Supplementary Material (ESI) for PCCP

Three-spin correlations in double electron electron resonance

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Supporting Information

1 Synthesis of bi- and triradicals

General information

All reactions were performed under argon. In case of alkynyl-aryl cross-coupling reactions, the solutions containing both coupling components, the solvent and the amine were degassed through several freeze-pump-thaw-cycles prior to addition of the catalysts. THF was distilled from sodium/benzophenone. Piperidine was distilled from CaH_2. Diethylamine and triethylamine were used as received. 1-Oxyl-2,2,5,5-tetramethylpyrroline-3-carboxylic acid was purchased from Acros. Triiodobenzene **1**[1] and the alkynes **7**[1, 2] were prepared as described in the literature.

For flash chromatography, Merck silica gel (40-63 μm) and Acros silica gel (35-70 μm) was used. For the preparation of the chromatotron plates (centrifugal preparative thin layer chromatography) Merck silica gel 60 PF_{254} was used. Thin layer chromatography (TLC) was carried out on silica gel coated aluminum foils (Merck, 60 F_{254}). Ratios of solvents in mixtures are given as volume to volume.

The melting points were determined in open capillaries. Elemental analyses were made at the analytical laboratory of Bielefeld University or at an external analytical laboratory. MALDI

TOF mass spectra were recorded with a Voyager DE Instrument mounted with a 1.2 m flight tube. Ionisation was achieved using an LSI nitrogen laser (337 nm beam wavelength, 3 ns pulse width, 3 Hz repetition rate). The ions were accelerated with 15 to 20 kV. 1,8,9-trihydroxyanthracene was used as the matrix and THF or $CHCl_3$ as the solvent to prepare the samples.

Unless specified otherwise, NMR spectra were recorded at 27-30 °C on a Bruker 250 or a Bruker 500 instrument. The solvent was used as an internal standard. The coupling constants are given in Hz. For ^{13}C NMR signal assignment the carbon multiplicity (quaternary carbon (C), tertiary carbon (CH), secondary carbon (CH_2), primary carbon (CH_3)) was determined by a DEPT-135 experiment. The detailed assignment is based on reported shift increments[3] and on our own data obtained from related compounds.[1, 2, 4, 5]

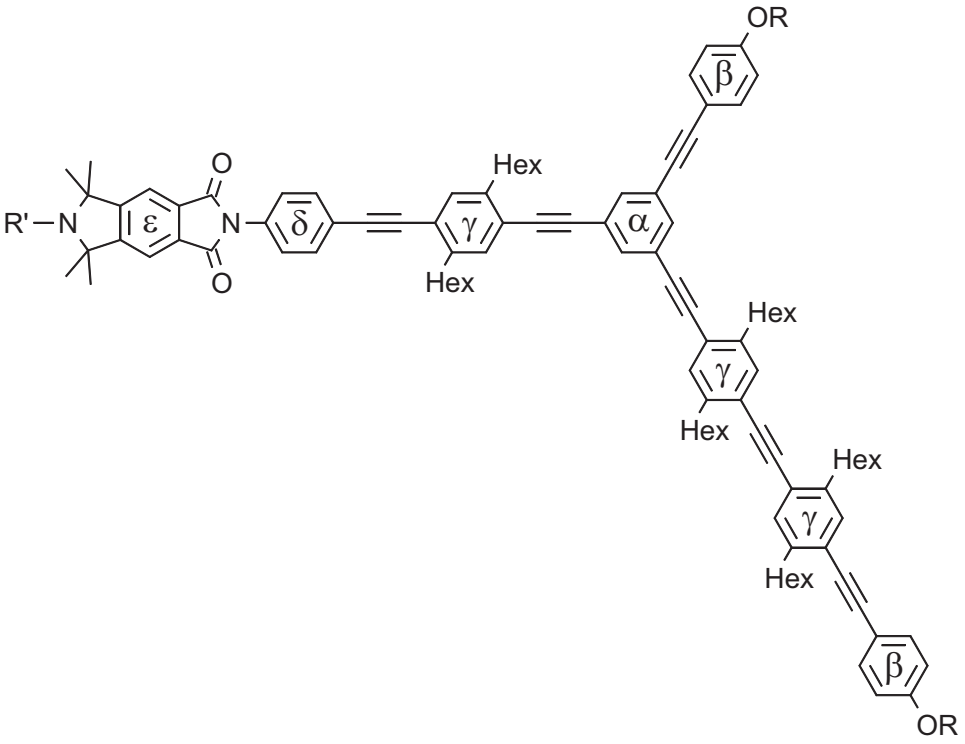

Figure S 1: A fictive molecule to define the labeling of the benzene moieties with α–ϵ.

Diiodo compound 2

$Pd(PPh_3)_2Cl_2$ (4 mg, 0.006 mmol) and CuI (3 mg, 0.02 mmol) were added to a degassed solution of alkyne $\mathbf{7_0}$ (81 mg, 0.40 mmol) and triiodobenzene **1** (609 mg, 1.34 mmol) in diethylamine (10 mL). After stirring the reaction mixture at room temperature for 16 h, Et_2NH was distilled

