Supporting Information

Contents

General Remarks

NMR (Nuclear Magnetic Resonance) spectra were recorded on a Bruker *Avance* 400 (^{1}H: 400 MHz, ^{13}C: 100 MHz) spectrometer. Chemical shifts δ were expressed in parts per million (ppm), referenced to deuterated dichloromethane (^{1}H: 5.32 ppm, ^{13}C: 54.0 ppm), chloroform (^{1}H: 7.27 ppm, ^{13}C: 77.0 ppm), and dimethyl sulfoxide (^{1}H: 2.50 ppm, ^{13}C: 39.5 ppm) as the internal standard. All coupling constants (*J*) are absolute values and *J* values are expressed in Hertz (Hz). The spectra were analyzed according to first order. All ^{1}H NMR data were reported as follows: chemical shift δ, multiplicity (m = multiplet, (b)s = (broad) singlet, d = doublet, q = quartet, sept = septet), multiplets (m) were given over the range (ppm).

FAB (Fast Atom Bombardment) and EI (Electron Impact) mass spectra, as well as HR-MS (High-Resolution Mass Spectra), were obtained using a Finnigan *MAT* 95 mass spectrometer. The indication of the molecular fragments was carried out as the ratio of mass to charge *m/z*; for EI mass the intensity of the signals was expressed in percent relative to the intensity of the base signal (100%). For High-Resolution Mass Spectrometry (HR-MS) the following abbreviations were used: calcd = calculated mass found = mass found in the analysis.

Attenuated Total Reflection Fourier Transform Infrared Spectroscopy (ATR-FTIR) was conducted on a Bruker *Alpha T* or *Tensor-27* at ambient temperature with the software

OPUS. The position of the absorption band was given in wavenumbers ν in cm^{-1}. The shapes and intensities of the bands were characterized as follows: vs = very strong 0-10% T (Transmittance), s = strong 11-40% T, m = medium 41-70% T, w = weak 71-90% T, vw = very weak, 91-100% T.

Argon sorption experiments and pore size analysis were conducted at 87 K using an *Autosorb-1* from Quantachrome Instruments. Before sorption measurements, the samples were degassed in vacuum for 72 h at room temperature. The surface area was calculated from a multipoint BET plot.

Electron Paramagnetic Resonance (EPR) spectroscopy was performed on a Bruker *EMXNano* spectrometer. If not otherwise noted, all liquid samples were measured in toluene at 23 °C. All solid samples were measured without solvent at 23 °C. The following parameters were used for the measurement: Centre-field: 3434 G; sweep width: 100 G; sweep time: 180 s; sample g-factor: 2.00; receiver gain: 40 dB; modulation amplitude: 0.452 G; number of scans: 1; microwave attenuation: 60 dB; number of points: 2212; modulation frequency: 100 kHz, modulation phase: 0; conversion time: 81.38 ms; time constant: 1.28 ms; points/modulation amplitude: 10.

SEM images were recorded using an FEI Philips XL30. Samples have been coated with a thin layer of a gold/palladium film to avoid charging and improve sample conductivity. Images were taken at an acceleration voltage of 15-20 kV with an SE detector.

TLC (Thin Layer Chromatography) reaction monitoring was carried out using silica gel coated aluminium plates (Merck, silica gel 60, F254) which were analyzed under UV light at 254 nm and/or stained by dipping the plate in a solution of vanillin (15 g vanillin in 250 mL ethanol with addition of two drops of sulfuric acid) followed by heating with a heat gun. Flash-chromatography was conducted on silica gel. Solvent mixtures for TLC and flash-chromatography are understood as volume/volume, with each volume measured separately.

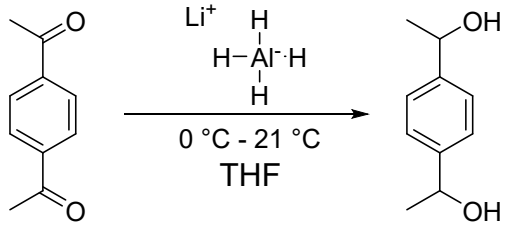
If not mentioned otherwise, all chemicals, solvents, and reagents were purchased from commercial sources (Sigma-Aldrich, Alfa Aesar, abcr, Thermo Fisher Scientific, or

VWR) and used without any further purification. Dry tetrahydrofuran and diethyl ether were prepared by refluxing over sodium with benzophenone as an indicator and distilled off freshly before use. For the synthesis of the frameworks, all solvents were degassed with at least three freeze-pump-thaw cycles before use, and all reactions were carried out under argon atmosphere using the Schlenk technique if not stated otherwise. Room temperature is understood as 21 °C. Strut length was estimated via Chem3D by measuring the distance between two nodes after minimizing the conformational energy.

Please note, that full experimental details and the original analytical data files can be accessed, examined, and downloaded from the repository Chemotion (https://www.chemotion-repository.net/) via the DOIs given at the end of the reaction procedure. For this supporting information, the reaction descriptions and analytical data were generated automatically via the repository Chemotion, adjusted, and enriched with additional information.

Building Block Synthesis

1-[4-(1-Hydroxyethyl)phenyl]ethanol (S1)



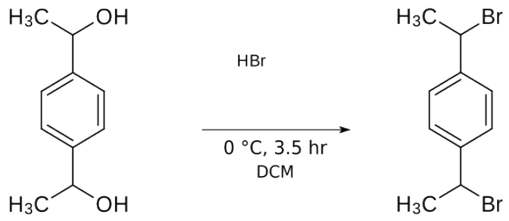
1-(4-Acetylphenyl)ethanone (3.00 g, 18.5 mmol, 1.00 equiv) was dissolved in 150 mL of dry THF and cooled to 0 °C before lithium aluminium hydride (1.05 g, 27.7 mmol, 1.50 equiv) was added in portions. The reaction mixture was slowly warmed to room temperature and then stirred for 1.5 h at this temperature. Afterwards, the mixture was hydrolyzed with ice water, acidified with conc. HCl (~ 16 mL) and the phases were separated. The aqueous phase was extracted with ethyl acetate three times and the combined organic phases were washed with water and brine. After drying over Na_2SO_4, the solvent was removed under reduced pressure. 2.92 g (17.6 mmol) of a colourless, crystalline solid were obtained and used without further purification. – Yield: 95%.

^{1}H NMR (400 MHz, Chloroform-d (s) [7.27 ppm], ppm) δ = 7.33 (s, 4H), 4.87 (q, *J* = 6.6 Hz, 2H), 2.36 (bs, 2H), 1.48 (d, *J* = 6.6 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$ [77.0 ppm], ppm) δ = 144.9 (2C), 125.5 (4C), 70.1, 70.1, 25.1 (2C); EI (m/z, 70 eV, 50 °C): 166 (30) [M^+], 151 (100) [$M^+ - CH_3$], 131 (18), 105 (63), 79 (28), 77 (21), 69 (32). HRMS–EI *(m/z)*: $[M]^+$ calcd for $C_{10}H_{14}O_2$, 166.0988; found 166.0990.

The experimental data are consistent with the literature.
J. S. Wallace, B. W. Baldwin, C. Morrow, *J. Org. Chem.* **1992**, *57*, 5231–5239. *Separation of remote diol and triol stereoisomers by enzyme-catalyzed esterification in organic media or hydrolysis in aqueous media*.

Additional information on the chemical synthesis is available via the Chemotion repository: https://doi.org/10.14272/reaction/SA-FUHFF-UHFFFADPSC-BHCGGVIVFX-UHFFFADPSC-NUHFF-NUHFF-NUHFF-ZZZ
Additional information on the analysis of the target compound is available via the Chemotion repository: https://doi.org/10.14272/BHCGGVIVFXWATI-UHFFFAOYSA-N.1

1,4-Bis(1-bromoethyl)benzene (S2)



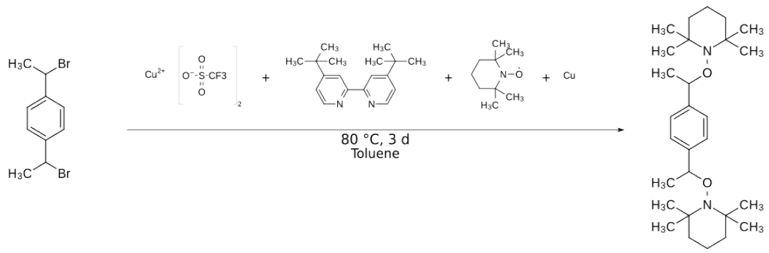
1-[4-(1-Hydroxyethyl)phenyl]ethanol (3.58 g, 21.5 mmol, 1.00 equiv) was dissolved in 150 mL of dichloromethane at 0 °C before hydron bromide (33% in glacial acetic acid) (14.2 g, 10.0 mL, 57.9 mmol, 2.69 equiv) was added. After the reaction was stirred for 3.5 h at this temperature, 70 mL of water were added. The phases were separated, and the organic phase was washed with a saturated $NaHCO_3$-solution, water and brine before being dried over Na_2SO_4. The solvent was removed under reduced pressure and the crude product was recrystallised from hexane to obtain 5.22 g (17.9 mmol) of a colourless, crystalline solid. – Yield: 83%.

^{1}H NMR (400 MHz, Chloroform-d (s), [7.27 ppm], ppm) δ = 7.42 (s, 4H), 5.21 (q, *J* = 7.1 Hz, 2H), 2.05 (d, *J* = 7.1 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$ [77.0 ppm], ppm) δ = 143.3 (2C), 127.1 (4C), 48.8, 48.8, 26.7, 26.7; EI (m/z, 70 eV, 40 °C): 294/292/290 (1/3/1) [M^+], 213/211 (84/76) [M^+ – Br], 132 (100) [M^+ – 2 Br], 117 (36) [M^+ – 2 Br – CH_3], 91 (17). HRMS–EI *(m/z)*: [M^+] calcd for $C_{10}H_{12}{}^{79}Br_2$, 289.9300; found, 289.9302.

The experimental data are consistent with the literature.
C. Zhang, J. Ling, Q. Wang, *Macromolecules* **2011**, *44*, 8739–8743. *Radical Addition-Coupling Polymerization (RACP) toward periodic copolymers*.

Additional information on the chemical synthesis is available via the Chemotion repository: https://doi.org/10.14272/reaction/SA-FUHFF-UHFFFADPSC-SPHVUXIZEZ-UHFFFADPSC-NUHFF-NUHFF-NUHFF-ZZZ
Additional information on the analysis of the target compound is available via the Chemotion repository: https://doi.org/10.14272/SPHVUXIZEZXNPH-UHFFFAOYSA-N.1

2,2,6,6-Tetramethyl-1-[1-[4-[1-(2,2,6,6-tetramethylpiperidin-1-yl)oxyethyl]phenyl]ethoxy]piperidine (1)



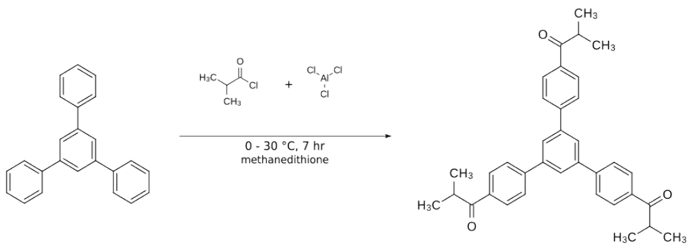
Under an argon atmosphere, 1,4-bis(1-bromoethyl)benzene (300 mg, 1.03 mmol, 1.00 equiv), 1-$l^{1}-oxidanyl-2,2,6,6-tetramethylpiperidine (485 mg, 3.10 mmol, 3.02 equiv), copper (196 mg, 3.08 mmol, 3.00 equiv), copper trifluoromethanesulfonate (18.6 mg, 51.4 µmol, 0.0501 equiv) and 4-tert-butyl-2-(4-tert-butylpyridin-2-yl)pyridine (27.6 mg, 103 µmol, 0.100 equiv) were suspended in 6 mL of abs. toluene. The reaction mixture was stirred for 3 days at 80 °C, before being cooled to room temperature and filtered over silica using dichloromethane. The solvent was removed under reduced pressure and the crude product recrystallised from acetonitrile to obtain 0.249 g (0.560 mmol) of a colourless, crystalline solid. – Yield: 55%.

