

EPR Probes with Well-Defined, Long Distances between Two or Three Unpaired Electrons

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The synthesis of rod- and star-shaped compounds carrying two or three spin labels as end groups is described. The unpaired electrons are 2.8–5.1 nm apart from each other. The shape-persistent scaffolds were obtained through Pd–Cu-catalyzed alkynyl–aryl coupling and Pd–Cu-catalyzed alkyne dimerization in the presence of oxygen using *p*-phenyleneethynylene as the basic shape-persistent building block. The spin label 1-oxyl-2,2,5,5-tetramethylpyrroline-3-carboxylic acid (**4**) was attached through esterification of the terminal phenolic OH groups of the scaffold.

Introduction

Electron paramagnetic resonance (EPR) is a versatile tool for investigating structure and dynamics of biomolecules such as proteins^{1–3} and DNA^{4,5} and of synthetic polymers.^{6–9} Important information can be obtained for example by measuring the distance between two or more radicals attached at specific sites of the macromolecule.^{3,10} To broaden the scope of such EPR techniques new pulse sequences are developed and existing sequences are improved.^{11–14} To explore the potential of new pulse sequences and to assess the upper limit of the measurable distances between unpaired electrons, well-defined compounds are highly desirable. The term “well-defined” particularly addresses the distance between the unpaired electrons. In the past, biradicals with distances of up to 2.77 nm were prepared. They are based on spacers such as tetraphenylporphyrin,¹⁵ hex-3-ene-1,5-diyne,¹⁶ dodeca-

3,9-diene-1,5,7,11-tetrayne,¹⁶ 1,4-diethynylbenzene,^{16–18} 1,4-bis(4-ethynylphenyl)butadiyne,^{16,18} or 2,6-dihydroxyanthracinone¹⁹ and the spin labels 1-oxyl-2,2,6,6-tetramethylpiperidine-4-yl,¹⁸ 1-oxyl-2,2,6,6-tetramethylazacyclohex-3-en-4-yl,^{17,18} and 1-oxyl-2,2,5,5-tetramethylpyrroline-3-yl.^{12,19} The lately developed, very efficient strategies for the preparation of monodisperse rod-shaped compounds such as oligo(*p*-phenyleneethynylene)s (oligo-PPE)^{20–22} and oligo(*p*-phenylene)s²³ with a wide range of lengths are an ideal starting point for the synthesis of well-defined biradicals with a larger spacing between the two unpaired electrons. Furthermore, these strategies offer a convenient access to molecules with architectures other than rods.^{22,24} For instance, star-shaped triradicals are required to check whether and how precisely the angle between molecular fragments with a distance in the nanometer range can be determined by EPR. Such angle measurements could finally be used to determine the relative orientation of protein subunits or dendrimer arms. Herein we report on the preparation of the biradicals **1** and **2a,b** with a spacing of 2.8–5.1 nm¹² and of the star-shaped triradical **3** with *p*-phenyleneethynylene as the building block for the spacer and 1-oxyl-2,2,5,5-tetramethylpyrroline-3-yl as the spin label.

Results and Discussion

1-Oxyl-2,2,5,5-tetramethylpyrroline-3-carboxylic acid (**4**) was selected as the spin label for reasons of avail-

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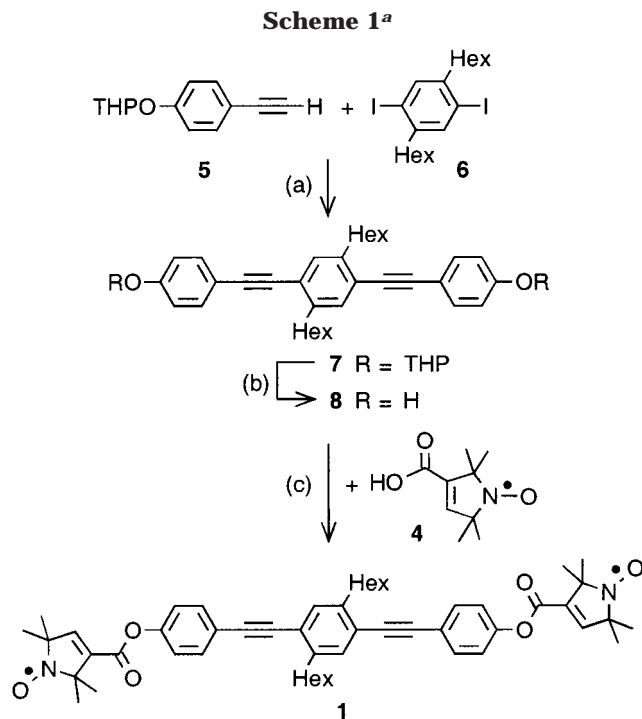
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ability, easily addressable carboxylic acid functionality, its restricted conformational flexibility, and the expected low exchange coupling. A restricted conformational flexibility is important to allow for a well-defined spacing. Hence, 3-ethynyl-1-oxyl-2,2,5,5-tetramethylpyrroline²⁵ and the corresponding six-membered-ring compound 4-ethynyl-1-oxyl-2,2,6,6-tetramethylazacyclohex-3-en²⁶ might be even better labels when attached to oligoPPEs through an alkynyl-aryl coupling.²⁷ However, if one considers the exchange coupling between the unpaired electron spins these labels are less favorable. The exchange coupling should be much smaller than the dipole-dipole coupling. Otherwise, the measurement of the distance will be more complicated and the precision that can be achieved will be lowered. Spin label **4** is expected to couple less unpaired spin density into the conjugated scaffold than the other labels mentioned above.¹⁸ Furthermore, calculations show that the error of the distance measurements by EPR is in the range or larger than the uncertainty of the spacing of the unpaired electron spins due to different conformers when using **4** as the spin label, especially for distances larger than 3 nm.¹²

A functionality that corresponds to the carboxylic acid group of the spin label **4** is the phenolic OH group. Thus, appropriate rod-shaped diphenols were prepared. The smallest diphenol **8** was obtained through an alkynyl-aryl coupling of protected monophenol **5** and diiodo compound **6** and subsequent removal of the tetrahydropyran-2-yl protecting groups from coupling product **7** (Scheme 1).²⁸

The analogous approach to longer diphenols with five or seven phenyleneethynylene units through a reaction starting from protected monophenol **13** and diiodo compound **6** should be possible. However, it is expected that separation of the intended products and the butadiynes **14**, which will be formed as byproducts,^{20,30} will be rather troublesome because of very similar polarity. Another option is the preparation of a sufficiently long oligoPPE **9** with $n = 3$ or 5, successive deprotections of the alkyne moieties and couplings with iodophenol **11**. A very different, much more straightforward approach to long, rod-shaped diphenols is the oxidative dimerization of protected monophenols **13** which yields the protected diphenols **14** that are finally O-deprotected to obtain the diphenols **15** (Scheme 2). The protected monophenols **13** were prepared through coupling of TIPS-protected oligoPPEs **10** with protected iodophenol **11** followed by the



^a Key: (a) Pd(PPh₃)₂Cl₂, CuI, Et₂NH (74%); (b) TsOH, methanol, THF (85%); (c) DCC, DMAP, THF (76%).

reaction of the obtained monofunctionalized oligoPPEs **12** with *n*-Bu₄NF in THF. Protected monophenol **13a** was also synthesized via the reaction of protected monophenol **5** with iodo compound **16** and subsequent removal of the hydroxymethyl group from coupling product **17** through treatment with MnO₂ and powdered KOH. However, in this case the overall yield is lower than with the former strategy and chromatographic purification of **17** turned out to be difficult.

The protected monophenols **13** can be dimerized through treatment with CuCl and CuCl₂ in pyridine.³¹ However, these reactions were very slow. They took several days for completion and yielded mixtures of protected diphenols **14** and partially O-deprotected diphenols. The reaction with CuCl, TMEDA in THF at air³² resulted in incomplete conversion and in the formation of side products. For the coupling reactions of alkynes **10** with iodobenzene derivatives such as **6** or **16** the alkynes **10** had been used in excess. Nevertheless, no residual alkynes **10** but their oxidative dimerization products, i.e., the butadiene derivatives, were detected in the reaction product mixture.²⁰ This observation led to the idea of using the conditions of alkynyl-aryl coupling for purposeful alkyne dimerization. Dimerization, also called homocoupling, of terminal alkynes as a side reaction in alkynyl-aryl coupling reactions in the presence of Pd complexes and CuI is well documented.^{20,30} Nonetheless, we found only a few reports on making use of these reaction conditions for alkyne dimerization.^{33–38} Chloro-

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(28) We have not tested whether unprotected 4-ethynylphenol (ref 29) can be coupled with diiodo compound **6**. Unprotected 4-ethynylphenol is reported to be very susceptible to hydration. In contrast, **5** could be stored for several month without any sign of decomposition. According to ref 29, for preparing 4-ethynylphenol from 4-iodophenol and trimethylsilylethyne (**20**) the latter reagent was used in large excess. As we found, this is necessary because first the phenol is silylated by **20** and then the resulting O-silylated 4-iodophenol reacts with **20** through alkynyl-aryl coupling. The waste of precious **20** and problems associated with the reactivity of the final compound can be avoided by using the THP-protected iodophenol.