off at room temperature and slightly reduced pressure. The residue was dissolved in Et_2O, THF and water, the aqueous phase was extracted with a mixture of Et_2O and THF, and the combined organic extracts were washed with saturated aqueous NH_4Cl, dried over Na_2SO_4, and concentrated at reduced pressure giving a colorless solid. This crude product was adsorbed onto a small quantity of silica gel through dissolving it in CH_2Cl_2, adding silica gel to this solution, and removing the solvent (40 °C, reduced pressure). The resulting freely flowing powder was applied to a silica gel column by pouring it into a small amount of solvent overlaying the silica gel column. Column chromatography (*n*-pentane/Et_2O 12:1) yielded triiodobenzene **1** (347 mg, 57%; $R_f = 0.72$) as a colorless solid and diiodo compound **2** (121 mg, 57%; $R_f = 0.52$) as a colorless solid (mp 122 °C; Found C, 43.15; H, 3.06. Calc. for $C_{19}H_{16}O_2I_2$ (530.145): C, 43.04; H, 3.04%) containing a trace (about 1 % as judged from ^{1}H NMR spectrum) of disubstitution product **3**. Analytical data of diiodo compound **2**: δ_H(250 MHz; $CDCl_3$) 7.97 (1 H, t, *J* 1.5, H_α ortho to both I), 7.80 (2 H, d, *J* 1.5, H_α ortho to one I and to C≡C), 7.41 and 7.02 (2 H each, AA'XX' spinsystem, H_β meta to OTHP and H_β ortho to OTHP, respectively), 5.44 (1 H, t-shaped, *J* 3, O_2CH), 3.87 and 3.61 (1 H each, 2 m, OCH_2), 2.1-1.5 (6 H, m, CH_2); δ_C(62.8 MHz; CD_2Cl_2) 158.2 (C, $C_\beta O$), 144.9 and 139.6 (CH, $C_\alpha H$), 133.5 (CH, $C_\beta H$ meta to OTHP), 127.6 (C, $C_\alpha C{\equiv}C$), 117.0 (CH, $C_\beta H$ ortho to OTHP), 115.4 (C, $C_\beta C{\equiv}C$), 96.8 (CH, O_2CH), 94.3 and 92.4 (C, C≡C), 85.2 (C, $C_\alpha I$), 62.5 (CH_2, OCH_2), 30.6, 25.5, and 19.1 (CH_2, CH_2 of THP).

Protected triol 5a

To a degassed solution of alkyne $\mathbf{7_1}$ (136 mg, 0.29 mmol) and diiodo compound **2** (60 mg, 0.11 mmol) in diethylamine (5 mL), $Pd(PPh_3)_2Cl_2$ (3 mg, 0.004 mmol) and CuI (2 mg, 0.01 mmol) were added. The reaction mixture was stirred at room temperature for 15 h. Then Et_2NH was distilled off at slightly reduced pressure/room temperature, the residue was dissolved in Et_2O and water, the aqueous phase was extracted with Et_2O, the combined organic extracts were washed with saturated aqueous NH_4Cl, dried over Na_2SO_4, and concentrated under reduced pressure giving a yellow oil. This was diluted with a very small amount of CH_2Cl_2 and applied as such to a chromatotron plate. Chromatography (*n*-pentane/CH_2Cl_2 5:1 → 1:1) yielded **5a** (126 mg, 92%; R_f(*n*-pentane/CH_2Cl_2 1:1) = 0.08) as a yellowish fluorescent oil (Found C, 83.97; H, 8.26. Calc. for $C_{85}H_{98}O_6$ (1215.713): C 83.98, H 8.13%). Ahead of this product, diiodo compound **2** in mixture of an unidentified compound (27 mg, R_f(*n*-pentane/CH_2Cl_2 1:1) = 0.35 and 0.29), oxidative dimer (Glaser coupling product) of the alkyne $\mathbf{7_1}$ (10 mg, 7%; R_f(*n*-pentane/CH_2Cl_2 1:1) = 0.26), and the monocoupling product **3** (2 mg, 1%; R_f(*n*-pentane/CH_2Cl_2 1:1) = 0.17) were eluted. Analytical data of protected triol **5a**: δ_H(250 MHz; $CDCl_3$) 7.60-7.57 (3 H, m, H_α), 7.46 (2 H, half of AA'XX' spinsystem, H_β meta to OTHP; short arm), 7.44 (4 H, 2 halves of 2 AA'XX' spinsystems, H_β meta to OTHP; long arms), 7.34 (4 H, slightly broadened s, H_γ), 7.03 (6 H, 3 halves of 3 AA'XX' spinsystems, H_β ortho to OTHP; short and long arms), 5.45 (3 H, t-shaped, *J* 3, O_2CH), 3.89 and 3.62 (3 H each, 2 m,

OCH_2), 2.78 (8 H, m, $ArCH_2$), 2.1-1.2 (50 H, m, CH_2), 0.885 and 0.875 (6 H each, t, J 6.9, CH_3); δ_C(62.8 MHz; CD_2Cl_2) 158.1 and 157.8 (C, $C_\beta O$), 143.0 and 142.6 (C, C_γHex), 134.0 - 132.5[6] (CH, $C_\alpha H$, $C_\beta H$ meta to OTHP, $C_\gamma H$), 124.9 and 124.7 (C, $C_\alpha C{\equiv}C$), 123.8 and 122.1 (C, $C_\gamma C{\equiv}C$), 117.0 (CH, $C_\beta H$ ortho to OTHP), 116.7 and 115.9 (C, $C_\beta C{\equiv}C$), 96.9 (CH, O_2CH), 94.6, 92.5, 91.1, 90.0, 87.4, and 86.9 (C, C≡C), 62.5 (CH_2, OCH_2), 34.5, 32.20, 32.17, 31.12, 31.0, 30.7, 29.6, 25.6, 23.1, 23.0, and 19.2 (CH_2, CH_2 of THP and Hex), 14.32 and 14.26 (CH_3).