^{1}H NMR (400 MHz, Chloroform-d [7.27 ppm], ppm) δ = 7.25 (s, 4H, $C_{ar.}H$), 4.75 (q, J = 6.57 Hz, 2H, CHCH$_3$), 1.44–1.59 (m, 12H, CH_3 TEMPO + CH_3 Sidechain), 1.35 (bs, 4H, CH_2), 1.30 (bs, 8H, CH_2), 1.17 (bs, 6H, CH_3 TEMPO), 1.02 (bs, 6H, CH_3 TEMPO), 0.60 (bs, 6H, CH_3 TEMPO); ^{13}C NMR (100 MHz, $CDCl_3$, 77 ppm) δ = 144.2 (2C, C_q), 126.3 (4C. $C_{ar.}$H), 83.1 (2C, CHCH$_3$), 59.7 (2C, C_q TEMPO), 59.4 (2C, C_q TEMPO), 40.4 (4C, CH$_2$ TEMPO), 34.4 (2C, CH$_3$ TEMPO), 34.3 (2C, CH$_3$ TEMPO), 23.3 (2C, CH$_3$), 20.3 (4C, CH$_3$ TEMPO), 17.2 (2C, CH$_2$ TEMPO); EI (m/z, 70 eV, 120 °C): 288 (4) [M$^+$ – TEMPO], 156 (100) [TEMPO$^+$], 142 (7), 132 (4) [M$^+$ – 2 TEMPO]. HRMS–EI *(m/z)*: [M$^+$] calcd for $C_{19}H_{30}NO$, 288.2322; found 288.2320; IR (ATR, ṽ) = 2999, 2969, 2930, 2870, 2846, 1463, 1443, 1371, 1358, 1347, 1332, 1289, 1273, 1259, 1240, 1231, 1208, 1182, 1130, 1089, 1082, 1056, 1046, 1018, 995, 984, 971, 953, 932, 881, 834, 789, 748, 691, 605, 572, 506, 429, 392 cm^{-1}.

The experimental data are consistent with the literature.
Y. Jia, Y. Matt, Q. An, I. Wessely, H. Mutlu, P. Theato, S. Bräse, A. Llevot, M. Tsotsalas, *Polym. Chem.* **2020**, *11*, 2502–2510. *Dynamic Covalent Polymer Networks via Combined Nitroxide Exchange Reaction and Nitroxide Mediated Polymerization.*

Additional information on the chemical synthesis is available via the Chemotion repository: https://doi.org/10.14272/reaction/SA-FUHFF-UHFFFADPSC-WMQIFFUHJF-UHFFFADPSC-NUHFF-NUHFF-NUHFF-ZZZ
Additional information on the analysis of the target compound is available via the Chemotion repository: https://doi.org/10.14272/WMQIFFUHJFOQPZ-UHFFFAOYSA-N.1

1,3,5-Tris(4'-isobutyronylphenyl)benzene (S3)



Under an argon atmosphere, aluminium trichloride (34.8 g, 261 mmol, 4.00 equiv) was suspended in 150 mL of methanedithione. 2-Methylpropanoyl chloride (28.4 g, 28.1 mL, 266 mmol, 4.08 equiv) was added dropwise under ice bath cooling, followed by 1,3,5-

triphenylbenzene (20.0 g, 65.3 mmol, 1.00 equiv) dissolved in 250 mL of methanedithione over 1 h, also under ice-bath cooling. The mixture was stirred under cooling until the end of gas evolution and then slowly warmed to room temperature. Stirring was repeated until no significant gas evolution was observed anymore. The mixture was then heated to 30 °C until no further gas evolution was observed (~2 hours) either. After cooling to 21 °C, the supernatant was decanted from the formed solid and the solid was mixed with 500 g of ice water, 100 mL of conc. HCl and 400 mL of methylene chloride. This mixture was stirred until the solid was completely dissolved. The organic phase was separated, washed with 10% NaOH solution, water, saturated NaCl solution, dried over Na_2SO_4, and the solvent was removed under reduced pressure. The residue was refluxed in a mixture of ethanol/ethyl acetate (200 mL/ 30 mL) and filtered after cooling to give 24.3 g (46.9 mmol) of a colourless solid. – Yield: 72%.
R_f = 0.53 (methylene chloride).

^{1}H NMR (400 MHz, Chloroform-d [7.27 ppm], ppm) δ = 8.12–8.09 (m, 6H, $C_{ar}H$), 7.89 (s, 3H, $C_{ar}H$), 7.83–7.79 (m, 6H, $C_{ar}H$), 3.63 (sept, J = 6.9 Hz, 3H, $CH(CH_3)_2$), 1.28 (d, J = 6.9 Hz, 18H, CH_3); ^{13}C NMR (100 MHz, Chloroform-d [77.0 ppm], ppm) δ = 204.0 (3C, CO), 144.8 (3C, C_q), 141.6 (3C, C_q), 135.4 (3C, C_q), 129.1 (6C, C_{ar}H), 127.5 (6C, C_{ar}H), 126.0 (3C, C_{ar}H), 35.5 (3C, $CH(CH_3)_2$), 19.2 (6C, CH_3); EI (m/z, 70 eV, 200 °C): 516 (20) [M^+], 474 (38) [$M^+ – C_3H_7 + H$], 473 (100) [$M^+ – C_3H_7$], 446 (20) [$M^+ – C_4H_7O + H$], 404 (30), 403 (95) [$M^+ – C_3H_7 – C_4H_7O + H$], 332 (20) [$M^+ – C_3H_7 – 2\ C_4H_7O + H$]. HRMS–EI *(m/z)*: [M]$^+$ calcd for $C_{36}H_{36}O_3$, 516.2664; found, 516.2665; IR (ATR, ṽ) = 2968 (w), 2931 (w), 2871 (w), 1676 (vs), 1596 (vs), 1561 (w), 1465 (w), 1443 (w), 1408 (w), 1381 (m), 1368 (w), 1350 (w), 1286 (w), 1248 (w), 1220 (vs), 1159 (s), 1119 (w), 1084 (w), 979 (vs), 931 (w), 905 (w), 892 (w), 871 (w), 849 (s), 827 (s), 761 (vs), 721 (w), 697 (s), 669 (w), 663 (w), 640 (w), 620 (w), 608 (w), 572 (w), 521 (w), 490 (m), 455 (w), 446 (w), 435 (w), 418 (w), 407 (w), 395 (w), 377 (w) cm^{-1}.

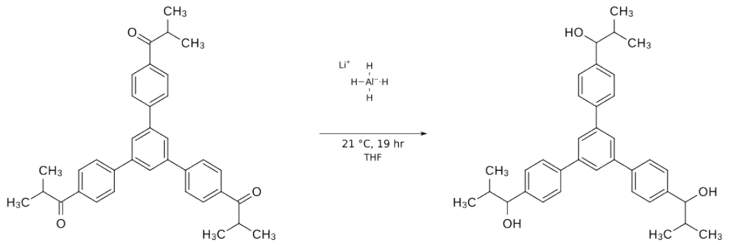
The experimental data are consistent with the literature.
Q. An, I. D. Wessely, Y. Matt, Z. Hassan, S. Bräse, M. Tsotsalas, *Polym. Chem.* **2019**, *10*, 672–678. *Recycling and self-healing of dynamic covalent polymer networks with a precisely tuneable crosslinking degree.*

Additional information on the chemical synthesis is available via the Chemotion repository:

https://doi.org/10.14272/reaction/SA-FUHFF-UHFFFADPSC-SASADIUGQA-UHFFFADPSC-NUHFF-NUHFF-NUHFF-ZZZ

Additional information on the analysis of the target compound is available via the Chemotion repository: https://doi.org/10.14272/SASADIUGQAVSRR-UHFFFAOYSA-N.1

1,3,5-Tris(4'-(1''-hydroxy-2''-methylpropyl)phenyl)benzene (S4)



Under an argon atmosphere, lithium aluminium hydride (3.53 g, 93.0 mmol, 1.98 equiv) was suspended in 700 mL of dry THF and 1,3,5-tris(isopropyl 4'-phenyl ketone)benzene (24.3 g, 47.0 mmol, 1.00 equiv) was added in portions. The reaction mixture was stirred for 19 h at 21 °C. Subsequently, the reaction was quenched with water and 10% NaOH solution was added until everything was dissolved. The phases were separated and the aqueous phase was extracted with ethyl acetate. The combined organic layers were washed with saturated NaCl solution, dried over Na_2SO_4 and the solvent was removed under reduced pressure. The residue was absorbed in a few mL of an ethyl acetate/cyclohexane mixture (1:1) and treated in an ultrasonic bath, filtered off, and dried to give 24.3 g (46.5 mmol) of a colourless solid. – Yield: 99%.
R_f = 0.88 (ethyl acetate).

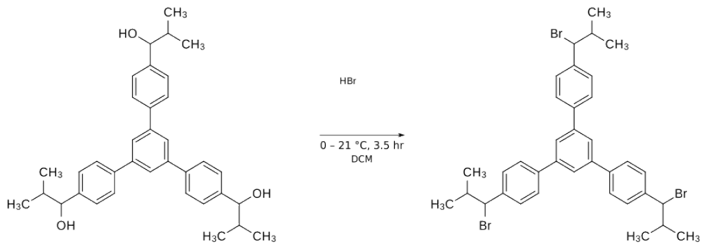
^{1}H NMR (400 MHz, DMSO-d_6 [2.50 ppm], ppm) δ = 7.86 (s, 3H, $C_{ar.}H$), 7.82–7.79 (m, 6H, $C_{ar.}H$), 7.42–7.40 (m, 6H, $C_{ar.}H$), 5.14 (d, J = 4.4 Hz, 3H, O*H*), 4.33–4.31 (m, 3H, C*H*OH), 1.92–1.80 (m, 3H, C*H*$(CH_3)_2$), 0.90 (d, J = 6.6 Hz, 9H, CH_3), 0.80 (d, J = 6.8 Hz, 9H, CH_3). ^{13}C NMR (100 MHz, DMSO-d_6 [39.5 ppm], ppm) δ = 144.6 (3C, C_q), 141.5 (3C, C_q), 138.4 (3C, C_q), 127.1 (6C, $C_{ar.}$H), 126.4 (6C, $C_{ar.}$H), 123.8 (3C, $C_{ar.}$H), 77.2 (3C, *C*HOH), 35.0 (3C, *C*H$(CH_3)_2$), 19.1 (3C, *C*H_3), 17.9 (3C, *C*H_3). FAB (3-NAB, m/z): 523 [M^+ + H], 522 [M^+], 506 [M^+ – O], 505 [M^+ – OH], 480 [M^+ – C_3H_7 + H], 479 [M^+ – C_3H_7], 433 [M^+ – C_4H_9O – CH_3 – H], 407 [M^+ – C_4H_9O – C_3H_7]. HRMS–FAB *(m/z)*: [M^+] calcd for $C_{36}H_{42}O_3$, 522.3134; found, 522.3133; IR (ATR, ṽ) = 3292 (w), 3247 (w), 3241 (w), 2961 (w), 2925 (m), 2907 (w), 2898 (w), 2868 (w), 2850 (w), 1595 (w), 1513 (w), 1468 (w), 1449 (w), 1384 (m), 1366 (w), 1324

(w), 1275 (w), 1239 (w), 1205 (w), 1033 (s), 1020 (vs), 935 (w), 864 (w), 841 (w), 824 (vs), 792 (s), 761 (w), 727 (w), 722 (w), 705 (m), 662 (w), 646 (w), 636 (w), 612 (m), 579 (s), 555 (w), 538 (w), 504 (m), 401 (w) cm^{-1}.