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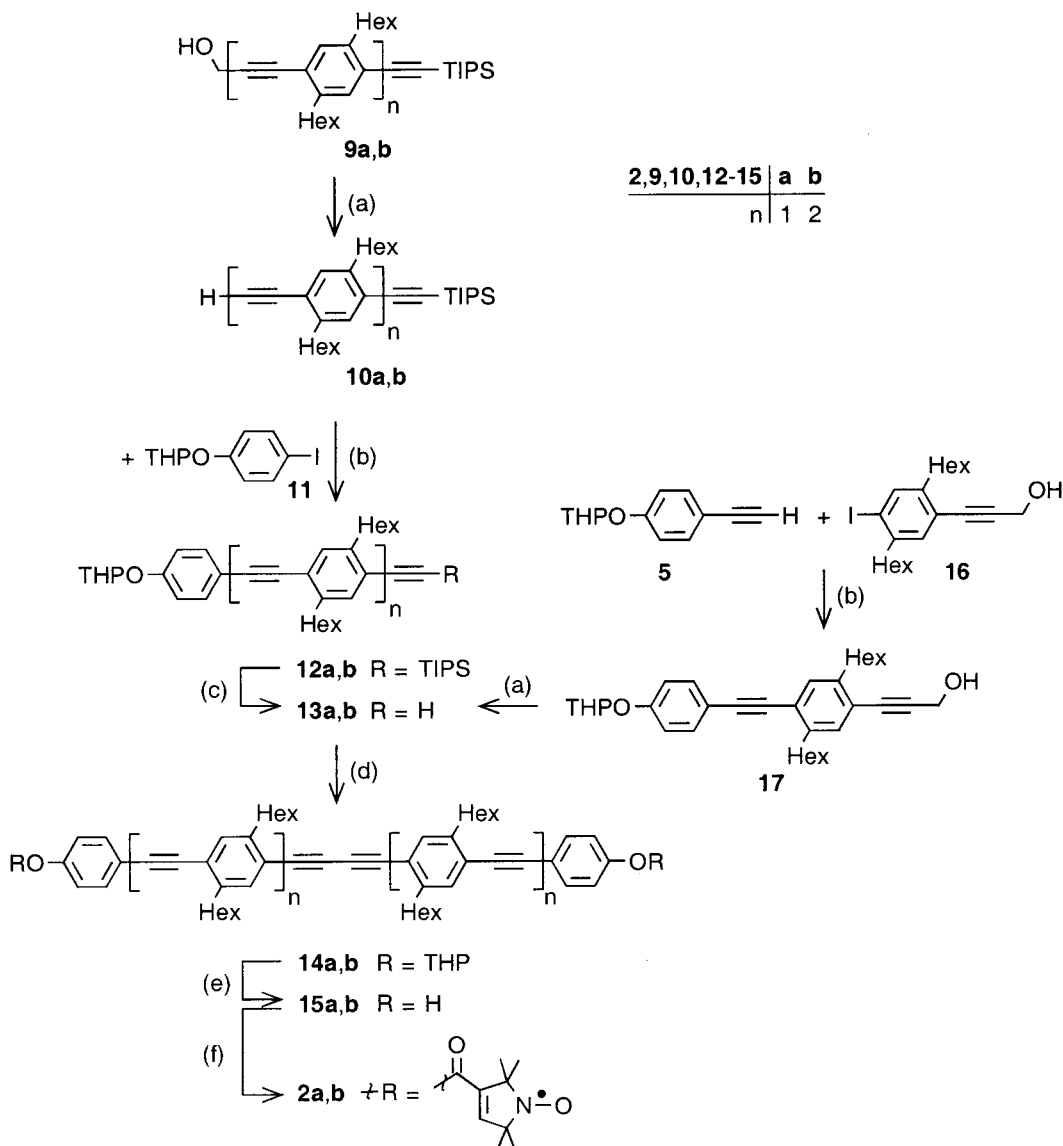
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Scheme 2^a

^a Key: (a) MnO₂, KOH, Et₂O (**10**: 75–80%, **13a**: 94%); (b) Pd(PPh₃)₂Cl₂, CuI, piperidine, THF (**12a**: 92%, **12b**: 93%, **17**: 66%); (c) *n*-Bu₄NF, THF (**13a**: 81%, **13b**: 93%); (d) Pd(PPh₃)₂Cl₂, CuI, piperidine, THF, air (**14a**: 90%, **14b**: 96%); (e) TsOH, methanol, THF (**15a**: 87%, **15b**: 71%); (f) spin label **4**, DCC, DMAP, THF (**2a**: 78%, **2b**: 48%).

acetone,³⁷ trimethylsilylethyne,³⁵ and allyl bromide³⁸ have been used as additional reagents. Intuitively more obvious reagents that have been used in addition to Pd complexes and CuI are iodine³⁶ and oxygen.^{33,34} We found that stirring a solution of the protected monophenols **13**, Pd(PPh₃)₂Cl₂ (ca. 2 mol %) and CuI (ca. 4 mol %) in THF and piperidine under air resulted in a quantitative and well-defined dimerization giving the protected diphenols **14**. As early as a few minutes after addition of the catalysts, the highly fluorescent protected diphenol **14** could be detected. This suggests that the dimerization reaction is a fast reaction. Therefore, the butadiynes found as byproducts of alkynyl–aryl coupling reactions are most probably, at least partially formed upon the workup which is carried out under air.³⁹

Treatment of protected diphenols **14** with toluenesulfonic acid in the presence of methanol gave the diphenols **15**.

For the star-shaped triradical **3** (Scheme 3), the protected monophenol **13a** was coupled with 1,3,5-triodobenzene. The product **18** was easily separated from the accompanying protected diphenol **14a** by column chromatography because of their distinctly different polarity. The triphenol **19** was obtained through treatment of **18** with toluenesulfonic acid in the presence of methanol.

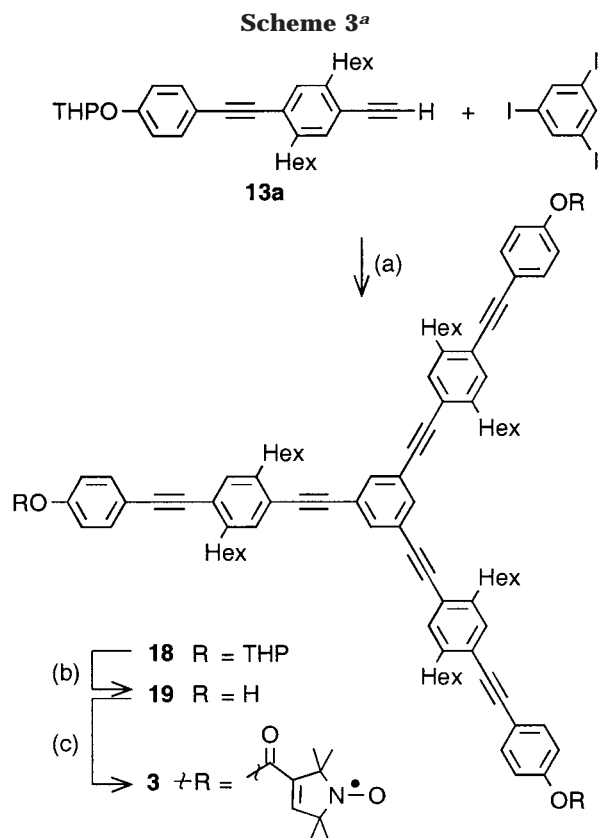
The last step in the preparation of the EPR probes is the attachment of the spin label **4** to the diphenols **8** and **15** and to the triphenol **19** (Schemes 1–3). Attachment via the acid chloride of **4**^{13,19} gave incomplete substitution. Almost quantitative⁴⁰ derivatization was achieved through reaction of the diphenols with a large excess of acid **4** in

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(40) Based on TLC and FD-MS spectra. The intensity of the FD-MS signals corresponding to **8** or **15** and the corresponding monoesterification products was 1–2% of the signal intensity of **1** and **2**.