Triol 5b

To a solution of protected triol **5a** (110 mg, 0.09 mmol) in THF (10 mL) and methanol (7 mL) toluenesulphonic acid monohydrate (47 mg, 0.25 mmol) was added. The reaction mixture was stirred at room temperature for 5 h (TLC monitoring; n-pentane/Et_2O 1:3). Then Et_2O and water were added, the phases were separated, the aqueous phase was extracted with Et_2O, and the combined organic extracts were washed with saturated aqueous K_2CO_3, then 2 N HCl, and finally brine. After drying over $MgSO_4$, the solvents were removed under reduced pressure and the residue was freeze-dried from benzene giving triol **5b** (86 mg, 99%) as a slightly yellow solid (mp 138 °C). The elemental analysis of this material deviated largely from the expected values. The ^{1}H NMR spectrum showed an intense peak for silicon grease which may account for the elemental analysis result. However other experiments in which THP was removed from similar compounds indicate that in general the material obtained in the way that is described above is impure. A satisfying elemental analysis (Found C, 87.08; H, 87.86. Calc. for $C_{70}H_{74}O_3$ (963.359): C 87.27, H 7.74%) was obtained from material which had been chromatographed (n-pentane/Et_2O 1:1). The crude triol **5b** was used as obtained for the next synthetic step, i.e. the preparation of triradical **T111**. δ_H(250 MHz; $CDCl_3$) 7.60-7.57 (3 H, m, H_α), 7.43 (2 H, half of AA'XX' spinsystem, H_β meta to OH, short arm), 7.42 (4 H, 2 halves of 2 AA'XX' spinsystems, H_β meta to OH, long arms), 7.35 and 7.34 (2 H each, 2 s, H_γ), 6.82 (6 H, 3 halves of 3 AA'XX' spinsystems, H_β ortho to OH; short and long arms), 4.92 (1 H, s, OH of short arm), 4.89 (2 H, s, OH of long arms), 2.79 (8 H, m, $ArCH_2$), 1.69 (8 H, m, CH_2), 1.34 (24 H, m, CH_2), 0.885 and 0.875 (6 H each, 2 t, J 6.9, CH_3); δ_C(62.8 MHz; CD_2Cl_2) 156.7 and 156.4 (C, $C_\beta O$), 143.0 and 142.6 (C, C_γHex), 133.8, 133.7, and 133.5 (CH, $C_\alpha H$, $C_\beta H$ meta to OH), 132.8 and 132.5 (CH, $C_\gamma H$) 124.9 and 124.7 (C, $C_\alpha C{\equiv}C$), 123.8 and 122.1 (C, $C_\gamma C{\equiv}C$), 116.1 (C, $C_\beta C{\equiv}C$), 116.02 and 115.99 (CH, $C_\beta H$ ortho to OH), 115.4 (C, $C_\beta C{\equiv}C$), 94.5, 92.5, 90.9, 90.0, 87.3, and 86.8 (C, C≡C), 34.5, 32.20, 32.17, 31.12, 31.0, 29.6, 23.1, and 23.0 (CH_2), 14.33 and 14.26 (CH_3); m/z (MALDI-TOF) 964.1 (100%, M^+. $C_{70}H_{74}O_3$ requires 963.4).

Triradical T011

N,N'-Dicyclohexylcarbodiimide (45.0 mg, 0.22 mmol) was added to a solution of triol **5b** (35 mg, 0.036 mmol), 1-oxyl-2,2,5,5-tetramethylpyrroline-3-carboxylic acid (40.5 mg, 0.220 mmol), and DMAP (26.8 mg, 0.22 mmol) in THF (5 mL). After stirring of the reaction mixture at room temperature for 3 days, the precipitate was filtered off and washed with THF until the

solid was colorless. The solvent of the filtrate, which contained the triradical, was removed. In order to get rid of trapped THF, the crude product was dissolved in CH_2Cl_2 and the solvent was removed. The crude product was suspended in a small amount of CH_2Cl_2 (the colorless insoluble material is most probably the urea compound) and applied to a chromatotron plate. Elution with CH_2Cl_2 (R_f = 0.12) gave triradical **T011** (25 mg, 47%) as a yellow oil which soldified upon freeze-drying from benzene (mp 54-56 °C; Found C, 78.95; H, 7.80; N, 3.09. Calc. for $C_{97}H_{110}O_9N_3$ (1461.959): C, 79.69; H, 7.58; N, 2.87%). Ahead of the triradical **T011** a yellow oil (12 mg) containing unidentified compounds was eluted.[7] Analytical data of triradical **T011**: δ_H(250 MHz; CD_2Cl_2) All signals are broad and structureless. 7.68 (3 H, H_α), 7.64 (6 H, H_β meta to OR), 7.42 (4 H, H_γ), 7.23 (very broad, 6 H, H_β ortho to OR), 2.85 (8 H, $ArCH_2$), 1.73 (8 H, $ArCH_2$), 1.38 (about 24 H, CH_2), 0.90 (12 H, CH_3); *m/z* (MALDI-TOF) 1465.6 (100%, M^+. $C_{97}H_{110}N_3O_9$ requires 1462.0), 1449.4 (37), 1434.6 (25), 1297.1 (75, [M - spin label]$^+$), 1282.8 (45), 1267.4 (22), 1130.4 (30, [M - 2 spin labels]$^+$, 1115.4 (27), 963.4 (30, [M - 3 spin labels]$^+$.[8]