The experimental data are consistent with the literature.
Q. An, I. D. Wessely, Y. Matt, Z. Hassan, S. Bräse, M. Tsotsalas, *Polym. Chem.* **2019**, *10*, 672–678. *Recycling and self-healing of dynamic covalent polymer networks with a precisely tuneable crosslinking degree.*

Additional information on the chemical synthesis is available via the Chemotion repository: https://doi.org/10.14272/reaction/SA-FUHFF-UHFFFADPSC-GZTZPWJYEB-UHFFFADPSC-NUHFF-NUHFF-NUHFF-ZZZ
Additional information on the analysis of the target compound is available via the Chemotion repository: https://doi.org/10.14272/GZTZPWJYEBUERP-UHFFFAOYSA-N.1

1,3,5-Tris(4'-(1''-bromo-2''-methylpropyl)phenyl)benzene (S5)



To a suspension of 1,3,5-tris(4'-(1''-hydroxy-2''-methylpropyl)phenyl)benzene (35.2 g, 67.3 mmol, 1.00 equiv) in 600 mL of methylene chloride, hydron bromide (33% in glacial acetic acid) (98.1 g, 69.1 mL, 400 mmol, 5.94 equiv) was slowly added via a dropping funnel at 0 °C. The reaction mixture was stirred for 3.5 h at 21 °C. Afterwards, water was added, the phases were separated and the organic phase was washed with saturated $NaHCO_3$ solution, water, saturated NaCl solution, and dried over Na_2SO_4. The solvent was removed under reduced pressure. The residue was recrystallised from acetone and washed with cyclohexane to give 38.9 g (54.7 mmol) of a colourless solid. – Yield: 81%.

^{1}H NMR (400 MHz, Chloroform-d [7.27 ppm], ppm) δ = 7.78 (s, 3H, $C_{ar}H$), 7.66 (d, J = 8.3 Hz, 6H, $C_{ar}H$), 7.49 (d, J = 8.3 Hz, 6H, $C_{ar}H$), 4.80 (d, J = 8.5 Hz, 3H, C*H*Br), 2.46–2.34 (m,

3H, C*H*(CH_3)$_2$), 1.25 (d, *J* = 6.5 Hz, 9H, CH_3), 0.94 (d, *J* = 6.6 Hz, 9H, CH_3); ^{1}H NMR (400 MHz, Dichloromethane-d_2 [5.32 ppm], ppm) δ = 7.82 (s, 3H, $C_{ar.}H$), 7.69 (d, *J* = 8.3 Hz, 6H, $C_{ar.}H$), 7.50 (d, *J* = 8.3 Hz, 6H, $C_{ar.}H$), 4.82 (d, *J* = 8.6 Hz, 3H, C*H*Br), 2.46–2.34 (m, 3H, C*H*(CH_3)$_2$), 1.24 (d, *J* = 6.5 Hz, 9H, CH_3), 0.92 (d, *J* = 6.8 Hz, 9H, CH_3); ^{13}C NMR (100 MHz, Chloroform-d [77.0 ppm], ppm) δ = 141.7 (3C, C_q), 141.1 (3C, C_q), 140.6 (3C, C_q), 128.4 (6C, $C_{ar.}$H), 127.3 (6C, $C_{ar.}$H), 125.1 (3C, $C_{ar.}$H), 63.9 (3C, *C*HBr), 36.6 (3C, *C*H(CH_3)$_2$), 21.6 (3C, *C*H_3), 20.6 (3C, *C*H_3); FAB (3-NBA, m/z): 709/711/713/715 [M^+ + H] 633/631/629 [M^+ – Br], 552/550 [M^+ – 2 Br]. HRMS–FAB *(m/z)*: [M + H]$^+$ calcd for $C_{36}H_{40}{}^{79}Br_2{}^{81}Br$, 711.0660; found, 711.0660; IR (ATR, ṽ) = 2959 (m), 2931 (w), 2907 (w), 2867 (w), 1595 (w), 1565 (vw), 1510 (m), 1465 (w), 1445 (w), 1414 (w), 1397 (w), 1384 (m), 1366 (w), 1317 (vw), 1307 (vw), 1244 (w), 1211 (w), 1170 (m), 1120 (w), 1068 (vw), 1018 (w), 942 (w), 928 (w), 887 (vw), 839 (m), 822 (vs), 803 (m), 786 (vs), 771 (m), 744 (m), 707 (m), 669 (vs), 653 (s), 635 (s), 613 (m), 575 (m), 534 (w), 507 (w), 476 (w), 452 (vw), 405 (vw) cm^{-1}.

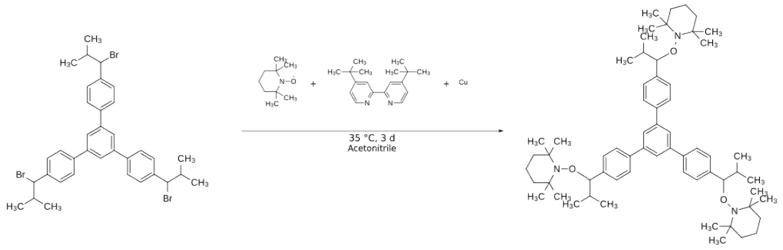
The experimental data are consistent with the literature.

Q. An, I. D. Wessely, Y. Matt, Z. Hassan, S. Bräse, M. Tsotsalas, *Polym. Chem.* **2019**, *10*, 672–678. *Recycling and self-healing of dynamic covalent polymer networks with a precisely tuneable crosslinking degree.*

Additional information on the chemical synthesis is available via the Chemotion repository: https://doi.org/10.14272/reaction/SA-FUHFF-UHFFFADPSC-AAFJWSUJJW-UHFFFADPSC-NUHFF-NUHFF-NUHFF-ZZZ

Additional information on the analysis of the target compound is available via the Chemotion repository: https://doi.org/10.14272/AAFJWSUJJWIJEW-UHFFFAOYSA-N.1

1,1'-(((5'-(4-(2-Methyl-1-((2,2,6,6-tetramethylpiperidin-1-yl)oxy)propyl)phenyl)-[1,1':3',1''-terphenyl]-4,4''-diyl)bis(2-methylpropane-1,1-diyl))bis(oxy))bis(2,2,6,6-tetramethylpiperidine) (**2**)



Under an argon atmosphere, 1,3,5-tris(4'-(1''-bromo-2''-methylpropyl)phenyl)benzene (1.00 g, 1.41 mmol, 1.00 equiv), 1-oxidanyl-2,2,6,6-tetramethylpiperidine (696 mg, 4.46 mmol, 3. 17 equiv), copper (134 mg, 2.11 mmol, 1.50 equiv) and 4-*tert*-butyl-2-(4-*tert*-butylpyridin-2-yl)pyridine (1.13 g, 4.22 mmol, 3.00 equiv) were suspended in 30 mL of dry acetonitrile. The reaction mixture was degassed for 10 minutes by bubbling with argon, before being stirred at 35 °C for 3 days. Afterwards, methylene chloride was added, and the mixture was washed with semi-concentrated ammonia, water, and saturated NaCl solution, and dried over Na_2SO_4. The solvent was removed under reduced pressure. The crude product was passed through a short column (methylene chloride/ethyl acetate 4:1) to remove 4-*tert*-butyl-2-(4-*tert*-butylpyridin-2-yl)pyridine. The residue was recrystallised from ethanol to give 1.02 g (1.09 mmol) of a colourless solid. – Yield: 77%.

R_f = 0.40 (methylene chloride/cyclohexane 1:1).

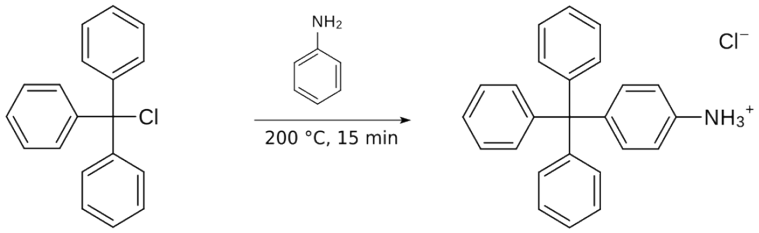
^{1}H NMR (400 MHz, Dichloromethane-d_2 [5.32 ppm], ppm) δ = 7.84 (s, 3H, $C_{ar.}H$), 7.67 (d, J = 8.3 Hz, 6H, $C_{ar.}H$), 7.35 (d, J = 8.3 Hz, 6H, $C_{ar.}H$), 4.60 (d, J = 5.5 Hz, 3H, C*H*O), 2.65–2.53 (m, 3H, C*H*$(CH_3)_2$), 1.70–0.97 (m, 45H, CH_2 CH_3 TEMPO), 0.85 (m, 18H, CH_3 Sidechain), 0.67 (s, 9H, CH_3 TEMPO); ^{13}C NMR (100 MHz, Dichloromethane-d_2 [54.0 ppm], ppm) δ = 142.6 (3C, C_q), 140.5 (3C, C_q), 139.9 (3C, C_q), 130.0 (6C, $C_{ar.}H$), 126.4 (6C, $C_{ar.}H$), 125.1 (3C, $C_{ar.}H$), 91.5 (3C, *C*HO), 60.3 (6C, C_q TEMPO), 41.2 (6C, *C*H_2 TEMPO), 35.2 (3C, *C*H_3 TEMPO), 34.4 (3C, *C*H_3 TEMPO), 31.8 (3C, *C*H$(CH_3)_2$), 20.9 (3C, *C*H_3 TEMPO), 20.7 (3C, *C*H_3 TEMPO), 20.6 (3C, *C*H_3 Sidechain), 17.8 (3C, *C*H_2 TEMPO), 16.7 (3C, *C*H_3 Sidechain); FAB (3-NBA, m/z): 941 [M^+ + H], 784 [M^+ – TEMPO], 628 [M^+ – 2 TEMPO], 488, 472 [M^+ – 3 TEMPO + H], 471 [M^+ – 3 TEMPO], 456 [M^+ – 3 TEMPO – CH_3], 441 [M^+ – 3 TEMPO – 2 CH_3], 158, 157, 156 [$TEMPO^+$], 140 [$TEMPO^+$ – O]. HRMS–FAB *(m/z)*: [M + H]$^+$ calcd

for $C_{63}H_{94}N_3O_3$, 940.7295; found, 940.7293; IR (ATR, $\tilde{\nu}$) = 3002 (w), 2963 (s), 2929 (vs), 2870 (m), 2847 (w), 1596 (w), 1568 (vw), 1510 (w), 1468 (m), 1460 (m), 1375 (m), 1360 (s), 1350 (m), 1313 (w), 1258 (w), 1241 (m), 1208 (w), 1180 (w), 1133 (s), 1079 (w), 1011 (s), 987 (s), 976 (s), 953 (s), 912 (w), 878 (w), 841 (m), 817 (vs), 744 (w), 707 (m), 616 (w), 584 (w), 557 (w), 507 (w), 452 (w), 424 (w), 375 (w) cm^{-1}.

The experimental data are consistent with the literature.
Q. An, I. D. Wessely, Y. Matt, Z. Hassan, S. Bräse, M. Tsotsalas, *Polym. Chem.* **2019**, *10*, 672–678. *Recycling and self-healing of dynamic covalent polymer networks with a precisely tuneable crosslinking degree.*

Additional information on the chemical synthesis is available via the Chemotion repository: https://doi.org/10.14272/reaction/SA-FUHFF-UHFFFADPSC-UODLICXQAZ-UHFFFADPSC-NUHFF-NUHFF-NUHFF-ZZZ
Additional information on the analysis of the target compound is available via the Chemotion repository: https://doi.org/10.14272/UODLICXQAZWDDJ-UHFFFAOYSA-N.1

4-Tritylaniline;hydrochloride (S6)



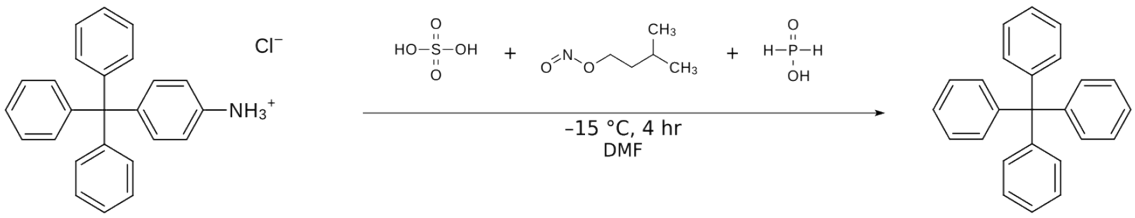
In a 500 mL round-bottomed flask with reflux condenser, [chloro(diphenyl)methyl]benzene (25.0 g, 89.7 mmol, 1.00 equiv) and aniline (21.7 g, 21.3 mL, 233 mmol, 2.60 equiv) were stirred for 15 min. at 200 °C. The reaction mixture was cooled down to room temperature. A mixture of 200 mL of 2M HCl and 300 mL of EtOH was then added to the solid and the reaction mixture was heated to 80 °C for 30 min. After the mixture was cooled down to 0 °C, the resulting solid was filtered, washed with 150 mL of EtOH, and dried under vacuum to give 25.0 g (67.2 mmol) of a grey solid. – Yield: 75%.