^a Key: (a) Pd(PPh₃)₂Cl₂, CuI, piperidine, THF (87%); (b) TsOH, methanol, THF (89%); (c) spin label **4**, DCC, DMAP, THF (84%).

the presence of dicyclohexylcarbodiimide and DMAP. The products were identified by NMR spectroscopy and field desorption mass spectrometry (FD-MS).

Mass spectrometry is of special value because the signals in ¹H NMR spectra are broad and signals resulting from the spin label moiety were not detected. Usually, the most intense signal in the FD-MS spectra corresponds to M⁺. Additional, significant signals, besides the signals that are due to dicationic species, correspond to [M - 15]⁺, [M - 30]⁺, and [M + 15]⁺. Their intensity relative to the signal intensity of M⁺ varied considerably. For example, in two FD-MS spectra of diradical **2b** the signal of [M - 15]⁺ was found to reach 14% and 40% of the intensity of the M⁺ signal, respectively. Loss of one methyl group, i.e., a signal for [M - 15]⁺ is commonly found for *N*-oxyl radicals with methyl groups at the α -position to the nitrogen atom under the conditions of electron impact or chemical ionization mass spectrometry.⁴¹ The signals [M - 30]⁺ in the spectra of diradicals **1** and **2** and triradical **3** are assigned to the loss of two methyl groups, one per spin label and not to the loss of NO. This interpretation is based on the finding that the M_m⁺-signals of the monoesterification products of diphenols **8** and **15** are accompanied by signals corresponding to [M_m - 15]⁺ and [M_m + 15]⁺ but not by [M_m - 30]⁺. The signals corresponding to [M + 15]⁺ are assigned to diradicals which have added a methyl group, most probably by radical recombination of **1**, **2** or **3** with an in situ formed methyl radical and thus formation of an

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NO-C bond. The methyl transfer seems to be a rather efficient process under the conditions of FD-MS. For example, in a mass spectrum of **2a** signals for M⁺, [M - 15]⁺, [M - 30]⁺, and [M + 15]⁺ were found with intensities of 100%, 19%, 5%, and 8%, respectively. Occasionally signals of low intensity for [M - 45]⁺ and [M + 30]⁺ were detected. The former is assigned to [M - 2CH₃ - NO]⁺ and the latter to [M + 2CH₃]⁺.

From the shortest diradical **1** single crystals were obtained. X-ray structure analysis⁴² (Supporting Information) reveals a nearly coplanar arrangement of the three phenylene rings (torsion angles of 4° and 6°). The planes of the pyrroline and the phenylene rings are roughly perpendicular to each other (torsion angles of 76–109°). The carbonyl group and the N-O bond are approximately coplanar with the pyrroline ring as has been found in other derivatives of spin label **4**.⁴³ The carbonyl group and the double bond in the pyrroline ring adopt an *s*-trans conformation. The two pyrroline moieties are transoidally arranged, representing the conformer with the largest distance between the unpaired electrons ($d_{\text{N1-N1}} = 2.78$ nm, $d_{\text{O1-O1}} = 3.01$ nm). In solution a shorter distance is expected because of a rotation around the bond C_{aryl}-C_{ethynylene}⁴⁴ and deviation from the *s*-cis conformation of the ester moiety. Nevertheless, despite this conformational flexibility the distances between the unpaired electrons are rather narrowly distributed as shown by force field calculations and a Monte Carlo conformational search.¹² With the longer compounds **2** this uncertainty becomes insignificant in comparison to the experimental error.¹²

In conclusion, we have developed a convenient route to rod-shaped diphenols **8** and **15a,b** based on phenyleneethynylene as the building blocks and Pd-Cu catalyzed alkynyl-aryl and alkynyl-alkynyl coupling chemistry. Extension of this strategy gave the star-shaped triphenol **19**. These compounds were used for the preparation of the diradicals **1**, **2a,b** and the triradical **3** with distances of 2.8–5.2 nm between the unpaired electrons. Minor changes of the discussed synthetic routes will allow for the preparation of oligoPPEs with only one spin label and either a terminal aryl or alkynyl unit. Such compounds may be of interest as shape anisotropic and shape persistent spin probes. Furthermore, these compounds will enable a combination of spin- and fluorescence⁴⁵ labeling of biomolecules with the additional advantage of a rigidly attached spin label.⁵ As shown with the synthesis of the spinlabeled compounds **1**, **2a,b**, and **3**, the corresponding phenols **8**, **15a,b**, and **19** are easily derivatized and can therefore be used as photoluminescent modules for the preparation of, e.g., photoluminescent rod-coil blockcopolymers⁴⁶ and polymer additives.⁴⁷

Experimental Section

General Methods. The reactions were performed under argon unless otherwise described. Solutions for coupling

(42) The crystallographic data have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-146143. A Copy of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: (+44) 1223-336-033. E-mail: deposit@ccdc.cam.ac.uk).

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reactions were carefully degassed through several freeze–pump–thaw cycles. THF was distilled from sodium/benzophenone. The petroleum ether used had a boiling range of 30–40 °C. For flash chromatography, Merck silica gel (40–63 μm) was used. Thin-layer chromatography (TLC) was carried out on silica gel coated aluminum foils (Merck, 60F₂₅₄). Unless otherwise specified, NMR spectra were recorded at room temperature in CD₂Cl₂ as solvent and internal standard on a 300 MHz instrument. For signal assignment the carbon multiplicity was determined by a DEPT-135 experiment. The UV/vis and fluorescence spectra were recorded in CH₂Cl₂. The melting points were determined in open capillaries. The starting compounds 1-iodo-4-(tetrahydropyran-2-yloxy)benzene (**11**),⁴⁸ [4-(tetrahydropyran-2-yloxy)phenyl]ethyne (**5**),⁴⁸ 1,4-dihexyl-2,5-diiodobenzene (**6**),²⁰ and the alkynes **10a**,**b**²⁰ were prepared as described in the literature. 1-Oxyl-2,2,5,5-tetramethylpyrrolidine-3-carboxylic acid (**4**) was purchased from Acros.

Protected Diphenol 7. To a solution of diiodo compound **6** (2.00 g, 4.01 mmol) and protected monophenol **5** (1.62 g, 8.01 mmol) in diethylamine (30 mL) were added Pd(PPh₃)₂Cl₂ (56 mg, 0.08 mmol) and CuI (30 mg, 0.16 mmol). After the reaction mixture was stirred overnight at room temperature, the solvent was removed under reduced pressure. The residue was dissolved in diethyl ether and water and the aqueous phase was extracted with diethyl ether. The combined organic phases were washed with saturated aqueous NH₄Cl, dried (Na₂SO₄) and concentrated in vacuo. Flash chromatography (petroleum ether/CH₂Cl₂ 2:1 v/v; *R_f* = 0.10) gave **7** as an offwhite solid (1.9 g, 74%). Mp: 141.5–142.8 °C. ¹H NMR: δ 7.46 (half of AA'XX', 4 H, H meta to OTHP), 7.35 (s, 2 H, C₆H₂), 7.05 (half of AA'XX', 4 H, H ortho to OTHP), 5.45 (t, *J* = 3.2 Hz, 2 H, O₂CH), 3.87 and 3.62 (2 m, 2 H each, OCH₂), 2.81 (m, 4 H, ArCH₂), 2.1–1.2 (m, 28 H, CH₂), 0.88 (t, *J* = 7.0 Hz, 6 H, CH₃). ¹³C NMR: δ 157.8 (C_{Ar}-O), 142.5 (C_{Ar}-Hex), 133.1 (CH meta to OTHP), 132.5 (CH of C₆H₂), 123.0 (C_{Ar}-C≡C of C₆H₂), 117.0 (CH ortho to OTHP), 116.8 (C_{Ar}-C≡C of C₆H₄), 96.9 (O₂CH), 94.3 and 87.6 (C≡C), 62.5 (OCH₂), 34.5, 32.2, 31.1, 30.7, 29.7, 25.6, 23.1 and 19.2 (CH₂), 14.3 (CH₃). Anal. Calcd for C₄₄H₅₄O₄ (646.912): C, 81.69; H, 8.41. Found: C, 81.68; H, 8.51.