Monoiodo compound 3

Starting from alkyne $\mathbf{7_1}$ (114 mg, 0.24 mmol), diiodo compound **2** (256 mg, 0.48 mmol), $Pd(PPh_3)_2Cl_2$ (3 mg, 0.004 mmol) and CuI (2 mg, 0.01 mmol) in diethylamine (10 mL) and working as described for the synthesis of protected triol **5a**, with the difference that the crude product was dissolved in *n*-pentane/Et_2O 12:1 for being applied onto the chromatotron plate and the compounds were eluted with *n*-pentane/Et_2O 12:1, monoiodo compound **3** (92 mg, 44%; R_f = 0.14) was obtained as a yellow solid (mp 49-50 °C; Found C, 71.30; H, 6.61. Calc. for $C_{52}H_{57}O_4I$ (872.929): C, 71.55; H, 6.58%). Ahead of the product **3**, diiodo compound **2** (107 mg, 42%; R_f = 0.30) and the oxidative dimer (Glaser coupling product) of alkyne $\mathbf{7_1}$ (4 mg, 4%; R_f = 0.19) were eluted. As a last fraction protected triol **5a** (15 mg, 10%; R_f = 0.05) was isolated. Analytical data of monoiodo compound **3**: δ_H(250 MHz; $CDCl_3$) 7.80 and 7.78 (1 H each, 2 dd, *J* 1.5 and 1.5, H_α ortho to I), 7.59 (1 H, t, *J* 1.5, H_α para to I), 7.44 (4 H, 2 halves of 2 AA'XX' spinsystems, H_β meta to OTHP), 7.33 and 7.32 (1 H each, 2 s, H_γ), 7.03 (4 H, 2 halves of 2 AA'XX' spinsystems, H_β ortho to OTHP), 5.44 (2 H, t-shaped, *J* 3, O_2CH), 3.89 and 3.61 (2 H each, 2 m, OCH_2), 2.77 (4 H, m, $ArCH_2$), 2.1-1.5 (16 H, m, CH_2 of THP and Hex), 1.34 (12 H, m, CH_2 of Hex), 0.89 and 0.87 (3 H each, 2 t, *J* 6.9, CH_3); δ_C(62.8 MHz; CD_2Cl_2) 158.2 and 157.8 (C, C_βO), 143.0 and 142.6 (C, C_γHex), 139.9 and 139.6 (CH, C_αH), 133.6 - 132.5 [6] (CH, C_βH meta to OTHP, C_αH, C_γH), 126.1 and 125.9 (C, C_αC≡C), 123.9 and 121.8 (C, C_γC≡C), 117.0 (CH, C_βH ortho to OTHP), 116.6 and 115.7 (C, C_βC≡C), 96.9 (CH, O_2CH), 94.7, 93.6, 91.8, 91.7, 90.7, and 87.4 (C, C≡C), 86.1 (C, *C*-I), 62.5 (CH_2, OCH_2), 34.5, 32.19, 32.18, 31.12, 31.0, 30.7, 29.6, 25.6, 23.1, 23.0, and 19.2 (CH_2, CH_2 of THP and Hex), 14.35 and 14.27 (CH_3).

Protected triol 4a

$Pd(PPh_3)_2Cl_2$ (9 mg, 0.01 mmol) and CuI (5 mg, 0.03 mmol)[12] were added to a degassed solution of monoiodo compound **3** (115 mg, 0.13 mmol) and alkyne $\mathbf{7_2}$ (107 mg, 0.14 mmol) in piperidine (3 mL) and THF (10 mL). The reaction mixture was stirred at room temperature for 23 h. Et_2O and water were added, the aqueous phase was extracted with Et_2O, the combined organic extracts were washed with saturated aqueous NH_4Cl, dried over Na_2SO_4, and the solvents were removed under reduced pressure. The dirty-yellow colored solid residue was dissolved in a minimum amount of CH_2Cl_2 and applied to a chromatotron plate. Chromatography (*n*-pentane/CH_2Cl_2 2:1 → 1:1) furnished protected triol **4a** (95 mg, 48%; R_f(*n*-pentane/CH_2Cl_2 1:1) = 0.32) as a yellow oil. Ahead of **4a**, the oxidative dimer (Glaser coupling product) of alkyne $\mathbf{7_2}$ (37 mg, 34%; R_f = 0.58) was eluted. Analytical data of protected triol **4a**: δ_H(250 MHz; $CDCl_3$) 7.61-7.58 (3 H, m, H_α), 7.46 (2 H, half of AA'XX' spinsystem, H_β meta to OTHP; short arm), 7.45 (4 H, 2 halves of 2 AA'XX' spinsystems, H_β meta to OTHP; medium and long arm), 7.37 and 7.36 (1 H each, 2 s, H_γ), 7.35 and 7.34 (allover 4 H, 2 s, H_γ), 7.03 (6 H, 3 halves of 3 AA'XX' spinsystems, H_β ortho to OTHP), 5.45 (3 H, t-shaped, *J* 3, O_2CH), 3.89 and 3.62 (3 H each, 2 m, OCH_2), 2.80 (12 H, m, ArCH_2), 2.1-1.5 (30 H, m, CH_2), 1.34 (36 H, m, CH_2), 0.88 (18 H, m, CH_3); δ_C(62.8 MHz; CD_2Cl_2) 158.1, 157.80 and 157.78 (C, C_βO), 143.00, 142.96, 142.61, 142.57, 142.50, and 142.46 (C, C_γHex), 134.0 -132.5 [6] (CH, C_βH meta to OTHP, C_αH, C_γH), 125.0, 124.8, 124.7 (C, C_αC≡C), 123.8, 123.7, 123.4, 122.8, 122.4, and 122.1 (C, C_γC≡C), 117.0 (CH, C_βH ortho to OTHP), 116.70, 116.65, and 115.9 (C, C_βC≡C), 96.9 (CH, O_2CH), 94.6, 94.5, 93.7, 93.1, 92.7, 92.5, 91.1, 90.05, 89.98, 87.5, 87.4, and 86.9 (C, C≡C), 62.5 (CH_2, OCH_2), 34.5, 32.25, 32.21, 32.18, 31.13, 31.08, 31.02, 30.7, 29.7, 29.6, 25.6, 23.1, and 19.2 (CH_2), 14.33 and 14.27 (CH_3); *m/z* (MALDI-TOF) 1488.1 (35%, M^+. $C_{105}H_{126}O_6$ requires 1484.2), 1404.1 (45, [M - dihydropyrane]$^+$), 1319.1 (30, [M - 2 dihydropyranes]$^+$), 1234.4 (100, [M - 3 dihydropyranes]$^+$).

