ESI for

Contrasting behaviour of TCNE and TCNQ zwitterionic benzoquinonemonoimine derivatives and coordination of a tricyanoethyl substituent to Pd(0)

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Experimental

General information: NMR spectra were recorded at room temperature on a Bruker AVANCE 400 $^1$H NMR (400.13 MHz) and $^{13}$C NMR (100.61 MHz) on a Bruker AVANCE 300 $^1$H NMR (300.17 MHz) and $^{13}$C NMR (75.49 MHz), respectively and referenced using the residual solvent proton ($^1$H) or solvent ($^{13}$C) resonance. Mass spectrometric measurements were recorded on a microTOF (Bruker Daltonics, Bremen, Germany) using nitrogen as drying agent and nebulising gas. Elementary analyses were performed by the “Service de Microanalyse, Université de Strasbourg” (Strasbourg, France). Solvents were freshly distilled under argon prior to use. 4,6 Diaminorecorcinoldihydrochloride was purchased from Acros. All reactions for air- and water-sensitive compounds were performed using standard Schlenk techniques under dry argon atmosphere.

Improved Synthesis of 1a

n-Butylamine (3.24 ml, 2.40 g, 32.8 mmol) was added to a solution of 2,4-diaminoresorcinoldihydrochloride (1.00 g, 4.69 mmol) in water (20 mL). The solution was stirred for 2 h at room temperature. The product was isolated by filtration, washed with water and dried in air to give a red powder (1.15 g, 4.60 mmol, 98%). $^1$H-NMR (300 MHz, CDCl$_3$): $\delta$ 0.99 (t, $^3$J(H,H) = 7.3 Hz, 6H, CH$_3$), 1.40-1.52 (m, 4H, CH$_2$CH$_3$), 1.69-1.79 (m, 4H, NCH$_2$CH$_2$), 3.38
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(q owing to overlap dt, $^3J(H,H) = 6.7$ Hz, 4H, NCH$_2$), 5.15 (s, 1H, N–C=CH), 5.55 (s, 1H, O=O–C=CH), 8.23 (br s, 2H, NH) ppm.

**Synthesis of 2a**

Zwitterion 1a (0.674 g, 26.9 mmol) and TCNE (0.344 g, 26.9 mmol) were dissolved in THF (50 mL) and the solution was stirred at room temperature for 2 h. It was then concentrated to about 10 mL and hexane (20 mL) was added. The red precipitate was isolated by filtration, washed with hexane and dried under reduced pressure to give a red powder of 2a (0.990 g, 26.1 mmol, 97%). $^1$H NMR (300 MHz, CDC$_3$): δ 1.01 (t, $^3J(H,H) = 7.3$ Hz, 6H, CH$_3$), 1.42-1.55 (m, 4H, CH$_2$CH$_3$), 1.72-1.82 (m, 4H, NCH$_2$CH$_2$), 3.44 (q owing to overlap dt, $^3J(H,H) = 6.8$ Hz, 4H, NCH$_2$), 5.35 (s, 1H, C(sp$^3$)-H), 5.98 (s, 1H, N=C–C), 8.15 (br s, 2H, N-H) ppm; $^{13}$C($^1$H) NMR (100 MHz, acetone): δ 14.95 (CH$_3$), 21.75 (CH$_2$), 31.98 (CH$_2$), 33.12 (C(C-sp$^3$)-H), 44.96 (CH$_2$), 45.96 (HC-C(CN)), 84.98 (N=C–C), 85.02 (O=C–C), 112.04 (CN), 113.85 (CN), 156.46 (C–N), 171.76 (C=O) ppm; FTIR: $\nu_{\text{max}}$ (pure, diamond orbit)/cm$^{-1}$ 3290m, 3193m, 2957w, 2934w, 2896w, 2875w, 2362vw, 2340vw, 1649w, 1612m, 1558vs, 1493s, 1462m, 1366w, 1306w, 1288m, 1269m, 1225m, 1143w, 1113w, 1003w, 900w, 870w, 812m, 789w, 774w, 737m, 712brs; MS (ESI): $m/z$ = 401.17 ([M+Na]$^+$). Anal. calcd for C$_{26}$H$_{22}$N$_6$O$_2$: C, 63.65; H, 5.61; N, 22.27%; found: C, 63.71; H, 5.60; N, 22.17%.