Diphenol 8. To a solution of **7** (900 mg, 1.39 mmol) in methanol (30 mL) and THF (40 mL) was added *p*-toluenesulfonic acid monohydrate (27 mg, 0.14 mmol). After 4 h at room temperature, the reaction mixture was cooled with an ice bath, and water was added. The product was extracted into diethyl ether. The combined organic phases were washed with brine, dried (Na₂SO₄) and concentrated in vacuo. Flash chromatography (petroleum ether/diethyl ether 1:1 v/v; *R_f* = 0.26) gave **8** (563 mg, 85%) as an offwhite solid. Mp: 159.2–159.9 °C. ¹H NMR (CDCl₃): δ 7.41 (half of AA'XX', 4 H, H meta to OH), 7.32 (s, 2 H, C₆H₂), 6.81 (half of AA'XX', 4 H, H ortho to OH), 4.84 (s, 2 H, OH), 2.77 (m, 4 H, ArCH₂), 1.67 (m, 4 H, CH₂), 1.5–1.2 (m, 12 H, CH₂), 0.87 (t, *J* = 7.0 Hz, 6 H, CH₃). ¹³C NMR (CDCl₃): δ 155.6 (C_{Ar}-O), 142.0 (C_{Ar}-Hex), 133.1 (CH meta to OH), 132.1 (CH of C₆H₂), 122.5 (C_{Ar}-C≡C of C₆H₂), 116.1 (C_{Ar}-C≡C of C₆H₄), 115.5 (CH ortho to OH), 93.6 and 87.2 (C≡C), 34.1, 31.8, 30.6, 29.2 and 22.6 (CH₂), 14.1 (CH₃). UV/vis: λ_{max} [nm] (ϵ [10⁶ cm² mol⁻¹]) = 313 (38.7; shoulder), 333 (55.9), 352 (40.5; shoulder). Emission ($\lambda_{\text{excitation}}$ = 330 nm): λ = 363 (maximum), 382 nm. Anal. Calcd for C₃₄H₃₈O₂ (478.676): C, 85.31; H, 8.00. Found: C, 84.00; H, 8.22. FD-MS: *m/z* = 956.5 (6%, [2M]⁺), 478.1 (100%, M⁺), 239.1 (24%, M²⁺).

Diradical 1.⁴⁹ To a cooled (ice bath) solution of **8** (200 mg, 0.42 mmol), spin label **4** (230 mg, 1.25 mmol), and DMAP (171

mg, 1.40 mmol) in THF (6 mL) was added *N,N*-dicyclohexylcarbodiimide (258 mg, 1.25 mmol). The reaction mixture was stirred at room temperature for 20 h. The precipitate was filtered off and washed with diethyl ether and THF until the solid was colorless. The yellow filtrate was washed with 2 N HCl and subsequently with brine. The solution was dried (MgSO₄) and concentrated in vacuo. Flash chromatography (petroleum ether/diethyl ether 1:2 v/v; *R_f* = 0.52; The crude product was dissolved in a small amount of warm CH₂Cl₂ and applied in this form to the column.⁵⁰) gave diradical **1** (256 mg, 76%) as a yellow solid tenaciously including methylene chloride which had been used for the transfer of the material. An intensely yellow colored compound of unidentified structure was eluted first (*R_f* = 0.83). Crystals for X-ray analysis were obtained by recrystallization in ethanol containing a small amount of ethyl acetate. Mp (from ethanol/ethyl acetate): 176.7–178.0 °C. ¹H NMR: all signals are broad and structureless δ 7.63 (4 H), 7.42 (2 H), 7.21 (very broad, 4 H), 2.86 (4 H), 1.74 (4 H), 1.38 (15 H), 0.92 (6 H). ¹³C NMR: δ 148.4 (broad; C_{Ar}-O), 141.8 (C_{Ar}-Hex), 132.0 and 131.7 (C_{Ar}H), 121.8 (C_{Ar}-C≡C), 121.6 (CH ortho to OH), 120.7 (C_{Ar}-C≡C), 92.3 and 87.9 (C≡C), 33.4, 31.1, 30.0, 28.5, and 22.0 (CH₂), 13.2 (CH₃). UV/vis: λ_{max} [nm] (ϵ [10⁶ cm² mol⁻¹]) = 314 (46.9; shoulder), 332 (59.4), 350 (43.0; shoulder). Emission ($\lambda_{\text{excitation}}$ = 320 nm): λ = 366, 385 nm (maximum). Anal. Calcd for C₅₂H₆₂N₂O₆ (811.076) (recrystallized from ethanol/ethyl acetate): C, 77.00; H, 7.71; N, 3.45. Found: C, 77.17; H, 7.68; N, 3.64. FD-MS: *m/z* = 826.3 (20%, [M + CH₃]⁺), 811.2 (100%, M⁺), 796.2 (20%, [M - CH₃]⁺), 645.0 (3%, M⁺ of monoesterification product), 405.8 (23, M²⁺).

Monofunctionalized OligoPPE 12a. To a solution of alkyne **10a** (863 mg, 1.91 mmol) and 1-iodo-4-(tetrahydropyran-2-yloxy)benzene (**11**) (529 mg, 1.74 mmol) in THF (15 mL) and piperidine (5 mL) were added PdCl₂(PPh₃)₂ (13 mg, 0.02 mmol) and CuI (7 mg, 0.04 mmol) at room temperature. The reaction was stirred at room temperature for 21 h. The suspension was cooled (ice bath), and diethyl ether and water were added. The aqueous phase was extracted with diethyl ether. The combined organic phases were washed successively with water, saturated aqueous NH₄Cl, water, and brine and dried (Na₂SO₄). The solvent was removed in vacuo. Flash chromatography (petroleum ether/CH₂Cl₂ 2:1 v/v, *R_f* = 0.62) gave **12a** (1.0 g, 92%) as a pale yellow oil. ¹H NMR: δ 7.45 (half of AA'XX', 2 H, H meta to OTHP), 7.32 and 7.30 (2 s, 1 H each, C₆H₂), 7.04 (half of AA'XX', 2 H, H ortho to OTHP), 5.44 (t, *J* = 3.2 Hz, 1 H, O₂CH), 3.87 and 3.59 (2 m, 1 H each, OCH₂), 2.77 (m, 4 H, ArCH₂), 2.1–1.2 (m, 22 H, CH₂), 1.16 (s, 21 H, CH(CH₃)₂), 0.89 (m, 6 H, CH₃). ¹³C NMR: δ 157.8 (C_{Ar}-O), 143.1 and 142.5 (C_{Ar}-Hex), 133.3 (CH of C₆H₂), 133.2 (CH meta to OTHP), 132.4 (CH of C₆H₂), 123.4 and 122.9 (C_{Ar}-C≡C of C₆H₂), 117.0 (CH ortho to OTHP), 116.8 (C_{Ar}-C≡C of C₆H₄), 106.2 (C≡C-TIPS), 96.9 (O₂CH), 95.6 (C≡C-TIPS), 94.4, and 87.5 (ArC≡CAr), 62.6 (OCH₂), 34.8, 34.5, 32.3, 32.2, 31.3, 31.2, 30.7, 29.8, 29.7, 25.6, 23.1, and 19.2 (CH₂), 18.9 (CH(CH₃)₂), 14.2 (CH₂CH₃), 11.9 (SiCH). Anal. Calcd for C₄₂H₆₂O₂-Si (627.042): C, 80.45; H, 9.97. Found: C, 80.29; H, 9.91.

Compound 17. To a solution of protected monophenol **5** (2.72 g, 13.5 mmol) and iodo compound **16** (5.00 g, 11.7 mmol) in piperidine (20 mL) and THF (160 mL) were added PdCl₂(PPh₃)₂ (86 mg, 0.12 mmol) and CuI (44 mg, 0.23 mmol) at room temperature. The reaction mixture was stirred overnight. Aqueous workup as described for **12a** followed by flash chromatography (petroleum ether/CH₂Cl₂ 1:1 v/v; *R_f* = 0.09) gave **17** (3.9 g, 66%) as a slightly beige colored solid. Mp: 65.5–66.5 °C. ¹H NMR: δ 7.45 (half of AA'XX', 2 H, H meta to OTHP), 7.32 and 7.27 (2 s, 1 H each, C₆H₂), 7.04 (half of AA'XX', 2 H, H ortho to OTHP), 5.44 (t, *J* = 3.2 Hz, 1 H, O₂-CH), 4.51 (br s, 2 H, CH₂OH), 3.87 and 3.59 (2 m, 1 H each,

(46) E.g.: Kukulka, H.; Ziener, U.; Schöps, M.; Godt, A. *Macromolecules* **1998**, *31*, 5160. Benfaremo, N.; Sandman, D. J.; Tripathy, S.; Kumar, J.; Yang, K.; Rubner, M. F.; Lyons, C. *Macromolecules* **1998**, *31*, 3595. Francke, V.; Räder, H. J.; Geerts, Y.; Müllen, K. *Macromol. Rapid Commun.* **1998**, *19*, 275. Tew, G. N.; Li, L.; Stupp, S. I. *J. Am. Chem. Soc.* **1998**, *120*, 5601. Jenekhe, S., A.; Chen, X. L. *Science* **1999**, *283*, 372.