Triol 4b

Crude triol **4b** was obtained starting from protected triol **4a** (90 mg, 0.06 mmol) and toluenesulphonic acid monohydrate (36 mg, 0.19 mmol) in THF (10 mL) and methanol (7 mL), following the same procedure as described for the synthesis of triol **5b**, but omitting the freeze drying. Through twofold chromatography on a chromatotron plate (*n*-pentane/Et_2O 1:1) triol **4b** (55 mg, 74%; R_f = 0.10) was obtained as a yellow colored solid (mp 69-70 °C; Found C, 87.59; H, 8.47. Calc. for $C_{90}H_{102}O_3$ (1231.803): C, 87.76; H, 8.35%); δ_H(250 MHz; $CDCl_3$) 7.60-7.58 (3 H, m, H_α), 7.43 (2 H, half of AA'XX' spinsystem, H_β meta to OH; short arm), 7.42 (4 H, 2 halves of 2 AA'XX' spinsystems, H_β meta to OH; medium and long arm), 7.37 and 7.36 (1 H each, 2 s, H_γ), 7.34 (4 H, slightly broadened s, H_γ), 6.83 and 6.82 (allover 6 H, 3 halves of 3 AA'XX' spinsystems, H_β ortho to OH), 4.98, 4.95, 4.94 (1 H each, 3 s, OH), 2.81 (12 H, m, ArCH_2), 1.70 (12 H, m, CH_2), 1.34 (36 H, m, CH_2), 0.88 (18 H, m, CH_3); δ_C(125.6 MHz; CD_2Cl_2) 156.7, 156.41 and 156.38 (C, C_βO), 142.96, 142.92, 142.54, 142.50, 142.46, and 142.42

(C, C_γHex), 133.9, 133.8, 133.7, 133.48, and 133.47 (CH, C$_\beta$H meta to OH, C_αH), 132.84, 132.78, 132.5, and 132.4 (CH, C$_\gamma$H), 124.9, 124.7, and 124.6 (C, C_αC≡C), 123.7, 123.6, 123.3, 122.7, 122.3, and 122.0 (C, C_γC≡C), 116.00 (C, C_βC≡C), 115.96, and 115.92 (CH, C$_\beta$H ortho to OH), 115.2 (C, C_βC≡C), 94.4, 94.3, 93.6, 93.1, 92.7, 92.5, 90.9, 89.97, 89.92, 87.3, 87.2, and 86.7 (C, C≡C), 34.5, 32.21, 32.17, 32.14, 31.10, 31.06, 31.04, 30.99, 29.6, 23.07, 23.05, and 23.03 (CH_2), 14.32 and 14.26 (CH_3).

Triradical T012

The procedure reported for the synthesis of triradical **T011** was followed. Starting from triol **4b** (25 mg, 0.02 mmol), 1-oxyl-2,2,5,5-tetramethylpyrroline-3-carboxylic acid (22 mg, 0.12 mmol), DMAP (15 mg, 0.12 mmol), and N,N'-dicyclohexylcarbodiimide (25 mg, 0.12 mmol) in THF (5 mL), triradical **T012** (22 mg, 63%; $R_f(CH_2Cl_2) = 0.14$) was obtained as a yellow oil which solidified upon freeze-drying from benzene. (mp 63-64 °C; Found C, 80.61; H, 8.12; N, 2.47. Calc. for $C_{117}H_{138}N_3O_9$ (1730.403): C, 81.21; H, 8.04; N, 2.43%). Ahead of the triradical **T012** a yellow oil (7 mg) containing unidentified compounds was eluted [7]. Analytical data of triradical **T012**: δ_H(500 MHz; CD_2Cl_2) All signals are broadened. 7.68 and 7.67 (allover 3 H, 2 s, H$_\alpha$), 7.62 (6 H, very broad, H$_\beta$ meta to OR), 7.43, 7.42, 7.41, and 7.40 (allover 6 H, 4 s, H$_\gamma$), 7.21 (extremely broad, 6 H, H$_\beta$ ortho to OR), 2.86 (12 H, m, ArCH_2), 1.72 (12 H, m, ArCH_2), 1.44 and 1.35 (allover about 36 H, 2 m, CH_2), 0.90 (18 H, m, CH_3); *m/z* (MALDI-TOF) 1732.1 (95%, M^+. $C_{117}H_{138}N_3O_9$ requires 1730.4), 1716.6 (30), 1698.4 (20), 1669.3 (13), 1563.6 (55), 1549.2 (42), 1532.1(35, 1519.5 (23), 1397.7 (50), 1382.2 (50), 1366.6 (17), 1230.6 (100).

Triradical precursor 9

$Pd(PPh_3)_2Cl_2$ (3.7 mg, 0.005 mmol) and CuI (2.0 mg, 0.010 mmol) were added to a degassed solution of 1,3,5-triiodobenzene (**1**) (20.0 mg, 0.044 mmol) and alkyne **8**(121.0 mg, 0.197 mmol) in THF (10 mL) and Et_3N (5.0 mL). After two further freeze-pump thaw cycles the reaction mixture was stirred at room temperature for 5 days. The solvent was evaporated at 45°C and reduced pressure. The brown residue was dissolved in chloroform (5.0 mL) and applied as such onto a silica gel column. Chromatography ($CHCl_3$/MeOH 97:3) furnished triradical precursor **9** as a light-yellow colored solid (37 mg, 44%;R_F= 0.35; mp 143°C). Ahead of this product the oxidative dimer (Glaser coupling product) of the alkyne **9** was eluted (R_F = 0.28). Analytical data of triradical precursor **9**: δ_H(500 MHz; $CDCl_3$) 7.70 (6 H, s, H$_\varepsilon$), 7.65 (6 H, half of AA'XX' spinsystem, H$_\delta$ meta to N), 7.63 (3 H, s, H$_\alpha$), 7.47 (6 H, half of AA'XX' spinsystem,ortho to N), 7.40 and 7.38 (3 H each, 2 s, H$_\gamma$), 2.83 and 2.82 (6 H each, 2 t, *J* 6.4, ArCH_2), 1.78 (9 H, broad, NH and H_2O), 1.72 and 1.71 (6 H each, 2 quint, *J* 8, ArCH_2CH_2), 1.53 (36 H, s, CH_3 of isoindoline), 1.42 (12 H, CH_2), 1.35 (24 H, m, CH_2), 0.892 and 0.888 (9 H each, 2 t, *J* 7, CH_3 of Hex); δ_C(62.8 MHz; $CDCl_3$) 166.9 (C, CO), 156.4 (C, C$_\varepsilon$), 142.45 and 142.43 (C, C_γHex), 133.7 (C$_\alpha$H), 132.5 and 132.4 (CH, C$_\gamma$H), 132.1 (CH, C$_\delta$H meta to N), 131.6 (C, C$_\delta$N), 131.5 (C, C$_\varepsilon$), 126.2 (CH, C$_\delta$H ortho to N), 124.3 (C, C_αC≡C), 123.1 (C, C_δC≡C), 122.7 and 122.2 (C, C_γC≡C), 117.6 (CH, C$_\varepsilon$H), 93.4, 92.3, 89.7, and 89.3 (C, C≡C), 63.1 (C, Me_2CN),