**Synthesis of 3a**

A solution of TCNQ (0.395 g, 1.93 mmol) in ethanol (60 mL) was added to a solution of the zwitterion 1a (0.485 g, 1.94 mmol) in THF (10 mL). The reaction mixture was stirred for 3 h at room temperature, the red precipitate was isolated by filtration, washed with ethanol and dried in air to give product 3a (0.667 g, 1.47 mmol, 76%) as a red solid. $^1$H NMR (400 MHz, CDCl$_3$): δ 0.98 (t, $^3J(H,H) = 7.3$ Hz, 6H, CH$_3$), 1.41-1.50 (m, 4H, CH$_2$CH$_3$), 1.69-1.76 (m, 4H, NCH$_2$CH$_2$), 3.38 (q owing to overlapping dt, $^3J(H,H) = 6.8$ Hz, 4H, NCH$_2$), 5.11 (s, 1H, C(sp$^3$)-H), 5.25 (s, 1H, N=C–C), 7.53 (dt, AA' part of an AA'BB' spin system, 2H, $^3J(H,H) = 8.3$ Hz, $^4J(H,H) = 2.4$ Hz, aromatic C-H), 7.92 (dt, BB' part of an AA'BB' spin system, 2H, $^3J(H,H) = 8.9$ Hz, $^5J(H,H) = 2.2$ Hz, aromatic C-H), 8.16 (brt, $^3J(H,H) = 5.4$ Hz, calculation 2H, N-H) ppm; $^{13}$C($^1$H) NMR (100 MHz, CDCl$_3$): δ 13.54 (CH$_3$), 20.07 (CH$_2$), 27.75 (C(C-sp$^3$)-H), 30.12 (CH$_2$), 43.39 (CH$_2$), 81.41 (N=C–C), 101.61 (O=C–C), 111.37 (CN), 114.63 (CN), 126.75 (aromatic), 127.86 (aromatic C-H), 127.98 (aromatic C-H), 137.98 (aromatic), 155.06 (C–N), 168.03 (C=O) ppm; FTIR: $\nu_{\text{max}}$ (pure, diamond orbit)/cm$^{-1}$...
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3286w, 3222w, 2962w, 2931w, 2868m, 2256vw, 1650w, 1592m, 1548vs, 1473vs, 1463s, 1417 s, 1401m, 1366m, 1283m, 1221m, 1206m, 1187w, 1145w, 1111w, 1020m, 929m, 856m, 809m, 786m, 766 m, 705s, 670m. In the region 2260-2200 cm\(^{-1}\), only weak absorptions were observed, so that the signal at 2256 cm\(^{-1}\) was assigned to \(\nu(CN)\). MS (ESI): \(m/z = 477.20 ([M+Na]^+).\) Anal. calcd for C\(_{26}\)H\(_{26}\)N\(_6\)O\(_2\): C, 68.70; H, 5.77; N, 18.49%; found: C, 68.44; H, 5.48; N, 18.95%.

Synthesis of 4

To a solution of 2a (1.93 g, 5.10 mmol) in THF (110 mL) were added 18 drops of NEt\(_3\) (0.188 g, 1.63 mmol) and the mixture was stirred for 1 h at room temperature. Water was added and the mixture was extracted with CH\(_2\)Cl\(_2\) (3 x 80 mL). The combined organic layers were dried over NaSO\(_4\), filtered and all volatile components were removed under reduced pressure. Compound 4 was obtained as a red powder with metallic appearance (1.67 g, 4.73 mmol, 93%). \(^1H\) NMR (300 MHz, CDCl\(_3\)): \(\delta 0.99 \text{ (t, } J(H,H) = 7.3 \text{ Hz, 6H, CH}_3\), 1.40-1.52 (m, 4H, CH\(_2\)CH\(_3\)), 1.73-1.81 (m, 4H, NCH\(_2\)C\(_2\)H\(_5\)), 3.50 (q owing to overlap dt, \(J(H,H) = 6.7 \text{ Hz, 4H, NCH}_2\) ppm; \(^{13}C\{^1H\} NMR (75 MHz, CDCl\(_3\)):\(\delta 13.54 \text{ (CH}_3\), 20.03 (CH\(_2\)), 30.07 (CH\(_2\)), 43.72 (CH\(_2\)), 48.45 (N\text{---C----CH}), 84.25 (O\text{---C----C}), 105.53 (NC\text{--C--CN}), 112.32 (CN), 113.23 (CN), 114.33 (CN), 134.21 \text{ (C-CN), 153.88 (C--N), 169.96 (C--O ppm); FTIR: } \nu_{\text{max}} \text{ (pure, diamond orbit)/cm}^{-1} \text{ 3234brs, 2959m, 2931m, 2873m, 2221m, 1563vs, 1497vs, 1469s, 1401vs, 1360s, 1307m, 1288m, 1260m, 1223m, 1155m, 1111m, 1019m, 815m, 800m, 761m, 733m; MS (ESI): } m/z 374.17 ([M+Na]^+)\). Anal. calcd for C\(_{19}\)H\(_{21}\)N\(_5\)O\(_2\): C, 64.94; H, 6.02; N, 19.93%; found: C, 64.66; H, 5.86; N, 19.91%.