(47) Palmans, A. R. A.; Eglin, M.; Montali, A.; Weder, C.; Smith, P. *Chem. Mater.* **2000**, *12*, 472.

(48) Godt, A. *J. Org. Chem.* **1997**, *62*, 7471.

(49) This is an improved procedure in comparison to the one given in ref 13.

(50) The diradicals were found to be labile when adsorbed onto silica gel. E.g., preparation of **1** as described, however applying the crude product adsorbed on silica gel (This freely flowing powder was obtained by dissolving the compound in CH₂Cl₂, adding some silica gel to this solution, and removing the solvent in vacuo) to a silica gel column resulted in a yield of only 12%.

CH₂CH₂O), 2.74 (m, 4 H, ArCH₂), 2.1–1.2 (m, 22 H, CH₂), 0.89 (m, 6 H, CH₃). ¹³C NMR: δ = 157.8 (C_{Ar}-O), 142.8 and 142.5 (C_{Ar}-Hex), 133.2 (CH meta to OTHP), 132.9 and 132.4 (CH of C₆H₂), 123.5 and 122.1 (C_{Ar}-C≡C of C₆H₂), 117.0 (CH ortho to OTHP), 116.7 (C_{Ar}-C≡C of C₆H₄), 96.9 (O₂CH), 94.4, 92.3, 87.4 and 84.5 (C≡C), 62.6 (CH₂CH₂O), 52.0 (CH₂OH) 34.5, 34.2, 32.2, 32.1, 31.0, 30.9, 30.7, 29.6, 29.5, 25.6, 23.05, 23.03 and 19.2 (CH₂), 14.3 (CH₃). Anal. Calcd for C₃₄H₄₄O₃ (500.723): C, 81.56; H, 8.86. Found: C, 81.63; H, 8.87.

Protected Monophenol 13a from 17. To a solution of **17** (3.88 g, 7.75 mmol) in diethyl ether (150 mL) were added a mixture of MnO₂ (10.8 g, 31 mmol) and powdered KOH (0.87 g, 15.5 mmol) in four portions over a period of 4 h.⁵¹ The reaction was monitored by TLC (petroleum ether/diethyl ether 6:1 v/v, R_f(**17**) = 0.08, R_f(**13a**) = 0.49). Filtration over silica gel with diethyl ether as solvent gave **13a** (3.5 g, 94%) as a colorless solid.

Protected Monophenol 13a from 12a. To a solution of **12a** (825 mg, 1.32 mmol) in THF (30 mL) was added 1 M *n*-Bu₄NF (2.6 mL, 2.6 mmol) in THF at room temperature. After 1.5 h, diethyl ether and then water was added. The aqueous phase was extracted with diethyl ether. The combined organic phases were washed with brine, dried (MgSO₄) and concentrated in vacuo. Recrystallization of the residual solid in methanol (40 mL) gave **13a** as a colorless solid (501 mg, 81%). Mp: 58.3–59.6 °C. ¹H NMR: δ 7.45 (half of AA'XX', 2 H, H meta to OTHP), 7.33 and 7.32 (2 s, 1 H each, C₆H₂), 7.04 (half of AA'XX', 2 H, H ortho to OTHP), 5.44 (t, *J* = 3.1 Hz, 1 H, O₂CH), 3.86 and 3.59 (2 m, 1 H each, OCH₂), 3.35 (s, 1 H, C∞CH), 2.76 (m, 4 H, ArCH₂), 2.1–1.2 (m, 22 H, CH₂), 0.89 (m, 6 H, CH₃). ¹³C NMR: δ 157.8 (C_{Ar}-O), 143.3 and 142.5 (C_{Ar}-Hex), 133.4 (CH of C₆H₂), 133.2 (CH meta to OTHP), 132.4 (CH of C₆H₂), 123.9 and 121.5 (C_{Ar}-C≡C of C₆H₂), 117.0 (CH ortho to OTHP), 116.7 (C_{Ar}-C≡C of C₆H₄), 96.9 (O₂CH), 94.5, 87.3, 82.8, 81.7 (C≡C), 62.5 (OCH₂), 34.5, 34.2, 32.2, 32.1, 31.0, 30.9, 30.7, 29.6, 29.5, 25.6, 23.05, 23.02 and 19.2 (CH₂), 14.3 (CH₃). Anal. Calcd for C₃₃H₄₂O₂ (470.697): C, 84.21; H, 8.99. Found: C, 84.29; H, 9.01.

Protected Diphenol 14a. To a solution of **13a** (500 mg, 1.06 mmol) in THF (19 mL) and piperidine (4.7 mL) were added PdCl₂(PPh₃)₂ (11 mg, 0.02 mmol) and CuI (7 mg, 0.04 mmol) at room temperature. The reaction mixture was stirred under air for 3.5 h. The reaction was monitored by TLC (petroleum ether/diethyl ether 5:1 v/v, R_f(**14a**) = 0.41, R_f(**13a**) = 0.59). Dichloromethane and then water were added. The aqueous phase was extracted with CH₂Cl₂. The combined organic phases were washed with saturated aqueous NH₄Cl and dried (MgSO₄). The solvent was removed in vacuo. Filtration over silica gel (CH₂Cl₂; R_f = 0.69) gave **14a** (451 mg, 90%) as an offwhite solid. Mp: 136.7–137.7 °C. ¹H NMR: δ 7.46 (half of AA'XX', 4 H, H meta to OTHP), 7.37 and 7.35 (2 s, 2 H each, C₆H₂), 7.05 (half of AA'XX', 4 H, H ortho to OTHP), 5.45 (t, *J* = 3.1 Hz, 2 H, O₂CH), 3.87 and 3.60 (2 m, 2 H each, OCH₂), 2.78 (m, 8 H, ArCH₂), 2.1–1.2 (m, 44 H, CH₂), 0.90 (m, 12 H, CH₃). ¹³C NMR: δ 157.9 (C_{Ar}-O), 143.2 and 142.6 (C_{Ar}-Hex), 133.6 (CH of C₆H₂), 133.2 (CH meta to OTHP), 132.5 (CH of C₆H₂), 124.4 (C-C≡C-C≡C), 121.1 (C_{Ar}-C≡C of C₆H₂), 117.0 (CH ortho to OTHP), 116.6 (C_{Ar}-C≡C of C₆H₄), 96.9 (O₂CH), 95.2 and 87.4 (ArC≡CAr), 82.1 (C≡C-C≡C), 78.5 (C≡C-C≡C), 62.5 (OCH₂), 34.5, 34.4, 32.2, 32.1, 31.0, 30.9, 30.7, 29.6, 29.5, 25.6, 23.0, and 19.2 (CH₂), 14.3 (CH₃). Anal. Calcd for C₆₆H₈₂O₄ (939.378): C, 84.39; H, 8.80. Found: C, 84.46; H, 8.88.

Diphenol 15a. The procedure for the preparation of diphenol **8** was followed. The reaction of protected diphenol **14a** (2.94 g, 3.13 mmol) with toluenesulfonic acid monohydrate (720 mg, 3.8 mmol) in THF (340 mL) and methanol (130 mL) gave after flash chromatography (CH₂Cl₂, R_f = 0.21) diphenol **15a** (2.1 g, 87%) as a pale yellow solid containing tetrahydropyran-2-yl-methyl ether (ca. 7 mol %).⁵² This product was used without further purification for the preparation of diradical **2a**. Re-

crystallization in ethanol (30 mL for 1.37 g of **15a**) gave analytically pure **15a** as a pale yellow solid. Mp: 119.3–121.4 °C. ¹H NMR: δ 7.43 (half of AA'XX', 4 H, H meta to OH), 7.37 and 7.34 (2 s, 2 H each, C₆H₂), 6.85 (half of AA'XX', 4 H, H ortho to OH), 5.21 (s, 2 H, OH), 2.78 (m, 8 H, ArCH₂), 1.68 (m, 8 H, CH₂), 1.36 (m, 24 H, CH₂), 0.89 (m, 12 H, CH₃). ¹³C NMR: δ 156.5 (C_{Ar}-O), 144.2 and 142.6 (C_{Ar}-Hex), 133.64 (CH of C₆H₂), 133.57 (CH meta to OH), 132.5 (CH of C₆H₂), 124.3 (C_{Ar}-C≡C-C≡C), 121.1 (C_{Ar}-C≡CAr of C₆H₂), 116.0 (CH ortho to OH); Most probably this signal covers up the signal of C-C≡C of C₆H₄), 95.0 and 87.2 (ArC≡CAr), 82.1 (C≡C-C≡C), 78.5 (C≡C-C≡C), 34.4, 34.3, 32.2, 32.1, 31.0, 30.9, 29.6, 29.5, and 23.0 (CH₂), 14.29 and 14.25 (CH₃). UV/vis: λ_{max} [nm] (ε [10⁶ cm² mol⁻¹]) = 338 (54.2; shoulder), 357 (83.1), 385 (62.2). Emission (λ_{excitation} = 360 nm): λ = 403 (maximum), 427 nm. Anal. Calcd for C₅₆H₆₆O₂ (771.142): C, 87.22; H, 8.63. Found: C, 87.17; H, 8.68.