EI (m/z, 70 eV, 110 °C): 336 (15) [M^+ of free base + H], 335 (52) [M^+ of free base], 259 (21) [M^+ of free base – C_6H_4], 258 (100) [M^+ of free base – C_6H_5], 180 (21), 165 (18), 58 (24). HRMS–EI *(m/z)*: $[M]^+$ calcd for $C_{25}H_{21}N$, 335.1674; found, 335.1675; IR (ATR, ṽ) = 2800 (s), 2582 (s), 1621 (w), 1591 (w), 1579 (w), 1527 (w), 1506 (s), 1490 (s), 1442 (m), 1417 (w), 1326 (w), 1279 (w), 1214 (w), 1186 (w), 1156 (w), 1128 (w), 1081 (w), 1033 (w), 1018 (w), 1001 (w), 986 (w), 892 (w), 847 (vw), 820 (m), 765 (w), 754 (m), 745 (s), 721 (w), 700 (vs), 683 (m), 629 (s), 584 (w), 540 (w), 516 (m), 496 (w), 482 (m), 416 (w) cm^{-1}.

Additional information on the chemical synthesis is available via the Chemotion repository: https://doi.org/10.14272/reaction/SA-FUHFF-UHFFFADPSC-GGYQDMHUVM-UHFFFADPSC-NUHFF-NUHFF-NUHFF-ZZZ

Additional information on the analysis of the target compound is available via the Chemotion repository: https://doi.org/10.14272/GGYQDMHUVMIEFM-UHFFFAOYSA-N.1

Tritylbenzene (S7)



In a 500 mL round-bottomed flask, 4-tritylaniline hydrochloride (25.0 g, 67.2 mmol, 1.00 equiv) was suspended in 235 mL of DMF and cooled to –15 °C. At this temperature, hydron sulfate (41.2 g, 22.5 mL, 420 mmol, 6.25 equiv) and 3-methylbutyl nitrite (14.6 g, 16.8 mL, 125 mmol, 1.86 equiv) were added. The reaction mixture was stirred for 1 h at this temperature and then phosphinic acid (22.9 g, 18.7 mL, 347 mmol, 5.16 equiv) was added carefully. The reaction mixture was then heated to 50 °C until no further gas evolution was observed (~ 4 h). The resulting solid was filtered off and washed twice with 250 mL of DMF, 250 mL of water, and 250 mL of ethanol to give 21.4 g (66.9 mmol) of a slightly beige solid. – Yield: 99%.

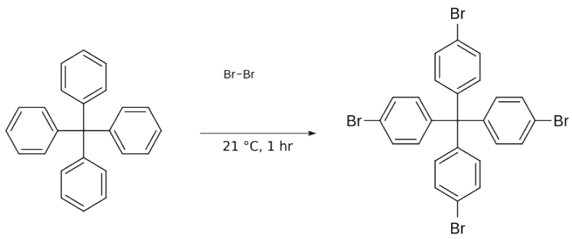
^{1}H NMR (300 MHz, DMSO-d_6 [2.50 ppm], ppm) δ = 7.33–7.28 (m, 8H, C_{ar}*H*), 7.23–7.20 (m, 4H, C_{ar}*H*), 7.18–7.13 (m, 8H, C_{ar}*H*); EI (m/z, 70 eV, 110 °C): 320 (56) [M^+], 243 (100) [M^+ – C_6H_5], 165 (60) [M^+ – 2 C_6H_5 –H]. HRMS–EI *(m/z)*: [M^+] calcd for $C_{25}H_{20}$, 320.1565; found,

320.1566; IR (ATR, $\tilde{\nu}$) = 3084 (vw), 3055 (w), 3029 (w), 3017 (w), 1672 (w), 1592 (w), 1490 (m), 1441 (w), 1385 (w), 1183 (w), 1081 (w), 1034 (w), 1002 (w), 765 (m), 749 (vs), 700 (vs), 633 (s), 620 (w), 588 (w), 564 (vw), 548 (vw), 524 (w), 511 (vw), 492 (w) cm^{-1}.

The experimental data are consistent with the literature.
O. Plietzsch, C. I. Schilling, M. Tolev, M. Nieger, C. Richert, T. Müller, S. Bräse, *Org. Biomol. Chem*.**2009**, *7*, 4734–4743. *Four-fold click reactions: Generation of tetrahedral methane- and adamantane-based building blocks for higher-order molecular assemblies.*

Additional information on the chemical synthesis is available via the Chemotion repository: https://doi.org/10.14272/reaction/SA-FUHFF-UHFFFADPSC-PEQHIRFAKI-UHFFFADPSC-NUHFF-NUHFF-NUHFF-ZZZ
Additional information on the analysis of the target compound is available via the Chemotion repository: https://doi.org/10.14272/PEQHIRFAKIASBK-UHFFFAOYSA-N.1

Tetrakis(4-bromophenyl)methane (**S8**)



Molecular bromine (29.9 g, 9.59 mL, 187 mmol, 12.0 equiv) was added slowly to tritylbenzene (5.00 g, 15.6 mmol, 1.00 equiv) with continuous stirring. The resulting slurry was stirred for exactly one hour and then quenched with ethanol (100 mL) which was cooled to –78 °C. The precipitated solid was filtered, washed with saturated aqueous $NaHSO_3$ solution, water, cold ethanol, and dried at 50 °C under vacuum to gain 8.81 g (13.9 mmol) of a colourless solid. – Yield: 89%.
R_f = 0.92 (cyclohexane/methylene chloride 1/1).

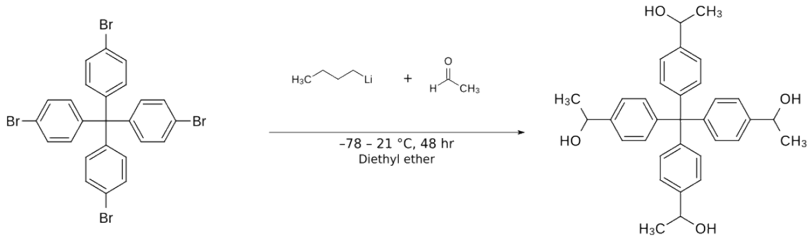
^{1}H NMR (400 MHz, Chloroform-d [7.27 ppm], ppm) δ = 7.42–7.39 (m, 8H, $C_{ar.}H$), 7.04–7.01 (m, 8H, $C_{ar.}H$); ^{13}C NMR (100 MHz, Chloroform-d [77.0 ppm], ppm) δ = 144.4 (4C, C_q), 132.3 (8C, $C_{ar.}$H), 131.1 (8C, $C_{ar.}$H), 120.8 (4C, C_q), 63.6 (1C, C_q); MS (EI, 70 eV, 170 °C), m/z (%):

640/638/636/634/632 (8/34/49/34/9) [M^+], 559/557/555/553 (6/12/12/3) [M^+ – Br], 483/481/479/477 (33/100/90/35) [M^+ – C_6H_4Br], 402/400/398 (5/9/4) [M^+ – C_6H_4Br – Br], 321/319 (35/27) [M^+ – C_6H_4Br – 2 Br]. HRMS–EI *(m/z)*: [M^+] calcd for $C_{25}H_{16}{}^{79}Br_2{}^{81}Br_2$ 635.7939; found 635.07937; IR (ATR, ṽ) = 1571 (vw), 1480 (m), 1460 (w), 1397 (w), 1184 (w), 1167 (w), 1139 (w), 1112 (w), 1078 (m), 1009 (vs), 949 (w), 914 (vw), 833 (w), 809 (vs), 727 (vw), 677 (vw), 629 (w), 533 (m), 510 (vs), 414 (w), 399 (vw) cm^{-1}.

The experimental data are consistent with the literature.
L. Zhu, D. Sheng, C. Xu, X. Dai, M. A. Silver, J. Li, P. Li, Y. Wang, Y. Wang, L. Chen, et al., *J. Am. Chem. Soc.***2017**, *139*, 14873–14876. *Identifying the Recognition Site for Selective Trapping of $^{99}TcO_4^-$ in a Hydrolytically Stable and Radiation Resistant Cationic Metal–Organic Framework.*

Additional information on the chemical synthesis is available via the Chemotion repository: https://doi.org/10.14272/reaction/SA-FUHFF-UHFFFADPSC-YBGIIZGNEO-UHFFFADPSC-NUHFF-NUHFF-NUHFF-ZZZ.1
Additional information on the analysis of the target compound is available via the Chemotion repository: https://doi.org/10.14272/YBGIIZGNEOJSRF-UHFFFAOYSA-N.1

1,1',1'',1'''-(Methanetetrayltetrakis(benzene-4,1-diyl))tetrakis(ethan-1-ol) (S9)



Under an argon atmosphere, butane; lithium (1.81 g, 11.3 mL, 28.3 mmol, 2.50M, 6.00 equiv) was added dropwise to a suspension of 1-bromo-4-[tris(4-bromophenyl)methyl]benzene (3.00 g, 4.72 mmol, 1.00 equiv) in 225 mL of dry diethyl ether at –78 °C. The resultant reaction mixture was then allowed to warm to 21 °C and stirred overnight. After cooling to –78 °C again, acetaldehyde (1.66 g, 2.13 mL, 37.7 mmol, 8.00 equiv) was added and the mixture was allowed to warm to 21 °C and stirred overnight. Afterwards, the reaction was quenched with water, phases separated with saturated NaCl solution and the aqueous phase further extracted

with THF. The combined organic phases were washed with water and saturated NaCl solution, dried over Na_2SO_4 and the solvent was removed under reduced pressure. The crude product was recrystallised from ethanol to give 990 mg (1.99 mmol) of a colourless solid. – Yield: 42%.

R_f = 0.39 (cyclohexane/acetone 4:3).

^{1}H NMR (400 MHz, DMSO-d_6 [2.50 ppm], ppm) δ = 7.25–7.23 (m, 8H, $C_{ar.}H$), 7.14–7.12 (m, 8H, $C_{ar.}H$), 5.08 (d, J = 4.1 Hz, 4H, O*H*), 4.63–4.69 (m, 4H, C*H*OH), 1.31 (d, J = 6.4 Hz, 12H, CH_3). ^{13}C NMR (100 MHz, DMSO-d_6 [39.5 ppm], ppm) δ = 145.1 (4C, C_q), 144.5 (4C, C_q), 129.9 (8C, $C_{ar.}$H), 124.7 (8C, $C_{ar.}$H), 67.7 (4C, *C*OH), 63.6 (1C, C_q), 25.6 (4C, *C*H$_3$); EI (m/z, 70 eV, 220 °C): 496 (18) [M^+], 387 (10), 376 (28) [$C_{25}H_{28}O_3^+$], 375 (100) [$C_{25}H_{27}O_3^+$], 331 (8) [$C_{23}H_{22}O_2^+$], 165 (12) [$C_{13}H_9^+$]. HRMS–EI *(m/z)*: [M^+] calcd for $C_{33}H_{36}O_4$, 496.2614; found, 496.2616; IR (ATR, ṽ) = 3264 (w), 3021 (w), 2969 (w), 2925 (w), 2870 (w), 1504 (w), 1446 (w), 1407 (w), 1368 (w), 1324 (w), 1306 (w), 1268 (w), 1213 (m), 1193 (w), 1086 (s), 1069 (vs), 1020 (m), 1004 (s), 955 (w), 894 (vs), 824 (vs), 788 (w), 768 (s), 732 (m), 704 (m), 619 (m), 578 (s), 555 (vs), 507 (m), 426 (m) cm^{-1}.