Synthesis of 5

To a solution of 3a (0.200 g, 0.440 mmol) in THF (15 mL) were added 8 drops of NEt\(_3\) (0.084 g, 0.726 mmol). The mixture was stirred for 45 min. and all volatile components were removed under reduced pressure to yield 5 as a red powder with metallic appearance (0.241 g, 0.434 mmol, 99%). \(^1H\) NMR (400 MHz, acetone): \(\delta 0.96 \text{ (t, } J(H,H) = 7.4 \text{ Hz, 6H, CH}_3\), 1.39 (t, \(J(H,H) = 7.3 \text{ Hz, 9H, NHCH}_2CH_3\)), 1.37-1.48 (m, partial overlap with NHCH\(_2\)CH\(_3\), 4H, CH\(_2\)CH\(_3\)), 1.76 (m, 4H, NCH\(_2\)CH\(_3\)), 3.07 (br s, 2H, NH), 3.40 (q, \(J(H,H) = 7.3 \text{ Hz, 6H, NHCH}_2CH_3\), 3.57 (t, \(J(H,H) = 7.4 \text{ Hz, 4H, NHCH}_2CH_3\)), 5.72 (s, 1H, N\text{--C----CH}), 6.87 (d, AA' part of an AA'BB' spin system, 2H, \(J(H,H) = 8.2 \text{ Hz, aromatic C-H}, 7.32 \text{ (d, BB' part of an AA'BB' spin system, 2H, } J(H,H) = 8.2 \text{ Hz, aromatic C-H), 8.61 (br s, 1H, NHCH}_2CH_3\) ppm;
\(^{13}\text{C}\{^1\text{H}\}\text{-NMR} (100 \text{ MHz, acetone}): \delta 10.46 (\text{CH}_3), 14.95 (\text{CH}_3), 21.76 (\text{CH}_2), 32.02 (\text{CH}_2), 44.67 (\text{CH}_2) 44.69 (\text{CH}_2), 48.83 (\text{CH}_2), 83.44 (\text{N}═\text{C}═\text{C}-\text{H}), 100.7 (\text{O}═\text{C}═\text{C}), 102.07 (\text{CN}), 103.64 (\text{CN}), 118.49 (\text{aromatic C}), 120.36 (\text{aromatic C}), 127.92 (\text{aromatic C}═\text{H}), 157.31 (\text{C}═\text{N}), 169.91 (\text{C}═\text{O}) \text{ ppm}; \text{we could not observe all }^{13}\text{C}\text{-NMR signals because of the low solubility in acetone. IR } \nu_{\text{max}} (\text{pure, diamond orbit})/\text{cm}^{-1}: 3227\text{br m}, 2956\text{m}, 2930\text{w}, 2869\text{w}, 2690\text{brm}, 2170\text{vs} (\nu_{\text{C}≡\text{N}}), 2121\text{vs} (\nu_{\text{C}≡\text{N}}), 1600\text{s}, 1545\text{vs}, 1500\text{vs}, 1481\text{vs}, 1459\text{vs}, 1395\text{s}, 1367\text{br s}, 1314\text{s}, 1288\text{w}, 1241\text{m}, 1224\text{m}, 1195\text{m}, 1164\text{m}, 1112\text{w}, 1084\text{w}, 1018\text{m}, 926\text{m}, 822\text{s}, 750\text{s}, 705\text{m}; \text{MS (ESI, negative mode): } m/z 453.21 ([M-HNEt}_3^+]^-). Satisfactory elemental analysis data could not be obtained because of the reactivity of the product.