34.2 and 34.1 (CH_2), 31.8 (CH_3 of isoindoline), 30.7, 30.6, 29.3, 29.2, 22.7, and 22.6 (CH_2), 14.2 and 14.1 (CH_3); *m/z* (MALDI-TOF) 1909.8 (100%, M^+. $C_{132}H_{144}N_6O_6$ requires 1910.6), 1893.8 (60%).

Triradical T111$_{inv}$

A solution of *m*-chloroperbenzoic acid (28 mg, 0.16 mmol) in CH_2Cl_2 (1.5 mL) was added to an ice bath cooled solution of triradical precursor **9** (29.0 mg, 0.015 mmol) in CH_2Cl_2 (3.0 mL). The reaction mixture was stirred at room temperature for 2 h. The solvent was evaporated at 40°C and reduced pressure. Methanol (5.0 mL) was added to the yellow residue, the precipitate was isolated through filtration and washed with methanol (10 mL). Surprisingly, the material was only partially soluble in solvents such as THF, $CHCl_3$, CH_2Cl_2, Et_2O, and toluene, despite the fact that the reaction mixture had been a clear solution (CH_2Cl_2) before work-up. The isolated solid was suspended in $CHCl_3$. The suspension was stirred at room temperature for overnight, then stirred at 80°C for 1 h, cooled to room temperature and filtered. The filtrate was concentrated (to about 5 mL) at room temperature and reduced pressure. The residual solution was diluted with THF (2.0 mL). This solution was applied to a silica gel column. Chromatography (CH_2Cl_2/Et_2O 10:1) yielded triradical **T111$_{inv}$** (9.3 mg, 31%; mp 132 °C; $R_F = 0.54$) as a yellow solid. δ_H(500 MHz; $CDCl_3$) All signals are broad and structureless. 8.0 (ca 4 H, extremely broad, H_ε), 7.67 (6 H, very broad, H_δ ortho to N), 7.63 (3 H, s, H_α), 7.48 (6 H, very broad, H_δ meta to N), 7.41 and 7.39 (3 H each, 2 s, H_γ), 2.82 (12 H, ArCH_2), 1.72 (ca. 12 H, ArCH$_2$CH_2), 1.53 (ca. 27 H, s, CH_3 of isoindoline), 1.43 and 1.34 (ca. 36 H, CH_2), 1.25 (ca. 4 H, sharp s, probably water), 0.89 (18 H, m, CH_3 of Hex); *m/z* (MALDI-TOF) 1984.5 (50), 1968.8 (70), 1955.3 (100%, M^+. $C_{132}H_{141}N_6O_9$ requires 1955.6), 1941.3 (90), 1924.1 (75); All signals are of very low absolute intensity.

Compound 10a

To a degassed solution of diiodo compound **2** (30.0 mg, 0.057 mmol) and alkyne **8** (99.3 mg, 0.162 mmol) in THF (6.0 mL) and Et_3N (3.0 mL) were added $Pd(PPh_3)_2Cl_2$ (3.2 mg, 0.005 mmol) and CuI (1.8 mg, 0.009 mmol). Two further freeze-pump-thaw cycles were pursued. The reaction mixture was stirred at room temperature for 5 days. The solvent was evaporated at 45 °C and reduced pressure. The lightly yellow colored solid residue was dissolved in $CHCl_3$ (5.0 mL) and applied as such to a silica gel column. Elution ($CHCl_3$/EtOH 97:3) gave two fractions of a faintly yellow solid (64 mg, 19 mg; $R_F = 0.32$) containing the coupling product **10a** and the oxidative dimer (Glaser coupling product) of the alkyne **8** in a ratio of 3:1 and 20:1 (^{1}H NMR spectroscopically determined), respectively. Ahead of this fraction a mixture (6 mg; $R_F = 0.38$ and 0.32) of these two products and an unidentified compound was eluted. Analytical data of compound **10a**: δ_H(500 MHz; $CDCl_3$) 7.70 (4 H, s, H_ε), 7.64 (4 H, half of AA'XX' spinsystem, H_δ meta to N), 7.62 and 7.60 (2 H and 1 H, respectively, AB_2 spinsystem, *J* 1, H_α), 7.471 (4 H, half of AA'XX' spinsystem, H_δ ortho to N), 7.466 (2 H, half of AA'XX' spinsystem, H_β meta to OTHP), 7.39 and 7.38 (2 H each, 2 s, H_γ), 7.04 (2H, half of AA'XX'

spinsystem, H_β ortho to OTHP), 5.46 (1 H, t-shaped, *J* 3, O_2CH), 3.89 and 3.62 (1 H each, 2 m, CH_2O) and 2.81 (8 H, m, $ArCH_2$), 2.1 - 1.5 (17 H, m, CH_2 of Hex and THP, NH), 1.52 (24 H, s, CH_3 of isoindoline), 1.42 and 1.34 (24 H, CH_2 of Hex), 0.899 and 0.886 (6 H each, 2 t, *J* 7, CH_3 of Hex); *m/z* (MALDI-TOF of the 20:1 mixture) 1499.3 (80%, M^+. $C_{103}H_{110}N_4O_6$ requires 1500.0), 1482.9 (40), 1414.5 (50, [M^+ - THP]), 1399.2 (100), 1383.9 (55,) 1370.1 (85).