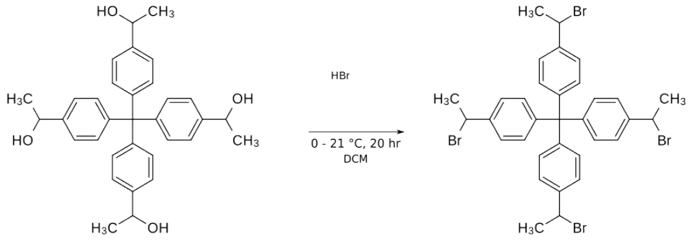
The experimental data are consistent with the literature.

Y. Matt, I. Wessely, L. Gramespacher, M. Tsotsalas, S. Bräse, *Eur. J. Org. Chem.* **2020**, DOI 10.1002/ejoc.202001415. *Rigid Multidimensional Alkoxyamines: A Versatile Building Block Library.*

Additional information on the chemical synthesis is available via the Chemotion repository: https://doi.org/10.14272/reaction/SA-FUHFF-UHFFFADPSC-NARYKPVJYV-UHFFFADPSC-NUHFF-NUHFF-NUHFF-ZZZ

Additional information on the analysis of the target compound is available via the Chemotion repository: https://doi.org/10.14272/NARYKPVJYVHZGI-UHFFFAOYSA-N.1

Tetrakis(4-(1-bromoethyl)phenyl)methane (S10)



To a suspension of tetrakis(4-(1-hydroxyethyl)phenyl)methane (2.20 g, 4.43 mmol, 1.00 equiv) in 40 mL of methylene chloride, hydron bromide (33% in glacial acetic acid) (6.52 g, 4.59 mL, 26.6 mmol, 6.00 equiv) was slowly added via a dropping funnel at 0 °C. The reaction mixture was stirred for 20 h at 21 °C. Afterwards, water was added, the phases were separated, and the organic phase was washed with saturated $NaHCO_3$ solution, water, saturated NaCl solution and dried over Na_2SO_4. The solvent was removed under reduced pressure. The residue was recrystallised from acetone to give 2.38 g (3.18 mmol) of a colourless solid. – Yield: 72%.

^{1}H NMR (400 MHz, CD_2Cl_2 [5.32 ppm], ppm) δ = 7.37–7.34 (m, 8H, $C_{ar.}H$), 7.26–7.23 (m, 8H, $C_{ar.}H$), 5.24 (q, *J* = 6.9 Hz, 4H, C*H*Br), 2.03 (d, *J* = 6.9 Hz, 12H, CH_3); ^{13}C NMR (100 MHz, CD_2Cl_2 [54.0 ppm], ppm) δ = 147.0 (4C, C_q), 141.7 (4C, C_q), 131.5 (8C, $C_{ar.}$H), 126.9 (8C, $C_{ar.}$H), 64.9 (1C, C_q), 50.0 (4C, *C*HBr), 27.1 (4C, *C*H_3); FAB (3-NBA, m/z): 671/669/667/665 [M^+ – Br], 589/587/585 [M^+ – Br – HBr], 565/563/561 [M^+ – C_8H_8Br], 509/507 [M^+ – 3 Br], 474, 403, 323. HRMS–FAB *(m/z)*: [M^+ – Br] calcd for $C_{33}H_{32}{}^{79}Br_3$, 665.0054; found, 665.0054; IR (ATR, ṽ) = 3024 (w), 2983 (w), 2970 (w), 2919 (w), 2859 (w), 1604 (w), 1568 (vw), 1504 (m), 1438 (w), 1409 (m), 1374 (w), 1340 (w), 1303 (w), 1282 (w), 1215 (m), 1197 (w), 1171 (vs), 1126 (w), 1067 (w), 1044 (s), 1016 (vs), 969 (w), 956 (w), 914 (w), 824 (vs), 779 (vs), 732 (m), 643 (w), 602 (vs), 581 (vs), 548 (m), 511 (m) cm^{-1}.

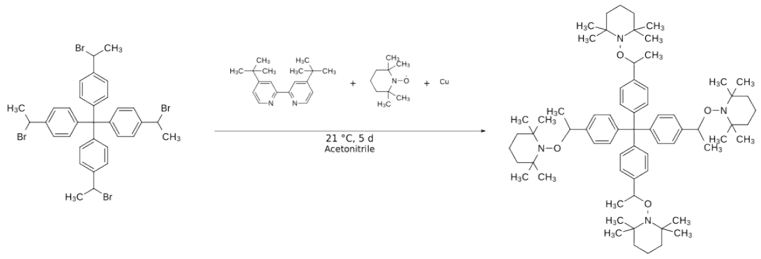
The experimental data are consistent with the literature.
Y. Matt, I. Wessely, L. Gramespacher, M. Tsotsalas, S. Bräse, *Eur. J. Org. Chem.* **2020**, DOI 10.1002/ejoc.202001415. *Rigid Multidimensional Alkoxyamines: A Versatile Building Block Library.*

Additional information on the chemical synthesis is available via the Chemotion repository:

https://doi.org/10.14272/reaction/SA-FUHFF-UHFFFADPSC-BKNFZNXZGI-UHFFFADPSC-NUHFF-NUHFF-NUHFF-ZZZ

Additional information on the analysis of the target compound is available via the Chemotion repository: https://doi.org/10.14272/BKNFZNXZGIKBEB-UHFFFAOYSA-N.1

2,2,6,6-Tetramethyl-1-[1-[4-[tris[4-[1-(2,2,6,6-tetramethylpiperidin-1-yl)oxyethyl]phenyl]methyl]phenyl]ethoxy]piperidine (3)



Under an argon atmosphere, tetrakis(4-(1-bromoethyl)phenyl)methane (250 mg, 334 µmol, 1.00 equiv), 1-oxidanyl-2,2,6,6-tetramethylpiperidine (211 mg, 1.35 mmol, 4.05 equiv), copper (42.5 mg, 668 µmol, 2.00 equiv) and 4-*tert*-butyl-2-(4-*tert*-butylpyridin-2-yl)pyridine (359 mg, 1.34 mmol, 4.00 equiv) were suspended in 6 mL of dry acetonitrile. The reaction mixture was degassed for 10 minutes by bubbling with argon, before being stirred at 21 °C for five days. Afterwards, methylene chloride was added, and the mixture was washed with semi-concentrated ammonia, water, saturated NaCl solution and dried over Na_2SO_4. The solvent was removed under reduced pressure. The crude product was passed through a short column (methylene chloride/ethyl acetate 4:1) to remove 4-*tert*-butyl-2-(4-*tert*-butylpyridin-2-yl)pyridine. The residue was recrystallized from ethanol to give 289 mg (274 µmol) of a colourless solid. – Yield: 82%.

R_f = 0.48 (methylene chloride).

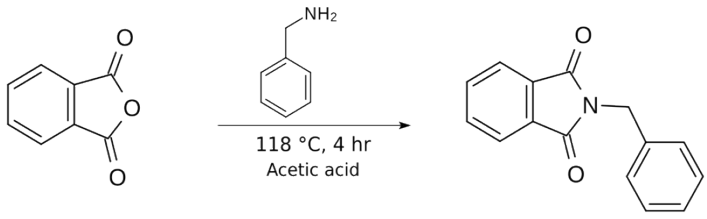
^{1}H NMR (400 MHz, Dichloromethane-d_2 [5.32 ppm], ppm) δ = 7.21–7.18 (m, 8H, $C_{ar.}H$), 7.11–7.09 (m, 8H, $C_{ar.}H$), 4.75 (q, J = 6.6 Hz, 4H, C*H*O), 1.49–1.27 (m, 48H, CH_3 Sidechain, CH_2 CH_3 TEMPO), 1.15 (bs, 12H, CH_3 TEMPO), 1.01 (bs, 12H, CH_3 TEMPO), 0.60 (bs, 12H, CH_3 TEMPO); ^{13}C NMR (100 MHz, Dichloromethane-d_2 [54.0 ppm], ppm) δ = 146.5 (4C, C_q), 143.4 (4C, C_q), 131.3 (8C, $C_{ar.}$H), 126.5 (8C, $C_{ar.}$H), 83.0 (4C, *C*HO), 64.7 (1C, C_q), 60.4 (4C, C_q TEMPO), 59.9 (4C, C_q TEMPO), 40.9 (8C, *C*H$_2$ TEMPO), 34.7 (4C, *C*H$_3$ TEMPO), 34.5 (4C, *C*H$_3$ TEMPO), 22.9 (4C, *C*H$_3$ Sidechain), 20.7 (4C, *C*H$_3$ TEMPO), 20.6 (4C, *C*H$_3$

TEMPO), 17.8 (4C, *C*H_2 TEMPO); FAB (3-NBA, m/z): 1054 [M^+ + H], 897 [M^+ – TEMPO], 741 [M^+ – 2 TEMPO], 584 [M^+ – 3 TEMPO], 443, 442, 428 [M^+ – 4 TEMPO], 324 [$C_{25}H_{24}^+$], 208, 158 [TEMPO$^+$ + 2H], 156 [TEMPO$^+$], 142 [TEMPO$^+$ – CH_3 + H], 140 [TEMPO$^+$ – O]. HRMS–FAB *(m/z)*: [M^+ + H] calcd for $C_{69}H_{105}N_4O_4$, 1053.8130; found, 1053.8132; IR (ATR, $\tilde{\nu}$) = 2996 (w), 2972 (m), 2927 (vs), 2885 (w), 2870 (w), 2846 (w), 1611 (vw), 1503 (w), 1453 (w), 1408 (w), 1374 (m), 1360 (s), 1349 (w), 1299 (w), 1278 (w), 1258 (w), 1242 (w), 1208 (w), 1183 (w), 1132 (s), 1099 (w), 1061 (vs), 1045 (w), 1020 (m), 989 (m), 975 (w), 956 (m), 935 (vs), 881 (w), 826 (vs), 793 (w), 779 (w), 737 (w), 708 (m), 628 (vw), 601 (w), 560 (m), 510 (w), 469 (vw), 419 (w) cm^{-1}.

The experimental data are consistent with the literature.
Y. Matt, I. Wessely, L. Gramespacher, M. Tsotsalas, S. Bräse, *Eur. J. Org. Chem.* **2020**, DOI 10.1002/ejoc.202001415. *Rigid Multidimensional Alkoxyamines: A Versatile Building Block Library.*

Additional information on the chemical synthesis is available via the Chemotion repository: https://doi.org/10.14272/reaction/SA-FUHFF-UHFFFADPSC-OMHGNVWHHA-UHFFFADPSC-NUHFF-NUHFF-NUHFF-ZZZ
Additional information on the analysis of the target compound is available via the Chemotion repository: https://doi.org/10.14272/OMHGNVWHHANWNN-UHFFFAOYSA-N.2

2-Benzylisoindole-1,3-dione (S11)



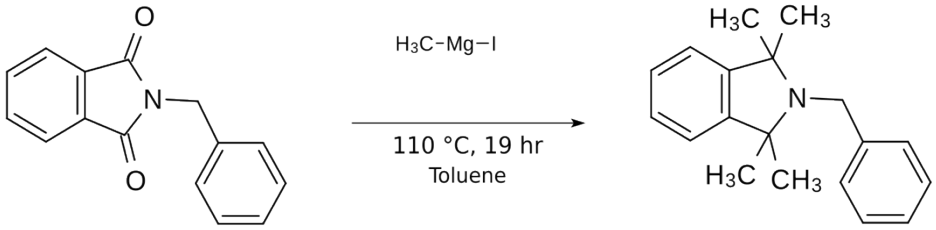
2-Benzofuran-1,3-dione (75.0 g, 506 mmol, 1.00 equiv) and phenylmethanamine (63.9 g, 65.0 mL, 596 mmol, 1.18 equiv) were dissolved in 300 mL of glacial acetic acid and refluxed for 4 h. After cooling to room temperature, 700 mL of water were added. The precipitate was filtered off and washed with water. The crude product was recrystallised from ethanol to give 106 g (447 mmol) of a colourless solid. – Yield: 88%.