\text{Synthesis of 6}

Under the exclusion of air and moisture, dimethoxyethane (1 mL) and solid NaN(SiMe}_3^2 (0.063 g, 0.34 mmol) were added successively to a solution of zwitterion 3a (0.156 g, 0.343 mmol) in THF (20 mL). The solution was stirred for 30 min and MeI (0.059 g, 0.41 mmol) was added. The solution was stirred for 1 h at room temperature and then heated for 16 h at 60 °C. Water was then added and the mixture was extracted with CH}_2Cl}_2 (3 x 50 mL). The combined organic layers were dried over Na}_2SO}_4, filtered and all volatile components were removed under reduced pressure. This afforded 6 as a red solid (0.127 g, 0.271 mmol, 79%).

\(^1\text{H}\text{NMR} (400 \text{ MHz, CDCl}_3): \delta 0.98 (\text{t, }^3J(\text{H,H}) = 7.3 \text{ Hz}, 6\text{H}, \text{CH}_3), 1.41-1.51 (\text{m, }4\text{H}, \text{C}_\text{H}_2\text{CH}_3), 1.69-1.76 \text{ (m, }4\text{H, NCH}_2\text{CH}_2\text{)}, 2.10 (\text{s, }3\text{H, CH}_3), 3.39 \text{ (owing to overlap dt, }^3J(\text{H,H}) = 6.8 \text{ Hz, }4\text{H, NCH}_2\text{H}), 5.25 (\text{s, }1\text{H, N}═\text{C}═\text{CH}), 7.60 (\text{AA' part of an AA'BB' spin system, }2\text{H, }^3J(\text{H,H}) = 8.8 \text{ Hz, }^4J(\text{H,H}) = 2.3 \text{ Hz, aromatic C-H}), 7.92 \text{ (BB' part of a AA'BB' spin system, }2\text{H, }^3J(\text{H,H}) = 8.8 \text{ Hz, }^4J(\text{H,H}) = 2.3 \text{ Hz, aromatic C-H}), 8.18 \text{ (br s, }2\text{H, NH) ppm; }^{13}\text{C}\{^1\text{H}\}\text{-NMR} (100 \text{ MHz, CDCl}_3): \delta 13.53 (\text{CH}_3), 20.06 (\text{CH}_2), 29.32 (\text{CH}_3), 30.12 (\text{CH}_2), 36.14 \text{ (aryl-C(CN)_2)}, 43.38 (\text{CH}_2), 81.38 (\text{N}═\text{C}═\text{C}), 101.64 (\text{O}═\text{C}═\text{C}), 114.66 (\text{CN}), 115.28 (\text{CN}), 126.06 \text{ and } 127.80 \text{ (aromatic C-H) }133.62 \text{ and } 137.60 \text{ (aromatic C), }155.07 (\text{C}═\text{N}) 168.02 (\text{C}═\text{O}) \text{ ppm; FTIR: } \nu_{\text{max}} \text{ (pure, diamond orbit)/cm}^{-1}: 3226\text{br m}, 2959\text{m}, 2930\text{m}, 2871\text{m}, 2360\text{w}, 2342\text{w}, 2244\text{w}, 2167\text{w}, 2123\text{w}, 1650\text{w}, 1597\text{w}, 1547\text{vs}, 1503\text{s}, 1488\text{s}, 1463\text{s}, 1397\text{m}, 1364\text{m}, 1352\text{w}, 1286\text{w}, 1259\text{m}, 1223\text{m}, 1174\text{w}, 1144\text{w}, 1088\text{m}, 1015\text{m}, 931\text{m}, 906\text{w}, 862\text{w}, 809\text{m}, 725\text{s}, 694\text{m}. \text{In the } \nu\text{(CN) region } 2260-2200 \text{ cm}^{-1}, \text{the absorptions at } 2244\text{w, } 2167\text{w} \text{ and } 2123\text{w cm}^{-1} \text{ are more intense than in } 3\text{a. MS (ESI): } m/z = 491.217 \text{ [M+Na]}^+\text{. Anal. calcd for C}_{27}\text{H}_{28}\text{N}_6\text{O}_2: C, 69.21; H, 6.02; N, 17.94\%. Found: C, 69.00; H, 6.06; N, 18.23\%.}
Synthesis of 8