Biradical B11$_{inv}$

A solution of metachloroperbenzoic acid (25.3 mg, 0.147 mmol) in dichloromethane (1.5 mL) was added to an ice-bath cooled solution of the 3:1 mixture (27.2 mg) of compound **10a** and the Glaser coupling product of the alkyne **8** dissolved in dichloromethane (2.0 mL). The reaction mixture was stirred at room temperature for 1.5 h. The solvent was evaporated at 40 °C and reduced pressure. Washing with methanol (8.0 mL) provided a yellowish solid (24 mg). This solid (23 mg) was dissolved in THF (2.0 mL) and CH_3OH (1.0 mL) and *p*-toluenesulphonic acid mono hydrate (5.6 mg, 0.03 mmol) was added. After stirring the reaction mixture at room temperature for 3 h, the solution was concentrated (to about 2 mL) at 38 °C and reduced pressure. The residual solution was diluted with $CHCl_3$ (5 mL). This solution was applied to a silica gel column. Chromatography (CH_2Cl_2/Et_2O 12:1) gave the oxidised Glaser coupling product of the alkyne **8** (R_F(CH_2Cl_2/Et_2O 10:1) = 0.73) and biradical **B11$_{inv}$** as a yellowish solid (13 mg, 63% over two steps; R_F(CH_2Cl_2/Et_2O 10:1) = 0.34; mp 125 °C). Analytical data of biradical **B11$_{inv}$**: δ_H(500 MHz; $CDCl_3$) All signals are broad and structureless. 8.0-10 (extremely broad, H_ε), 8.5-6.5 (extremely broad, H_β ortho to OH), 7.69 (4 H, very broad, H_δ meta to N), 7.63 and 7.62 (3 H, 2 s, H_α), 7.49 (6 H, very broad, H_δ ortho to N and H_β meta to OH), 7.42 and 7.40 (2 H each, 2 s, H_γ), 2.84 (8 H, $ArCH_2$), 1.73 (8 H, $ArCH_2CH_2$), 1.44 and 1.36 (allover ca. 28 H, CH_2, CH_3 of isoindoline), 1.26 (2 H, sharp s, probably water), 0.92 and 0.91 (12 H, CH_3 of Hex); *m/z* (MALDI-TOF) 1445.9 (55%, M^+. $C_{98}H_{100}N_4O_7$ requires 1445.9), 1430.7 (75), 1415.8 (100), 1400.2 (75).

2 Supporting figures

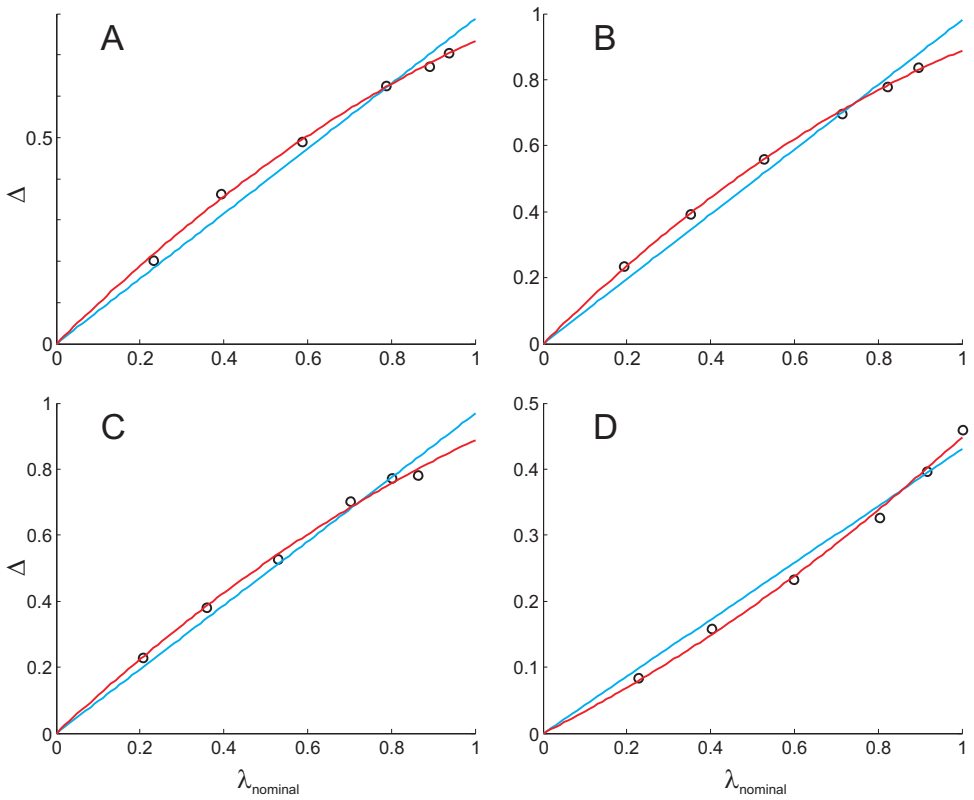

Figure S 2: Total modulation depth Δ as a function of nominal inversion efficiency λ_{nominal} for compounds **T011** (A), **T012** (B), **T111** (C), and **2a** from [1]. The data were fitted for models with up to two spins (blue lines) and up to three spins (red lines) by varying the polynomial coefficients and λ_{max}.