^{1}H NMR (400 MHz, Chloroform-d [7.27 ppm], ppm) δ = 7.87–7.27 (m, 2H, $C_{ar.}H$), 7.73–7.69 (m, 2H, $C_{ar.}H$), 7.45–7.47 (m, 2H, $C_{ar.}H$), 7.30–7.36 (m, 3H, $C_{ar.}H$), 4.86 (s, 2H, CH_2). ^{13}C NMR (100 MHz, Chloroform-d [77.0 ppm]) δ = 168.0 (2C, *C*O), 136.3 (2C, $C_{q.}$), 133.9 (1C, $C_{ar.}$H), 132.1 (1C, $C_{q.}$), 128.6 (2C, $C_{ar.}$H), 128.6 (2C, $C_{ar.}$H), 127.8 (2C, $C_{ar.}$H), 123.3 (2C, $C_{ar.}$H), 41.6 (1C, CH_2). EI (m/z, 70 eV, 60 °C): 238/237 (15/100) [M^+], 219 (20), 209 (8) [M^+ – CO], 208 (5). HRMS–EI *(m/z)*: [M]$^+$ calcd for $C_{15}H_{11}NO_2$, 237.0784; found 237.0784.

The experimental data are consistent with the literature.
K. N. de Oliveira, P. Costa, J. R. Santin, L. Mazzambani, C. Bürger, C. Mora, R. J. Nunes, M.M. de Souza, *Bioorganic & medicinal chemistry*, **2011**, *19(14)*, 4295–4306. *Synthesis and antidepressant-like activity evaluation of sulphonamides and sulphonyl-hydrazones*

Additional information on the chemical synthesis is available via the Chemotion repository: https://doi.org/10.14272/reaction/SA-FUHFF-UHFFFADPSC-WITXFYCLPD-UHFFFADPSC-NUHFF-NUHFF-NUHFF-ZZZ
Additional information on the analysis of the target compound is available via the Chemotion repository: https://doi.org/10.14272/WITXFYCLPDFRNM-UHFFFAOYSA-N.1

2-Benzyl-1,1,3,3-tetramethylisoindole (S12)



Under an argon atmosphere, CH_3IMg in Et_2O (399 g, 800 mL, 2.40 mol, 3.00M, 6.70 equiv) and 50 mL of dry toluene were placed in a 2 L three-necked flask with a reflux condenser, thermometer and attached cooling trap. The diethyl ether was distilled off the solution at vacuum and 30°C until the mixture was slightly cloudy. A solution of 2-benzylisoindole-1,3-dione (85.0 g, 358 mmol, 1.00 equiv) in 600 mL of dry toluene was added slowly. Afterwards, more solvent was removed by distillation until the reaction mixture refluxed at 110°C and it was refluxed for an additional 19 h. Then toluene was removed by distillation, cooled to room temperature and 1 L of *n*-hexane was added. The mixture was refluxed for another 16 h and

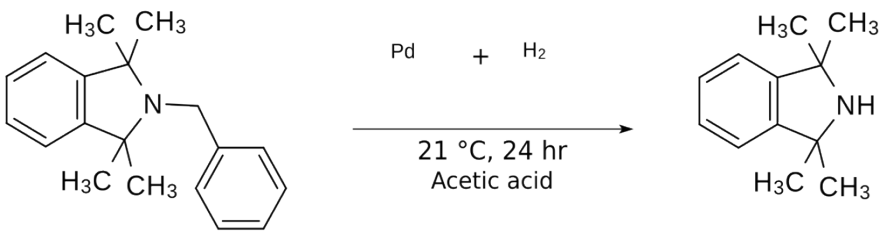
again cooled to room temperature. The mixture was filtered over Celite® and the filter cake was washed three times with *n*-hexane. Air was bubbled through the filtrate overnight and then passed over a column of basic alumina using *n*-pentane as eluent until the eluent was amine-free. The solvent was removed under reduced pressure and the crude product recrystallised from ethanol to give 20.6 g (77.7 mmol) of a slightly beige solid. – Yield: 22%.

^{1}H NMR (400 MHz, Chloroform-d [7.27 ppm], ppm) δ = 7.49–7.51 (m, 2H, $C_{ar.}H$), 7.25–7.34 (m, 5H, $C_{ar.}H$), 7.16 (dd, *J* = 5.6 Hz, *J* = 3.0 Hz, 2H, $C_{ar.}H$), 4.01 (s, 2H, CH_2), 1.32 (s, 12H, CH_3); ^{13}C NMR (100 MHz, Chloroform-d [77.0 ppm], ppm) δ = 147.8 (2C, $C_{q.}$), 143.4 (1C, $C_{q.}$), 128.3 (2C, $C_{ar.}$H), 127.9 (2C, $C_{ar.}$H), 126.7 (2C, $C_{ar.}$H), 126.4 (1C, $C_{ar.}$H), 121.3 (2C, $C_{ar.}$H), 65.2 (2C, $C_{q.}$), 46.2 (1C, CH_2), 28.4 (4C, CH_3); EI (m/z, 70 eV, 50 °C): 265 (3) [M^+], 251/250 (19/100) [$M^+ - CH_3$], 144 (3) [$M^+ - Bn - 2\ CH_3$], 92/91 (3/52) [Bn^+]. HRMS–EI *(m/z)*: [M]$^+$ calcd for $C_{19}H_{23}N$, 265.1825; found, 265.1825.

The experimental data are consistent with the literature.
M.-C. Frantz, E. M. Skoda, J. R. Sacher, M. W. Epperly, J. P. Goff, J. S. Greenberger, P. Wipf, *Organic & biomolecular chemistry*, **2013**, *11 (25)*, 4147–4153. *Synthesis of analogs of the radiation mitigator JP4-039 and visualization of BODIPY derivatives in mitochondria.*

Additional information on the chemical synthesis is available via the Chemotion repository: https://doi.org/10.14272/reaction/SA-FUHFF-UHFFFADPSC-PXORNCDWOH-UHFFFADPSC-NUHFF-NUHFF-NUHFF-ZZZ
Additional information on the analysis of the target compound is available via the Chemotion repository: https://doi.org/10.14272/PXORNCDWOHJSJD-UHFFFAOYSA-N.1

1,1,3,3-Tetramethyl-2H-isoindole (S13)



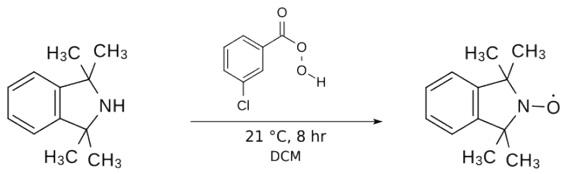
A suspension of 2-benzyl-1,1,3,3-tetramethylisoindole (9.28 g, 35.0 mmol, 1.00 equiv) and 1.12 g Pd/C (10%, 1.05 mmol (Pd), 3 mol%) in 120 mL of glacial acetic acid was stirred for 24 h under a hydrogen atmosphere at ambient pressure at room temperature. The reaction mixture was filtered over Celite® and the filter cake was washed with conc. acetic acid, water, and little diethyl ether. The filtrate was extracted with diethyl ether three times and the organic phase was discarded. Afterwards, the aqueous phase was alkalised(pH = 10) using NaOH and again extracted with diethyl ether three times. The organic phase was washed with brine and dried over Na_2SO_4. The solvent was removed under reduced pressure to give 4.36 g (24.9 mmol) of a colourless solid which was used without further purification. – Yield: 71%.

^{1}H NMR (400 MHz, Dichloromethane-d_2 [5.32 ppm], ppm) δ = 7.20–7.25 (m, 2H, $C_{ar.}H$), 7.10–7.15 (m, 2H, $C_{ar.}H$), 1.81 (bs, 1H, N*H*), 1.41 (s, 12H, CH_3); ^{13}C NMR (100 MHz, Dichloromethane-d_2 [54.0 ppm], ppm) δ = 149.6 (2C, $C_{q.}$), 127.5 (2C, $C_{ar.}$H), 121.9 (2C, $C_{ar.}$H), 63.1 (2C, $C_{q.}$), 32.5 (4C, CH_3); EI (m/z, 70 eV, 70 °C): 175 (1.7) [M^+], 174 (12) [M^+ – H], 161/160 (13/100) [$M^+ – CH_3$], 158 (10), 145 (33) [$M^+ – 2\ CH_3$], 144 (27) [$M^+ – 2\ CH_3$ – H]. HRMS–EI *(m/z)*: $[M]^+$ calcd for $C_{12}H_{17}N$, 175.1356; found, 175.1354.

The experimental data are consistent with the literature.
M.-C. Frantz, E. M. Skoda, J. R. Sacher, M. W. Epperly, J. P. Goff, J. S. Greenberger, P. Wipf, *Organic & biomolecular chemistry*, **2013**, *11 (25)*, 4147–4153. *Synthesis of analogs of the radiation mitigator JP4-039 and visualization of BODIPY derivatives in mitochondria.*

Additional information on the chemical synthesis is available via the Chemotion repository: https://doi.org/10.14272/reaction/SA-FUHFF-UHFFFADPSC-ZAHPSFHHFN-UHFFFADPSC-NUHFF-NUHFF-NUHFF-ZZZ
Additional information on the analysis of the target compound is available via the Chemotion repository: https://doi.org/10.14272/ZAHPSFHHFNVYAR-UHFFFAOYSA-N.1

2-Lambda1-oxidanyl-1,1,3,3-tetramethylisoindole (S14)



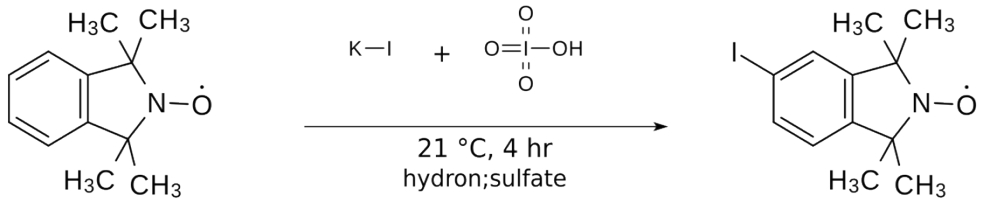
To a solution of 1,1,3,3-tetramethyl-2H-isoindole (4.35 g, 24.8 mmol, 1.00 equiv) in 150 mL of methylene chloride, 3-chlorobenzenecarboperoxoic acid (9.12 g, 37.0 mmol, 1.49 equiv) was added. After stirring at room temperature for 8 h, the reaction mixture was washed three times with 10% NaOH solution and brine and was dried over Na_2SO_4. The solvent was removed under reduced pressure to obtain 4.61 g (24.2 mmol) of a yellow solid, which was used without further purification. – Yield: 98%.

EI (m/z, 70 eV, 50 °C): 191/190 (9/68) [M^+], 176/175 (16/53) [$M^+ – CH_3$], 161/160 (9/55) [$M^+ – 2\ CH_3$], 158 (21), 146/145 (11/100) [$M^+ – 3\ CH_3$], 129 (10), 117 (16). HRMS–EI *(m/z)*: $[M]^+$ calcd for $C_{12}H_{16}NO$, 190.1226; found, 190.1225.

The experimental data are consistent with the literature.
M.-C. Frantz, E. M. Skoda, J. R. Sacher, M. W. Epperly, J. P. Goff, J. S. Greenberger, P. Wipf, *Organic & biomolecular chemistry*, **2013**, *11(25)*, 4147–4153. *Synthesis of analogs of the radiation mitigator JP4-039 and visualization of BODIPY derivatives in mitochondria.*

Additional information on the chemical synthesis is available via the Chemotion repository: https://doi.org/10.14272/reaction/SA-FUHFF-UHFFFADPSC-XWTBMUIROL-UHFFFADPSC-NUHFF-NUHFF-NUHFF-ZZZ
Additional information on the analysis of the target compound is available via the Chemotion repository: https://doi.org/10.14272/XWTBMUIROLHFGV-UHFFFAOYSA-N.1

5-Iodo-2-$l^{1}-oxidanyl-1,1,3,3-tetramethylisoindole (S15)



At 0 °C, potassium;iodide (2.21 g, 13.3 mmol, 0.549 equiv) was added in small portions to a solution of periodic acid (1.00 g, 5.21 mmol, 0.215 equiv) in 80 mL of conc. sulfuric acid. After the addition was completed, the mixture was stirred for a further 15 min. Then, 2-lambda1-oxidanyl-1,1,3,3-tetramethylisoindole (4.61 g, 24.2 mmol, 1.00 equiv) was added at 0 °C. The reaction mixture was warmed up slowly to room temperature while stirring for a further 3 h. Afterwards, the mixture was poured on 200 mL ice and was alkalised (pH = 10) using NaOH pellets and 7M NaOH-solution. The aqueous phase was extracted with methylene chloride three times and the combined organic phases were washed with saturated sodium thiosulfate solution, water and brine and dried over Na_2SO_4. The solvent was removed under reduced pressure. The crude product was purified by column chromatography (SiO_2, 7×20 cm, cyclohexane/dichloromethane 1:5). 3.05 g (9.65 mmol) of a yellow solid were obtained as a clean product as well as 0.725 g of starting material and a mixed fraction of both starting material and a small amount of the product (3%). – Yield: 40%.
R_f = 0.36 (cyclohexane/dichloromethane 1:5).