Method A
Zwitterion 1a (0.703 g, 2.83 mmol) was dissolved in THF (20 mL). A solution of TCNQ (0.577 g, 2.83 mmol) and NEt₃ (0.900 g, 8.89 mmol) in ethanol (200 mL) was added. The reaction mixture was stirred for 3 h at room temperature and the red solid formed was isolated by filtration and washed with ethanol and acetone to give compound 8 (0.190 g, 0.210 mmol, 15%). The filtrate was collected and the volatiles were removed under reduced pressure. The green black residue was washed with THF and dried in air to give compound 5 as a red powder (0.532 g, 0.960 mmol, 34%).

Method B:
Zwitterion 3a (0.200 g, 0.440 mmol) was dissolved in dry THF (20 mL) and NaN(SiMe₃)₂ (0.073 g, 0.40 mmol) was slowly added. The resulting mixture was stirred at room temperature for 2 h and the volatiles were removed under reduced pressure. The resulting violet solid was taken up in dry ethanol (20 mL), iodine (0.057 g, 0.22 mmol) was added and the mixture was stirred for 3 h. Then the reaction mixture was poured into ice water (100 mL). Filtration gave compound 8 (0.176 g, 0.194 mmol, 88%) as a pale red powder.

1H NMR (300 MHz, dmso): δ 0.89 (t, 3J(H,H) = 7.2 Hz, 6H, CH₃), 1.25-1.37 (m, 4H, C₆H₄CH₃), 1.55-1.64 (m, 4H, NCH₂CH₂), 3.44 (m owing to overlapping dt, 3J(H,H) = 5.9 Hz, 4H, NCH₂), 5.66 (s, 1H, N···C···CH), 7.55 (d, AA’ part of an AA’BB’ spin system, 2H, 3J(H,H) = 8.4 Hz, aromatic C-H), 7.81 (d, BB’ part of a AA’BB’ spin system, 2H, 3J(H,H) = 8.4 Hz, aromatic C-H), 9.36 (br t, 3J(H, H) = 6.0 Hz, 2H, NH) ppm; 13C{¹H} NMR (75 MHz, dmso): δ 13.52 (CH₃), 19.49 (CH₂), 29.79 (CH₂), 42.49 (CH₂), 52.85 (CN)₂C-C(CN)₂, 82.44(N—C—CH), 99.92 (O—C—C), 110.16 (CN), 115.09 (CN), 124.71 (aromatic C), 127.18 and 128.93 (aromatic C-H), 139.75 (aromatic C), 154.30 (C—N), 168.82 (C—O) ppm; FTIR: νmax (pure, diamond orbit)/cm⁻¹ 3225 br m, 2958 w, 2931 w, 2672 w, 2163 v, 1608 w, 1541 s, 1488 vs, 1463 vs, 1355 m, 1275 m, 1254 w, 1226 m, 1146 m, 1112 m, 1018 w, 947 w, 807m, 739 m; MS (ESI): m/z = 929.40 [M+Na]+. Anal. calcd for C₅₂H₅₀N₁₂O₄: C, 68.86; H, 5.56; N, 18.53. Found: C, 68.46; H, 5.49; N, 18.34%.

Synthesis of 10
Under the exclusion of air and moisture, zwitterion 4 (0.300 g, 0.853 mmol), [Pd(dba)₂] (0.490 g, 0.853 mmol) and dppe (0.340 g, 0.853 mmol) were dissolved in freshly distilled THF (20 mL) and the resulting solution was stirred for 3 h at room temperature. Then all volatile components were removed under reduced pressure. The residue was taken up in a