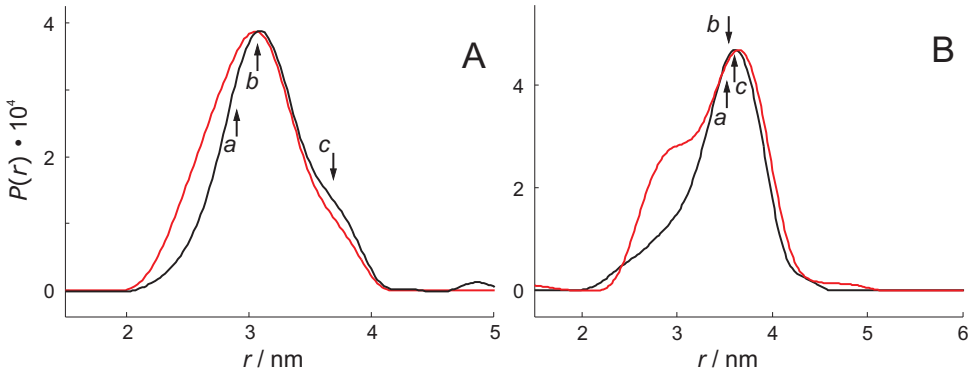

Figure S 3: Distance distributions for triradicals **T011** (A) and **T111** (B). Red lines correspond to distributions obtained from original DEER data and solid lines to distributions obtained from the extracted pair contribution. Vertical arrows correspond to side lengths found in model fits. (A) $a = 2.90$ nm, $b = 3.07$ nm, $c = 3.69$ nm. (B) $a = 3.52$ nm, $b = 3.54$ nm, $c = 3.60$ nm.

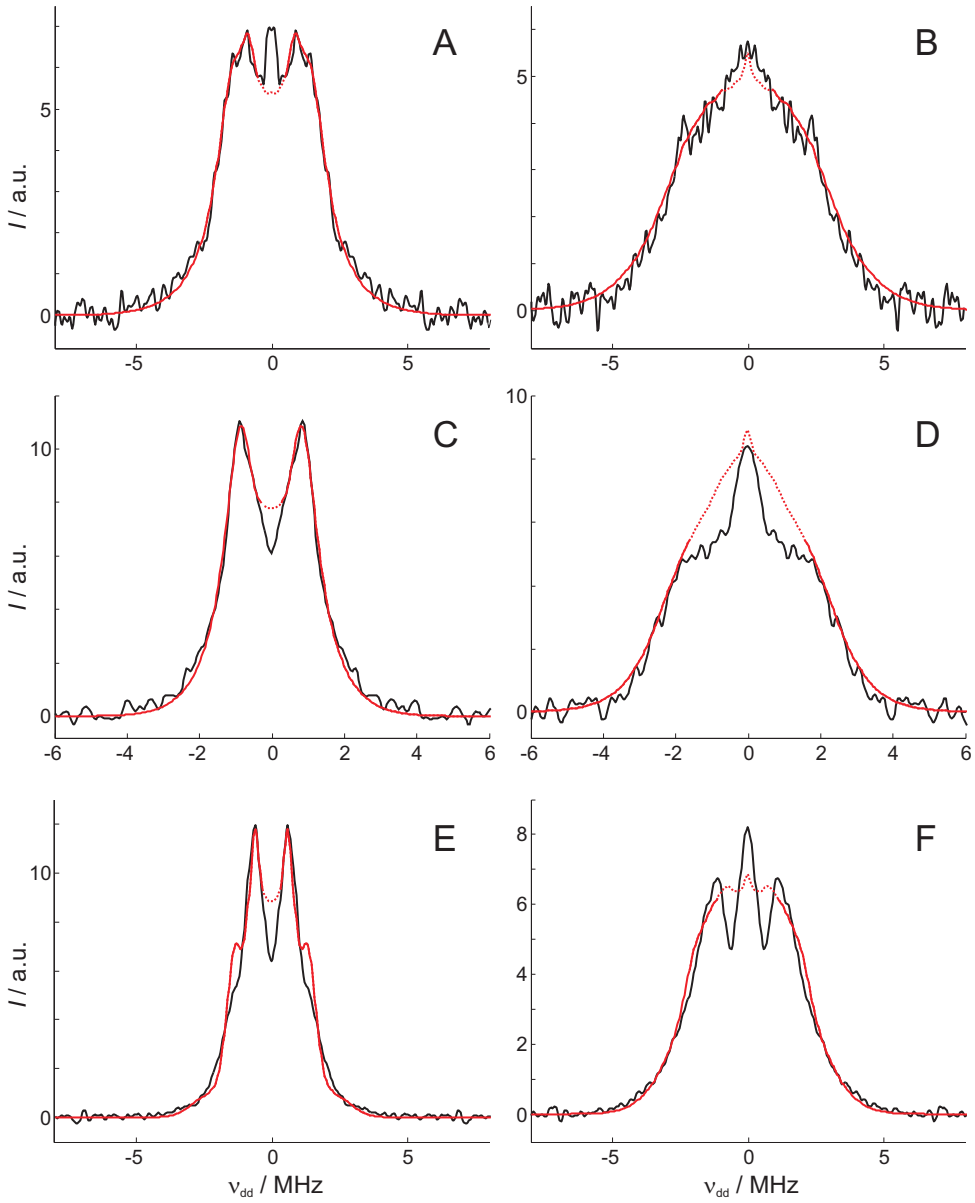

Figure S 4: Fit of dipolar spectra by scalene triangle models with uniform normal distribution of all side lengths. Experimental spectra are shown as black lines and fits as red lines. Dotted red lines correspond to a range that was excluded from the fits. (A) Pair contribution of **T011**. (B) Three-spin contribution of **T011**. (C) Pair contribution of **T111**. (D) Three-spin contribution of **T111**. (E) Pair contribution of **T012**. (F) Three-spin contribution of **T012**.

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[6] When recording the spectra on the 250 MHz instrument the decoupling power was insufficient which resulted in signal broadening or splitting in the case of aromatic CH groups.

[7] An intensely yellow prefraction has been observed in all reaction in which we attached 1-oxyl-2,2,5,5-tetramethylpyrroline-3-carboxylic acid to phenols in the way described here. See Refs. [1] and [5].

[8] This is a typical fragmentation pattern found for the esters of 1-oxyl-2,2,5,5-tetramethylpyrroline-3-carboxylic acid. See Refs. [1, 5, 9, 10, 11]

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[12] The large amounts of catalysts used in this reaction are due to a miscalculation.