Diradical 2a. The procedure for the preparation of diradical **1** was followed, however with a reaction time of 3 d. The reaction of **15a** (300 mg, 0.39 mmol) with spin label **4** (215 mg, 1.17 mmol) in the presence of *N,N*-dicyclohexylcarbodiimide (241 mg, 1.17 mmol) and DMAP (157 mg, 1.29 mmol) in THF (7 mL) gave after flash chromatography (petroleum ether/diethyl ether 1:1 v/v; R_f = 0.32)⁵⁰ diradical **2a** (335 mg, 78%) as a yellow solid. Mp: 164.0–164.8 °C. ¹H NMR: δ 7.61 (br s, 4 H, H meta to OR), 7.40 (s, 4 H, C₆H₂), 7.24 (very broad, 4 H, H ortho to OR), 2.80 (m, 8 H, ArCH₂), 1.69 (br s, 8 H, CH₂), 1.6–1.2 (m, 24 H, CH₂), 0.89 (m, 12 H, CH₃). ¹³C NMR: δ 148.8 (C_{Ar}-O), 143.4 and 142.0 (C_{Ar}-Hex), 132.9, 133.2, 131.9 (C_{Ar}-H), 122.9 (C_{Ar}-C≡C), 121.8 (broad, CH ortho to OR), 120.8 (C_{Ar}-C≡C); This signal splits into two when the compound is measured in CDCl₃), 93.2 and 88.0 (ArC≡CAr), 81.2 (C≡C-C≡C), 77.8 (C≡C-C≡C), 33.6, 33.5, 31.3, 31.24, 31.20, 30.1, 28.7, 28.6, and 22.2 (CH₂), 13.5 (CH₃). UV/vis: λ_{max} [nm] (ε [10⁶ cm² mol⁻¹]) = 286 (31.8), 338 (66.1; shoulder), 354 (91.7), 383 (64.9). Emission (λ_{excitation} = 355 nm): λ = 399 (maximum), 423 nm. Anal. Calcd for C₇₄H₉₀N₂O₆ (1103.542): C, 80.54; H, 8.22; N, 2.54. Found: C, 80.50; H, 8.26; N, 2.46. FD-MS: *m/z* = 1118.1 (7%, [M + CH₃]⁺), 1103.1 (100%, M⁺), 1088.1 (19%, [M - CH₃]⁺), 1073.6 (6%, [M - 2CH₃]⁺), 938.0 (1%, M⁺ of monoesterification product), 559.1 (3%, [M + CH₃]²⁺), 551.5 (17%, M²⁺).

Monofunctionalized OligoPPE 12b. To a solution of **10b** (2.25 g, 3.13 mmol) and 1-iodo-4-(tetrahydropyran-2-yloxy)benzene (**11**) (864 mg, 2.84 mmol) in THF (25 mL) and piperidine (8 mL) were added PdCl₂(PPh₃)₂ (20 mg, 0.03 mmol) and CuI (11 mg, 0.06 mmol) at 0 °C. The reaction mixture was stirred for 6 h at room temperature. Aqueous workup as described for **12a** followed by flash chromatography (petroleum ether/CH₂Cl₂ 4:1 v/v; R_f = 0.41) gave **12b** (2.4 g, 93%) as a pale yellow oil. ¹H NMR: δ 7.46 (half of AA'XX', 2 H, H meta to OTHP), 7.36 (s, 2 H, C₆H₂), 7.34 and 7.32 (2 s, 1 H each, C₆H₂), 7.05 (half of AA'XX', 2 H, H ortho to OTHP), 5.45 (t, *J* = 3.1 Hz, 1 H, O₂CH), 3.87 and 3.60 (2 m, 1 H each, OCH₂), 2.80 (m, 8 H, ArCH₂), 2.1–1.2 (m, 38 H, CH₂), 1.16 (s, 21 H, CH(CH₃)₂), 0.88 (m, 12 H, CH₂CH₃). ¹³C NMR: δ 157.8 (C_{Ar}-O), 143.1, 142.6, 142.44 and 142.36 (C_{Ar}-Hex), 133.3 (CH of C₆H₂), 133.2 (CH meta to OTHP), 132.82, 132.77 and 132.5 (CH of C₆H₂), 123.4, 123.3, 123.2 and 122.9 (C_{Ar}-C≡C of C₆H₂), 117.0 (CH ortho to OTHP), 116.8 (C_{Ar}-C≡C of C₆H₄), 106.2 (C≡C-TIPS), 96.9 (O₂CH), 95.8 (C≡C-TIPS), 94.5, 93.4, 93.2, and 87.6 (ArC≡CAr), 62.6 (OCH₂), 34.8, 34.6, 32.3, 32.2, 31.3, 31.2, 31.14, 31.08, 30.7, 29.8, 29.72, 29.68, 25.6, 23.1, 19.2 (CH₂), 18.9 (CH(CH₃)₂), 14.3 (CH₂CH₃), 11.9 (SiCH). Anal. Calcd for C₆₂H₉₀O₂Si (895.486): C, 83.16; H, 10.13. Found: C, 83.25; H, 10.12.

Protected Monophenol 13b. To a solution of **12b** (2.10 g, 2.35 mmol) in THF (40 mL) was added 1 M *n*-Bu₄NF (4.5 mL, 4.5 mmol) in THF at room temperature. The reaction mixture turned instantaneously dark red. After 3 h, diethyl ether and subsequently water were added. The aqueous phase was extracted with diethyl ether. The combined organic phases

(51) If the reaction is not complete, more MnO₂/KOH is added: see description in ref 20.

(52) Characteristic ¹H NMR signals of tetrahydropyran-2-yl-methyl ether: δ (CDCl₃) = 4.52 (t, 1H), 3.86 (m, 1H), 3.53 (m, 1H), 3.40 (s, 3H).

were washed with brine and dried (MgSO₄). The solvent was removed in vacuo. The residual, slightly red oil turned violet by storing overnight at room temperature in vacuo. To this violet oil was added methanol (10 mL). The methanol solution was removed from the oil with a pipet. Dissolving the residue again in methanol (30 mL) under heating gave, upon cooling to room temperature, **13b** as a violet solid (1.6 g, 93%). Mp: 43.4–43.6 °C. ¹H NMR: δ 7.46 (half of AA'XX', 2 H, H meta to OTHP), 7.37 (s, 2 H, C₆H₂), 7.36 and 7.34 (2 s, 1 H each, C₆H₂), 7.05 (half of AA'XX', 2 H, H ortho to OTHP), 5.45 (t, *J* = 3.1 Hz, 1 H, O₂CH), 3.87 and 3.60 (2 m, 1 H each, OCH₂), 3.37 (s, 1 H, C≡CH), 2.80 (m, 8 H, ArCH₂), 2.1–1.2 (m, 38 H, CH₂), 0.89 (m, 12 H, CH₃). ¹³C NMR: δ 157.8 (C_{Ar}-O), 143.3, 142.6, 142.5 and 142.4 (C_{Ar}-Hex), 133.4 (CH of C₆H₂), 133.2 (CH meta to OTHP), 132.84, 132.77 and 132.5 (CH of C₆H₂), 123.8, 123.5, 122.8 and 121.8 (C_{Ar}-C≡C of C₆H₂), 117.0 (CH ortho to OTHP), 116.8 (C_{Ar}-C≡C of C₆H₄), 96.9 (O₂CH), 94.5, 93.5, 93.0, and 87.5 (ArC≡CAr), 82.7 and 81.9 (C≡CH), 62.6 (OCH₂), 34.6, 34.5, 34.2, 32.3, 32.24, 32.21, 32.1, 31.14, 31.08, 30.9, 30.7, 29.7, 29.6, 29.5, 25.6, 23.1, 23.0, 19.2 (CH₂), 14.3 (CH₃). Anal. Calcd for C₅₃H₇₀O₂ (739.141): C, 86.12; H, 9.55. Found: C, 86.13; H, 9.53.