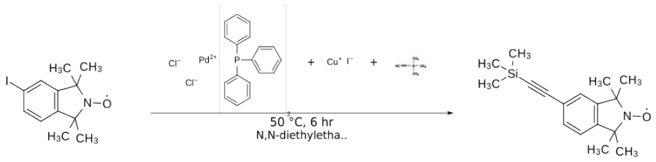
EI (m/z, 70 eV, 60 °C): 317/316 (17/100) [M^+], 302 (18) [$M^+ – CH_3 + H$], 301 (25) [$M^+ – CH_3$], 286 (39) [$M^+ – 2\ CH_3$], 271 (31) [$M^+ – 3\ CH_3$], 144 (17) [$M^+ – 3\ CH_3 – I$], 143 (9) [$M^+ – 2\ CH_3 – I – O$], 129 (15), 128 (11). HRMS–EI *(m/z)*: $[M]^+$ calcd for $C_{12}H_{15}NO^{127}I$, 316.0193; found, 316.0193.

The experimental data are consistent with the literature.

K. E. Fairfull-Smith, E. A. Debele, J. P. Allen, M. C. Pfrunder, J. C. McMurtrie, *Eur. J. Org. Chem.*, **2013**, *2013*(22), 4829–4835. *Direct Iodination of Isoindolines and Isoindoline Nitroxides as Precursors to Functionalized Nitroxides.*

Additional information on the chemical synthesis is available via the Chemotion repository: https://doi.org/10.14272/reaction/SA-FUHFF-UHFFFADPSC-ZEQLGGMCOX-UHFFFADPSC-NUHFF-NUHFF-NUHFF-ZZZ
Additional information on the analysis of the target compound is available via the Chemotion repository: https://doi.org/10.14272/ZEQLGGMCOXYGGY-UHFFFAOYSA-N.1

2-(2-$L^{1}-oxidanyl-1,1,3,3-tetramethylisoindol-5-yl)ethynyl-trimethylsilane (S16)



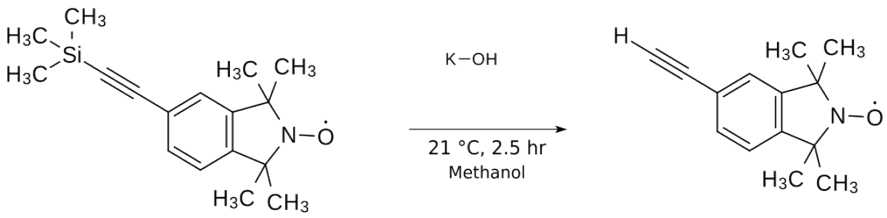
Under an argon atmosphere, 5-iodo-2-$l^{1}-oxidanyl-1,1,3,3-tetramethylisoindole (3.03 g, 9.58 mmol, 1.00 equiv), copper(1+);iodide (23.0 mg, 121 µmol, 0.0126 equiv) and $[Pd(PPh_3)_2Cl_2]$ (151 mg, 215 µmol, 0.0224 equiv) were placed in 10 mL of degassed triethylamine. Then, ethynyl(trimethyl)silane (1.93 g, 2.80 mL, 19.7 mmol, 2.05 equiv) was added and the reaction mixture was stirred at 50 °C for 6 h. After cooling to room temperature, the precipitate was filtered off and the solvent removed under reduced pressure. The residue was passed over a short column of neutral alumina (cyclohexane/ethyl acetate 15:1) and the solvent was again removed under reduced pressure. The crude product was purified by column chromatography (SiO_2, 5×20 cm, cyclohexane/ethyl acetate 9:1). 1.01 g of a yellow solid were obtained and used directly in the next step. A second mixed fraction was further purified by a second column (SiO_2, 4×20 cm, cyclohexane/ethyl acetate 15:1) to obtain an additional 1.16 g of a yellow solid with little impurities. – Yield: 79%.
R_f = 0.28 (cyclohexane/ethyl acetate 9:1).

EI (m/z, 70 eV, 80 °C): 287/286 (19/100) [M^+], 272 (29) [$M^+ - CH_3 + H$], 271 (96) [$M^+ - CH_3$], 256 (55) [$M^+ - 2\ CH_3$], 241 (63) [$M^+ - 3\ CH_3$]. HRMS–EI *(m/z)*: $[M]^+$ calcd for $C_{17}H_{24}NO^{28}Si$, 286.1622; found, 286.1622.

The experimental data are consistent with the literature.
I. Wessely, V. Mugnaini, A. Bihlmeier, G. Jeschke, S. Bräse, M. Tsotsalas, *RSC Adv*.**2016**, *57*, 55715–55719. *Radical exchange reaction of multi-spin isoindoline nitroxides followed by EPR spectroscopy.*

Additional information on the chemical synthesis is available via the Chemotion repository: https://doi.org/10.14272/reaction/SA-FUHFF-UHFFFADPSC-GCOXAOYAIW-UHFFFADPSC-NUHFF-NUHFF-NUHFF-ZZZ
Additional information on the analysis of the target compound is available via the Chemotion repository: https://doi.org/10.14272/GCOXAOYAIWZFRC-UHFFFAOYSA-N.1

5-Ethynyl-2-$l^{1}-oxidanyl-1,1,3,3-tetramethylisoindole (S17)



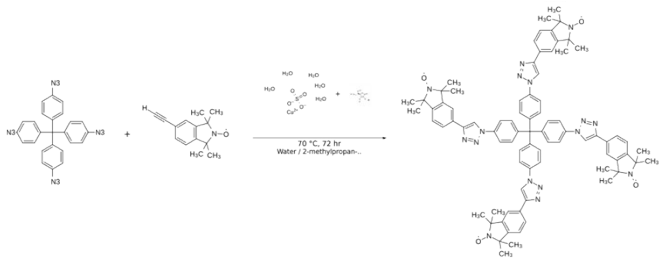
A solution of potassium;hydroxide in water (398 mg, 7.10 mL, 7.10 mmol, 1.00M, 2.01 equiv) was added to a solution of 2-(2-$l^{1}-oxidanyl-1,1,3,3-tetramethylisoindol-5-yl)ethynyl-trimethylsilane (1.01 g, 3.53 mmol, 1.00 equiv) in 50 mL of methanol. After stirring for 2.5 h at 21 °C the reaction mixture was diluted with 45 mL water and extracted with diethyl ether (50 mL) three times. The combined organic phases were washed with brine and dried over Na_2SO_4. The solvent was removed under reduced pressure and the crude product was purified by column chromatography (SiO_2, 4×20 cm, methylene chloride) to give 0.735 g (3.43 mmol) of a yellow solid. – Yield: 97%.
R_f = 0.41 (methylene chloride).

EI (m/z, 70 eV, 70 °C): 214 (93) [M^+], 200 (17) [$M^+ - CH_3 + H$], 199 (100) [$M^+ - CH_3$], 184 (49) [$M^+ - 2\ CH_3$], 182 (16) [$M^+ - CH_3 - O - H$], 169 (60) [$M^+ - 3\ CH_3$], 154 (16) [$M^+ - 4\ CH_3$], 153 (21) [$M^+ - 3\ CH_3 - O$], 152 (24) [$M^+ - 3\ CH_3 - O - H$], 141 (14), 115 (15). HRMS–EI *(m/z)*: $[M]^+$ calcd for $C_{14}H_{16}NO$, 214.1226; found, 214.1227; IR (ATR, ṽ) = 3196 (vs), 2978 (s), 2929 (w), 1487 (m), 1439 (w), 1428 (m), 1411 (w), 1375 (w), 1363 (vs), 1310 (m), 1292 (m), 1279 (m), 1164 (vs), 1122 (vs), 901 (s), 837 (vs), 744 (m), 700 (vs), 663 (m), 625 (s), 596 (m), 550 (vs), 411 (m) cm^{-1}.

The experimental data are consistent with the literature.
I. Wessely, V. Mugnaini, A. Bihlmeier, G. Jeschke, S. Bräse, M. Tsotsalas, *RSC Adv*.**2016**, *57*, 55715–55719. *Radical exchange reaction of multi-spin isoindoline nitroxides followed by EPR spectroscopy.*

Additional information on the chemical synthesis is available via the Chemotion repository: https://doi.org/10.14272/reaction/SA-FUHFF-UHFFFADPSC-MEBOKUYVJS-UHFFFADPSC-NUHFF-NUHFF-NUHFF-ZZZ
Additional information on the analysis of the target compound is available via the Chemotion repository: https://doi.org/10.14272/MEBOKUYVJSYXCR-UHFFFAOYSA-N.1

2-Lambda1-oxidanyl-1,1,3,3-tetramethyl-5-[1-[4-[tris[4-[4-(2-lambda1-oxidanyl-1,1,3,3-tetramethylisoindol-5-yl)triazol-1-yl]phenyl]methyl]phenyl]triazol-4-yl]isoindole (**4**)



In a closed vial, 1-azido-4-[tris(4-azidophenyl)methyl]benzene (226 mg, 466 µmol, 1.00 equiv), copper;sulfate;pentahydrate (11.7 mg, 46.9 µmol, 0.100 equiv), sodium;(2R)-2-[(1S)-1,2-dihydroxyethyl]-3-hydroxy-5-oxo-2H-furan-4-olate (37.0 mg, 187 µmol, 0.400 equiv) and 5-ethynyl-2-$l^{1}-oxidanyl-1,1,3,3-tetramethylisoindole (601 mg, 2.80 mmol, 6.01 equiv) in 17 mL of a ^{t}BuOH/H_2O-mixture (1:1) were stirred at 70 °C for 72 h. After cooling to room temperature, 15 mL of methanol were added and the precipitate was filtered off, washed with

50 mL of water, 50 mL of methanol and 15 mL of diethyl ether. The product was dried in vacuum to obtain 0.551 g (0.411 mmol) of a beige solid. – Yield: 88%.
R_f = 0.24 (ethyl acetate/dichloromethane 1:3).

FAB (3-NBA, m/z): 1344/1343/1342/1341/1340 [M^+], 1327/1326 [$M^+ - CH_3$], 1311 [$M^+ - CH_3 - O$]; IR (ATR, $\tilde{\nu}$) = 2973 (w), 2929 (w), 1700 (w), 1604 (w), 1511 (vs), 1483 (m), 1439 (m), 1404 (w), 1357 (m), 1315 (w), 1288 (w), 1230 (m), 1167 (w), 1123 (m), 1034 (vs), 993 (w), 980 (w), 902 (w), 824 (vs), 790 (m), 636 (w), 550 (vs), 501 (w) cm^{-1}.

The experimental data are consistent with the literature.
I. Wessely, V. Mugnaini, A. Bihlmeier, G. Jeschke, S. Bräse, M. Tsotsalas, *RSC Adv*.**2016**, *57*, 55715–55719. *Radical exchange reaction of multi-spin isoindoline nitroxides followed by EPR spectroscopy.*

Additional information on the chemical synthesis is available via the Chemotion repository: https://doi.org/10.14272/reaction/SA-FUHFF-UHFFFADPSC-YBFFHQQKFL-UHFFFADPSC-NUHFF-NUHFF-NUHFF-ZZZ
Additional information on the analysis of the target compound is available via the Chemotion repository: https://doi.org/10.14272/YBFFHQQKFLLCFZ-UHFFFAOYSA-N.1

Framework Synthesis

Synthesis of [2+4] NER framework:

Tetranitroxide **4** (60.0 mg, 0.045 mmol, 1.00 equiv.) and dialkoxyamine **1** (40.0 mg, 0.090 mmol, 2.00 equiv.) were dissolved in 0.9 mL of a toluene/methanol mixture (9:1) in a crimp vial. The vial was sealed and placed in an oven for 5 days at 100 °C. The crude product was washed with toluene five times. After washing, the framework was dried with a critical point dryer using supercritical CO_2 to give 33.1 mg of a pale beige solid. – Yield: 47%.

