, ArH), 7.47 (d, *J* = 8.1 Hz, 2 H, ArH), 7.75 (d, *J* = 8.2 Hz, 2 H, ArH). MS (EI, 70 eV): *m*/*z* (%) = 468 (22) [M^+, **19b**], 512 (22) [M^+, **19a**], 293 (100), 207 (30), 165 (62).
(36) To magnesium turnings (0.08 g, 3.3 mmol), activated with iodine, anhydrous THF (100 mL) was added under Ar. To this mixture, a few drops of 4-(11-bromoundecyl)-4′-pentylbiphenyl solution in THF was added. The mixture was heated to 80 °C

and a solution of 4-(11-bromoundecyl)-4′-pentylbiphenyl (**15**; 1.35 g, 2.9 mmol) was added dropwise during 1.5 h. The obtained Grignard reagent was pumped through a Teflon capillary tube into a dropping funnel under argon pressure. The Grignard reagent was then added dropwise at r.t. to a stirred degassed suspension of $PdCl_2$(dppf) catalyst (4 mol%) and 4-(11-haloundecil)-4′-iodobiphenyl (**19a**,**b**; 1.14 g, 2.2 mmol) for several minutes under Ar. The mixture was stirred for 1 h and then poured into 17% solution of ammonium chloride in water. The resulting mixture was extracted with toluene; the organic extracts were collected, washed with water, dried over Na_2SO_4, filtered, and evaporated to dryness. The crude product was recrystallized from a mixture of MeCN–CH_2Cl_2 (50%, 30 mL). Yield: 1.34 g (79%). According to HPLC analysis in combination with NMR spectroscopy (see the Supporting Information) the obtained mixture contained 33% **20b**. Mp 72–74 °C. IR (KBr): 3033, 2918, 2847, 1909, 1499, 1468, 1401, 1135, 1003, 809, 793, 763, 718, 648, 591, 516, 483 cm^{-1}. ^1H NMR ($CDCl_3$, 200 MHz): δ = 0.91 (br t, 3 H, CH_3), 1.18–1.50 [m, 32 H, $(CH_2)_{16}$], 1.65 [m, 8 H, $(CH_2)_4$], 1.86 (m, 2 H, CH_2), 2.64 [t, *J* = 7.7 Hz, 8 H, $(CH_2)_4$], 3.40 (t, *J* = 7.4 Hz, 1.41 H, CH_2), 3.53 (t, *J* = 6.6 Hz, 0.59 H, CH_2), 7.24 (d, *J* = 8.4 Hz, 8 H, ArH), 7.50 (d, *J* = 8.4 Hz, 8 H, ArH). MS (MALDI TOF): *m*/*z* = 718.5 $[M]^+$ ($C_{51}H_{71}Cl$), 757.5 $[M + K]^+$ ($C_{51}H_{71}ClK$), 764.5 $[M + 2H]^+$ ($C_{51}H_{73}Br$), 808.5 $[M+2Na]^+$ ($C_{51}H_{71}BrNa_2$), 840.5 $[M + 2K]^+$ ($C_{51}H_{71}BrK_2$).

(37) Prodanov, M. F.; Vashchenko, O. V.; Vashchenko, V. V. *Tetrahedron Lett.* **2014**, 275.