Protected Diphenol 14b. To a solution of **13b** (900 mg, 1.22 mmol) in THF (20 mL) and piperidine (5 mL) were added PdCl₂(PPh₃)₂ (13 mg, 0.02 mmol) and CuI (7 mg, 0.04 mmol) at room temperature. The reaction mixture was stirred under air for 3 h. The reaction was monitored by TLC (petroleum ether/diethyl ether 5:1 v/v, *R_f*(**14b**) = 0.48, *R_f*(**13b**) = 0.61). Diethyl ether and then water were added. Upon standing overnight a precipitate formed which was dissolved by addition of THF, diethyl ether, and CH₂Cl₂ (probably, workup with only CH₂Cl₂ is the best choice). The organic phase was washed with saturated aqueous NH₄Cl and brine and dried (MgSO₄). The solvent was removed in vacuo. Filtration over silica gel (CH₂-Cl₂; *R_f* = 0.84) gave **14b** (863 mg, 96%) as an intensely yellow colored solid. Mp: 120.7–121.6 °C. ¹H NMR: δ 7.46 (half of AA'XX', 4 H, H meta to OTHP), 7.40 and 7.38 (2 s, 2 H each, C₆H₂), 7.37 (s, 4 H, C₆H₂), 7.05 (half of AA'XX', 4 H, H ortho to OTHP), 5.45 (t, *J* = 3.1 Hz, 2 H, O₂CH), 3.88 and 3.60 (2 m, 2 H each, OCH₂), 2.81 (m, 16 H, ArCH₂), 2.1–1.2 (m, 76 H, CH₂), 0.89 (m, 24 H, CH₃). ¹³C NMR: δ 157.8 (C_{Ar}-O), 144.3, 142.6, and 142.5 (C_{Ar}-Hex), 133.7 (CH of C₆H₂), 133.2 (CH meta to OTHP), 132.9 and 132.5 (CH of C₆H₂), 124.3 (C_{Ar}-C≡C-C≡C), 123.6, 122.7, and 121.5 (C_{Ar}-C≡CAr of C₆H₂), 117.0 (CH ortho to OTHP), 116.7 (C-C≡C of C₆H₄), 96.9 (O₂CH), 94.6, 94.3, 93.0, and 87.5 (ArC≡CAr), 82.2 (C≡C-C≡C), 78.6 (C≡C-C≡C), 62.6 (OCH₂), 34.6, 34.4, 32.2, 32.1, 31.1, 30.7, 29.7, 29.5, 25.6, 23.1, 19.2 (CH₂), 14.3 (CH₃). Anal. Calcd for C₁₀₆H₁₃₈O₄ (1476.266): C, 86.24; H, 9.42. Found: C, 86.55; H, 9.54.

Diphenol 15b. The procedure for the preparation of diphenol **8** was followed, however with a longer reaction time of 19 h. The reaction was monitored by TLC (CH₂Cl₂; *R_f*(**15b**) = 0.12, *R_f*(**14b**) = 0.84). The reaction of **14b** (749 mg, 0.51 mmol) with toluenesulfonic acid monohydrate (20 mg, 0.11 mmol) in THF (40 mL) and methanol (15 mL) gave after flash chromatography (petroleum ether/diethyl ether 1:2 v/v; *R_f* = 0.48) diphenol **15b** (578 mg, 87%) containing tetrahydropyran-2-ylmethyl ether (ca. 3 mol %).⁵² The latter was removed by recrystallization in ethanol (7 mL) giving **15b** (473 mg, 71%) as an intensely yellow solid. Most probably, chromatography can be omitted because tetrahydropyran-2-yl-methyl ether is the only other product of the reaction. Mp: 157.7–159.0 °C. ¹H NMR: δ 7.43 (half of AA'XX', 4 H, H meta to OH), 7.40, 7.38, 7.37, and 7.36 (4 s, 2 H each, C₆H₂), 6.85 (half of AA'XX', 4 H, H ortho to OH), 5.20 (br s, 2H, OH), 2.81 (m, 16 H, ArCH₂), 1.70 (m, 16 H, CH₂), 1.34 (m, 48 H, CH₂), 0.88 (m, 24 H, CH₃). ¹³C NMR: δ 156.5 (C_{Ar}-O), 144.2, 142.6, 142.5 (C_{Ar}-Hex), 133.7 (CH of C₆H₂), 133.5 (CH meta to OH), 132.8, and 132.5 (CH of C₆H₂), 124.3 (C_{Ar}-C≡C-C≡C), 123.5, 122.7 and 121.4 (C_{Ar}-C≡CAr of C₆H₂), 116.1 (C_{Ar}-C≡C of C₆H₄), 116.0 (CH ortho to OH), 94.4, 94.2, 93.0, and 87.4 (ArC≡CAr), 82.2 (C≡C-C≡C), 78.6 (C≡C-C≡C), 34.52, 34.48, 34.36, 32.24, 32.19, 32.08, 31.13, 30.06, 30.99, 29.7, 29.5, 23.1, (CH₂), 14.3 (CH₃). UV/vis: λ_{max} [nm] (ε [10⁶ cm² mol⁻¹]) = 314 (38.1; shoulder), 382 (139.4),

401 (99.1). Emission (λ_{excitation} = 375 nm): λ = 419 (maximum), 446 nm. Anal. Calcd for C₉₆H₁₂₂O₂(1308.030): C, 88.15; H, 9.40. Found: C, 87.51; H, 9.46. FD-MS: *m/z* = 1308.9 (65%, M⁺), 811.1 (7%), 654.6 (100%, M²⁺).

Diradical 2b. The procedure for the preparation of diradical **1** was followed, however with a reaction time of 29 h. The reaction of **15b** (150 mg, 0.115 mmol) with spin label **4** (63 mg, 0.34 mmol) in the presence of *N,N*-dicyclohexylcarbodiimide (71 mg, 0.34 mmol) and DMAP (46 mg, 0.38 mmol) in THF (4 mL) gave after flash chromatography (petroleum ether/diethyl ether 1:1 v/v; *R_f* = 0.40; The crude material had been adsorbed onto silica gel prior to chromatography⁵⁰) diradical **2b** (91 mg, 48%) as a yellow solid. An intensely yellow colored compound of unidentified structure (20 mg) was eluted first. Mp: 148.0–148.7 °C. ¹H NMR: δ 7.61 (br s, 4 H, H meta to OR), 7.41 (s, 4 H, C₆H₂), 7.40 and 7.39 (2 s, 2 H each, C₆H₂), 7.2 (very broad, H ortho to OR), 2.84 (m, 16 H, ArCH₂), 1.71 (m, 16 H, CH₂), 1.6–1.2 (m, 50 H, CH₂), 0.89 (m, 24 H, CH₃). ¹³C NMR: δ 149.0 (C_{Ar}-O), 143.7, 142.3, 142.01, 141.98 (C_{Ar}-Hex), 133.1, 132.5, 132.4, 132.3, and 132.2 (C_{Ar}H), 123.7, 122.7, and 122.3 (C_{Ar}-C≡C), 122.0 (broad, CH ortho to OR), 121.2 and 121.0 (C_{Ar}-C≡C), 93.5, 92.9, 92.7, and 88.5 (ArC≡CAr), 81.6 (C≡C-C≡C), 78.1 (C≡C-C≡C), 34.0, 33.9, 33.8, 31.68, 31.67, 31.63, 31.5, 30.6, 30.5, 30.4, 29.1, 29.0, 28.9, 22.51, 22.48 (CH₂), 13.8 and 13.7 (CH₃). UV/vis: λ_{max} [nm] (ε [10⁶ cm² mol⁻¹]) = 314 (55.2; shoulder), 380 (144.3), 398 (102.6). Emission (λ_{excitation} = 370 nm): λ = 417 (maximum), 443 nm. Anal. Calcd for C₁₁₄H₁₄₆O₆N₂ (1640.430): C, 83.47; H, 8.97, N 1.71. Found: C, 83.26; H, 9.12, N 1.58. FD-MS: *m/z* = 1655 (7, [M + CH₃]⁺), 1640.01 (100%, M⁺), 1625.1 (13%, [M - CH₃]⁺), 1610 (3%, [M - 2CH₃]⁺), 1473.9 (1%, M⁺ of monoesterification product), 827.6 (7%), 820.1 (51%, M²⁺), 812.6 (16%, [M - 2CH₃]²⁺).