IR: ν_{max}/cm^{-1} = 2975 (asym. aliphatic-CH_3), 2929, 2863 (sym. aliphatic-CH_3), 2360, 2336, 1606, 1513, 1482, 1440, 1361 (NO), 1226, 1164 (CC), 1122 (1,4-aryl-CH), 1065, 877, 824.

SA_{BET}= 378 m^2/g – SA_L= 619 m^2/g – $V_{total\ pore}$ = 0.576 cm^3/g.

Synthesis of [3+4] NER framework:

Tetranitroxide **4** (60.0 mg, 0.045 mmol, 1.00 equiv.) and trialkoxyamine **2** (56.0 mg, 0.060 mmol, 1.33 equiv.) were dissolved in 0.9 mL of a toluene/methanol mixture (9:1) in a crimp vial. The vial was sealed and placed in an oven for 5 days at 100 °C. The crude product was washed with toluene five times. After washing, the framework was dried with a critical point dryer using supercritical CO_2 to give 18.4 mg of a pale beige solid. – Yield: 21%.

IR: ν_{max}/cm^{-1} = 2967 (asym. aliphatic-CH_3), 2925, 2870 (sym. aliphatic-CH_3), 2362, 2335, 1684, 1602, 1510, 1360 (NO), 1221, 1162 (CC), 1119 (1,4-aryl-CH), 1028 (1,3-aryl-CH), 990 (1,3,5-aryl-CH), 824 (1,3,5-aryl-CH).

SA_{BET}= 1200 m^2/g – SA_L= 1950 m^2/g – $V_{total\ pore}$ = 2.614 cm^3/g.

Synthesis of [4+4] NER framework:

Tetranitroxide **4** (37.0 mg, 0.028 mmol, 1.00 equiv.) and tetraalkoxyamine **3** (30.0 mg, 0.028 mmol, 1.00 equiv.) were dissolved in 0.9 mL of a toluene/methanol mixture (9/1) in a crimp vial. The vial was sealed and placed in an oven for 24 h at 100 °C. The crude product was washed with toluene five times. After washing, the framework was dried with a critical point dryer using supercritical CO_2 to give 20.2 mg of a pale beige solid. – Yield: 41%

IR: ν_{max}/cm^{-1} = 2975 (asym. aliphatic-CH_3), 2929, 2863 (sym. aliphatic-CH_3), 2122, 2089, 1684, 1604, 1360 (NO), 1270, 1188 (CC), 1122 (1,4-aryl-CH), 1004 (1,3-aryl-CH), 877, 824 (1,3,5-aryl-CH).

SA_{BET}= 923 m^2/g – SA_L= 1114 m^2/g – $V_{total\ pore}$ = 1.603 cm^3/g.

Scanning Electron Microscopy

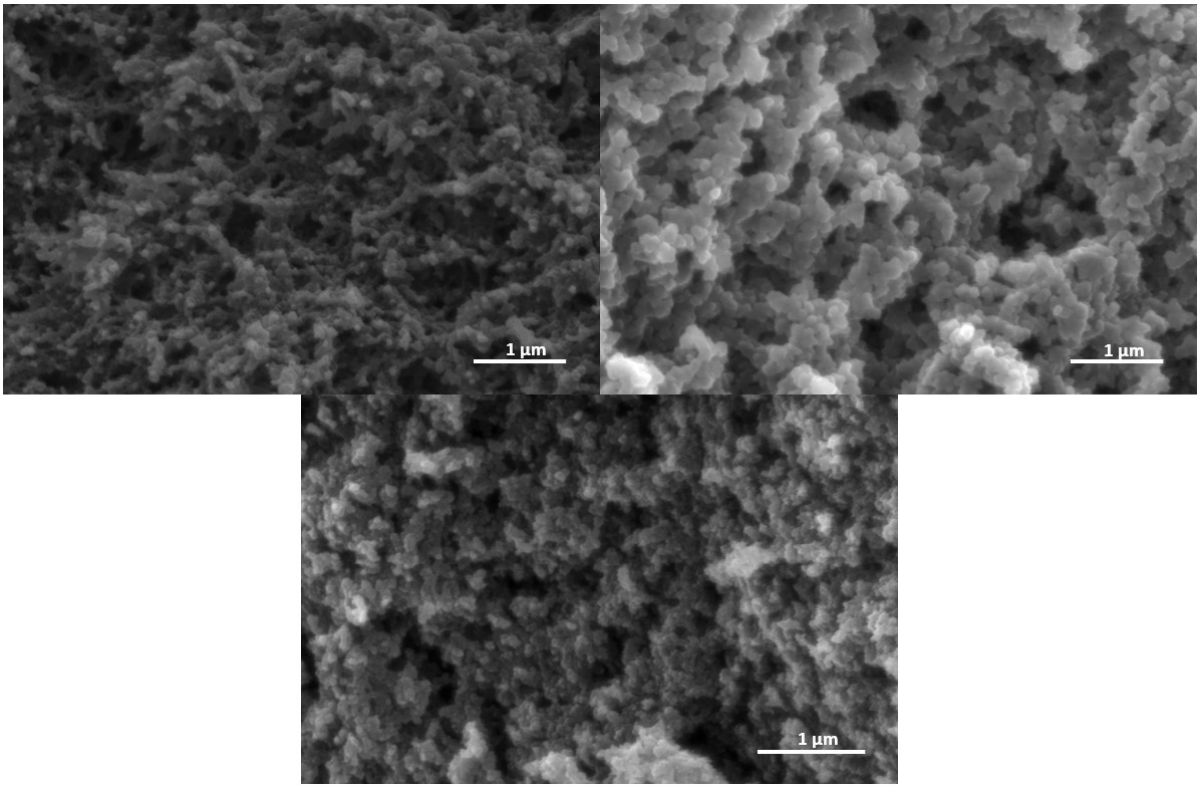


Figure S1: SEM analysis for [4+4], [3+4] and [2+4] frameworks (left to right and top to bottom).

Surface Area and Pore Size Distribution

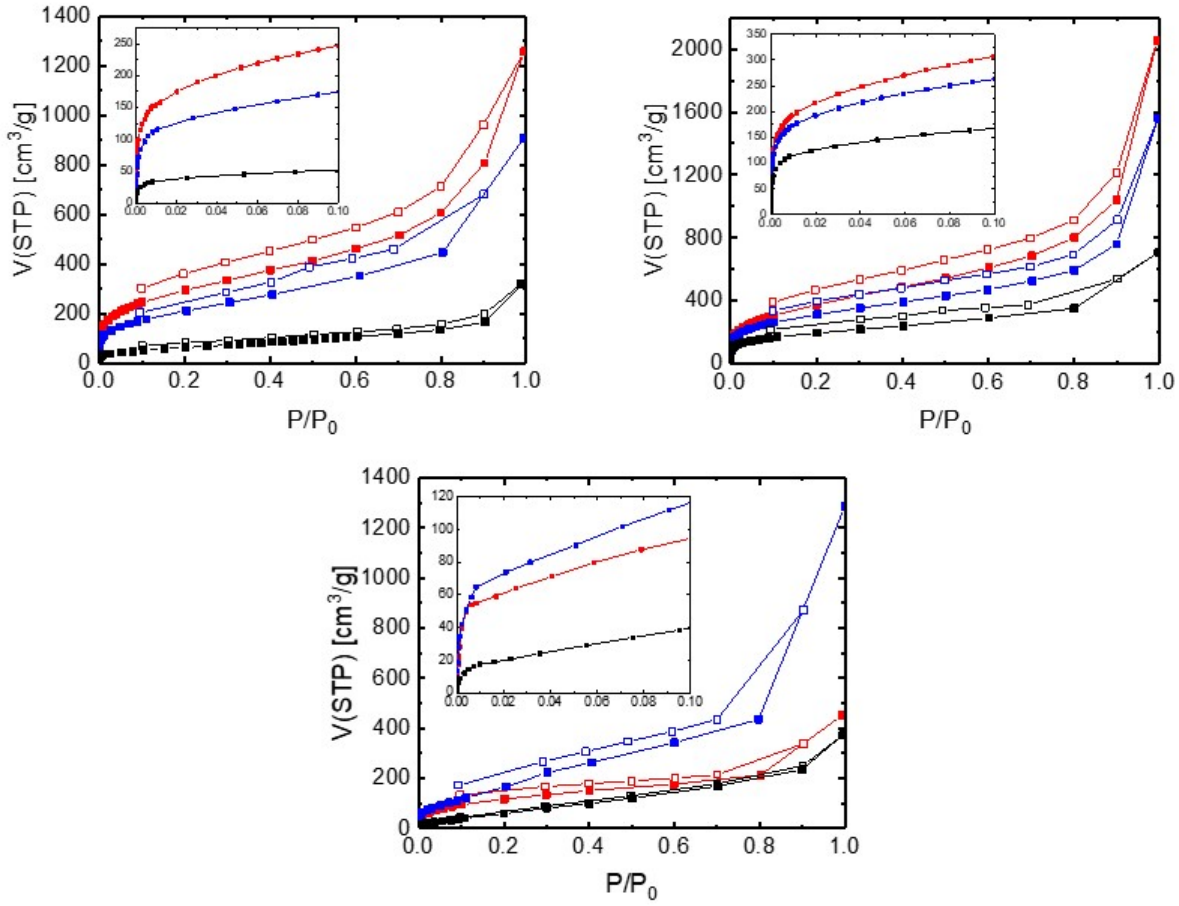


Figure S2: Argon adsorption and desorption isotherms of [4+4], [3+4] and [2+4] frameworks at pristine (red), annealed (blue) and de-crosslinked (black) states (left to right and top to bottom). The filled cubes represent the adsorption branch, and the empty cubes represent the desorption branch.

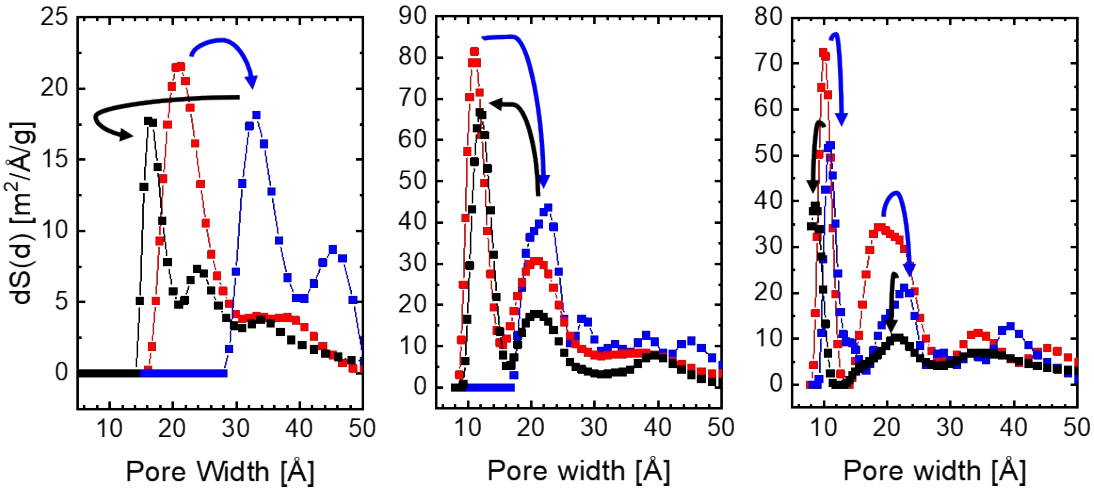


Figure S3: Pore size distribution of [2+4], [3+4], [4+4] frameworks at pristine (red), annealed (blue) and de-crosslinked (black) states (left to right). The annealing step is demonstrated as a blue arrow and the de-crosslinking step as a black arrow.