1,3,5-Triiodobenzene.^{53,54} A suspension of 1,3,5-tribromobenzene (6.00 g, 19 mmol), potassium iodide (142 g, 0.86 mol), and CuI (54 g, 0.28 mol) in 1,3-dimethyl-1,3-diazacyclohexane (180 mL) was heated to 155 °C for 24.5 h. After being cooled to room temperature, the brown, viscous reaction mixture was poured into water (800 mL). The precipitate was isolated, washed well with water, and dried (P₄O₁₀, vacuum). The obtained solid contained 1,3,5-triiodobenzene, 1,3-diiodobenzene and 1-bromo-3,5-diiodobenzene in a ratio of 11:6:1 (¹H NMR spectroscopically determined). Extraction in a Soxhlet apparatus with diethyl ether (400 mL) and concentration of the turbid solution to a volume of ca. 100 mL gave a colorless solid which was recrystallized from ethanol (350 mL) to give 1,3,5-triiodobenzene (2.9 g, 33%) as colorless needles contaminated with ca. 2 mol % of 1-bromo-3,5-diiodobenzene (determined with ¹H NMR spectroscopy).

Protected Triphenol 18. To a solution of **13a** (400 mg, 0.85 mmol) and 1,3,5-triiodobenzene (124 mg, 0.27 mmol) in THF (9 mL) and piperidine (4 mL) were added PdCl₂(PPh₃)₂ (6 mg, 0.09 mmol) and CuI (3 mg, 0.04 mmol) at 0 °C. The reaction mixture was stirred for 6.5 h at room temperature. Aqueous workup as described for **12a** followed by flash chromatography (petroleum ether/CH₂Cl₂ 10:8 → 1:2 v/v, *R_f* (petroleum ether/CH₂Cl₂ 10:8) = 0.37) gave **18** (350 mg, 87%) as a yellow-green fluorescent, very viscous oil. ¹H NMR: δ 7.64 (s, 3 H, C₆H₃), 7.46 (half of AA'XX', 6 H, H meta to OTHP), 7.40 and 7.38 (2 s, 3 H each, C₆H₂), 7.05 (half of AA'XX', 6 H, H ortho to OTHP), 5.45 (t, *J* = 3.1 Hz, 3 H, O₂CH), 3.87 and 3.60 (2 m, 3 H each, OCH₂), 2.83 (m, 12 H, ArCH₂), 2.1–1.2 (m, 66 H, CH₂), 0.89 (m, 18 H, CH₃).

Triphenol 19. The procedure for the preparation of diol **8** was followed, however with a reaction time of 5 h. The reaction of protected triphenol **18** (340 mg, 0.23 mmol) with toluenesulfonic acid monohydrate (10 mg, 0.05 mmol) in THF (11 mL) and methanol (10 mL) gave after chromatography on silica gel

(53) In analogy to bromine–iodine exchange described by Suzuki, H.; Kondo, A.; Ogawa, T. *Chem. Lett.* **1985**, 411. However, 1,3-dimethyl-1,3-diazacyclohexane was used instead of HMPA.

(54) Similar preparation: Schöberl, U.; Magnera, T. F.; Harrison, R. M.; Fleischer, F.; Pflug, J. L.; Schwab, P. F. H.; Meng, X.; Lipiak, D.; Noll, B. C.; Allured, V. S.; Rudalevige, T.; Lee, S.; Michl, J. *J. Am. Chem. Soc.* **1997**, *119*, 3907.

plates using a chromatotron (petroleum ether/diethyl ether 1:3, $R_f = 0.35$); the compound was applied as a solution in diethyl ether) triphenol **19** (250 mg, 89%) as a pale yellow solid. Mp: 145.8–146.9 °C. $^1\text{H NMR}$: δ 7.65 (s, 3 H, C_6H_3), 7.44 (half of AA'XX', 6 H, H meta to OH), 7.40 and 7.38 (2 s, 3 H each, C_6H_2), 6.85 (half of AA'XX', 6 H, H ortho to OH), 5.24 (br s, 3 H, OH), 2.83 (m, 12 H, ArCH_2), 1.72 (m, 12 H, ArCH_2), 1.37 (m, 36 H, CH_2), 0.89 (m, 18 H, CH_3). $^{13}\text{C NMR}$: δ 156.5 ($\text{C}_{\text{Ar-O}}$), 143.0 and 142.6 ($\text{C}_{\text{Ar-Hex}}$), 134.0 (CH of C_6H_3), 133.6 (CH meta to OH), 132.9 and 132.6 (CH of C_6H_2), 124.9 ($\text{C}_{\text{Ar-C}\equiv\text{C}}$ of C_6H_3), 123.8 and 122.1 ($\text{C}_{\text{Ar-C}\equiv\text{C}}$ of C_6H_2), 116.1 ($\text{C}_{\text{Ar-C}\equiv\text{C}}$ of C_6H_4), 116.0 (CH ortho to OH), 94.5, 92.5, 90.2, and 87.3 ($\text{ArC}\equiv\text{CAr}$), 34.5, 32.22, 32.20, 31.13, 31.0, 29.65, 29.63, 23.09, and 23.06 (CH_2), 14.33 and 14.27 (CH_3). Anal. Calcd for $\text{C}_{90}\text{H}_{102}\text{O}_3$ (1231.803): C, 87.75; H, 8.35. Found: C, 87.21; H, 8.34. FD-MS: $m/z = 1231.8$ (100%, M^+), 615.9 (44%, M^{2+}).

Starshaped Triradical 3. The procedure for the preparation of diradical **1** was followed, however with a reaction time of 17 h. The reaction of **19** (150 mg, 0.12 mmol) with spin label **4** (101 mg, 0.55 mmol) in the presence of *N,N*-dicyclohexylcarbodiimide (113 mg, 0.55 mmol) and DMAP (74 mg, 0.61 mmol) in THF (10 mL) gave after flash chromatography (petroleum ether/diethyl ether 2:1 v/v, $R_f = 0.40$); the crude product was dissolved in a small amount of CH_2Cl_2 and applied in this form to the column⁵⁰ triradical **3** (177 mg, 84%) as a yellow solid. An intensively yellow fraction (unidentified

compound, 21 mg, $R_f = 0.87$) was eluted first. Mp: 152.6–153.6 °C. $^1\text{H NMR}$: all signals are broad and structureless, δ 7.69 (3 H, C_6H_3), 7.64 (6 H, H meta to OR), 7.45 (6 H, C_6H_2), 7.23 (very broad, 6 H, H ortho to OR), 2.88 (12 H, ArCH_2), 1.76 (12 H, ArCH_2), 1.40 (36 H, CH_2), 3.6 (18 H, CH_3). $^{13}\text{C NMR}$: δ 148.7 ($\text{C}_{\text{Ar-O}}$), 142.2 and 142.0 ($\text{C}_{\text{Ar-Hex}}$), 133.2, 132.2, 132.1, 131.9 (C_6H_2 , C_6H_3 , CH meta to OR), 123.9 ($\text{C}_{\text{Ar-C}\equiv\text{C}}$ of C_6H_3), 122.4 ($\text{C}_{\text{Ar-C}\equiv\text{C}}$), 121.8 (CH ortho to OR), 121.7, 120.9 ($\text{C}_{\text{Ar-C}\equiv\text{C}}$), 92.7, 91.8, 89.2, and 88.1 ($\text{C}\equiv\text{C}$), 33.7, 31.3, 30.2, 28.8, 22.2 (CH_2), 13.51, 13.46 (CH_3). Anal. Calcd for $\text{C}_{117}\text{H}_{138}\text{N}_3\text{O}_9$ (1730.403): C, 81.21; H, 8.04, N 2.43. Found: C, 81.20; H, 7.99, N 2.46. FD-MS: $m/z = 1750.1$ (8%, $[\text{M} + \text{CH}_3]^+$), 1734.8 (100%, M^+), 1719.6 (3%, $[\text{M} - \text{CH}_3]^+$), 1704.1 (3%, $[\text{M} - 2\text{CH}_3]^+$), 868.6 (10%, M^{2+}).

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Supporting Information Available: Structure of diradical **1** in the crystal, X-ray crystallographic data, and figures showing the UV and fluorescence spectra of diphenols **8**, **15a,b** and diradicals **1**, **2a,b**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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