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minimum of CH$_2$Cl$_2$ and precipitated with pentane. The precipitate collected by filtration, washed with Et$_2$O and pentane and dried under vacuum. This afforded compound 10 (0.569 g, 0.665 mmol, 78%) as an orange powder. $^1$H NMR (300 MHz, CDCl$_3$): $\delta$ = 0.98 (t, $^3$J(H,H) = 7.3 Hz, 6H, CH$_3$), 1.34-1.46 (m, 4H, CH$_2$CH$_3$), 1.58 (s, partially overlap with NHCH$_2$CH$_3$, 4H, PCH$_2$), 1.58-1.69 (m, 4H, NHCH$_2$CH$_2$), 3.27 (“q” owing to overlap dt, $^3$J(H,H) = 6.8 Hz, 4H, NHCH$_2$), 5.00 (s, 1H, N—C—C—H), 7.18-7.22 (m, 2H, aromatic CH), 7.35-7.47 (m, 12H, aromatic CH), 7.54-7.72 (m, 4H, aromatic CH), 8.08 (brt, $^3$J(H,H) = 6.1 Hz, 2H, NH) ppm. $^{31}$P-NMR (121 MHz, CDCl$_3$): $\delta$ = 40.21 (d, $^2$J(P,P) = 27.8 Hz), 44.65 (d, $^2$J(P,P) = 27.8 Hz) ppm; IR $\nu$$_{max}$ (pure, diamond orbit)/cm$^{-1}$ 3170 brw, 3052w, 2957w, 2930w, 2870w, 2202m ($\nu$CN), 1586m, 1538s, 1471s, 1434s, 1399s, 1365m, 1308m, 1285w, 1244m, 1222w, 1186w, 1143w, 1101m, 1026w, 998w, 872w, 816m, 742s, 691s; MS (ESI): m/z = 856.22 ([M+H]$^+$), 878.20 ([M+Na]$^+$). Anal. calcd. for C$_{45}$H$_{45}$N$_5$O$_2$Pd, C 63.12; H 5.30, N 8.18. Found: C 63.00; H 5.10, N 8.25%.

**Diffusion ordered spectroscopy (DOSY)**

DOSY – spectra$^{1,2}$ of 3a and 8 were measured on a Bruker AVANCE III 600 (600.13 MHz) spectrometer in dimethylsulfoxide-D$_6$ at 298 K, using a static DOTTY 5 mm high gradient strength probe, able to deliver 500 G·cm$^{-1}$. The NMR experiments were performed with a standard LED-PFGSTE sequence, using a bipolar gradient. DOSY spectra were generated by using the DOSY module of NMRnotebook software (NMRTEC$^{TM}$)$^3$ using ILT (Inverse Lorentz Transformation) driven by maximum entropy.$^4$ Sequence delays were $\Delta$ = 40 ms (diffusion delay), $\tau$ = 1 ms (gradient recovery time) and eddy current delay = 5 ms. For each data set, 16 k complex points were collected for each 30 experiments in which the gradient strength was linearly incremented from 3 to 320 G·cm$^{-1}$. The gradient pulses were fixed to 2 x 600 $\mu$s. The hydrodynamic radii $R_H$ of the molecules were calculated by the Stokes-Einstein equation:

$$R_H = \frac{k_B T}{6 \pi \eta D}$$

Where, $k_B$ is the Boltzmann constant (in J·K$^{-1}$), $\eta$ (in cP) is the viscosity of the solvent, $D$ is the diffusion coefficient (in m$^2$·s$^{-1}$) and $T$ is the temperature (in K). The value of $\eta$ was set as 2.180 $\cdot$ 10$^{-3}$ cP, while $D$ was obtained from the spectra. The results of the calculations are stated in Table S2.
The calculation led to a diffusion coefficient $D$ of $1.90 \cdot 10^{-10}$ m$^2$/s for 3a and $1.35 \cdot 10^{-10}$ m$^2$/s for 8. The hydrodynamic radii were calculated as $5.27 \cdot 10^{-10}$ Å and $7.41 \cdot 10^{-10}$ Å, respectively, which corresponds to a molecular volume of $V = 612$ Å$^3$ for 3a and $V = 1706$ Å$^3$ for 8, assuming a spherical model for the molecules. From the crystal structure the molecular volume of 3a was determined as $V_{XRD} = 607$ Å$^3$. This is in good agreement with the value for the molecular volume calculated by the Stokes-Einstein equation for 3a and shows the reliability of the obtained values.

The ratio of the calculated molecular volumes is $V_8/V_{3a} = 2.79$, which indicates that molecule 8 has about twice the size of 3a. The use of spherical models of the molecular volume and the hydrodynamic radius is a good approach for compound 3a, the corresponding values for compound 8, rather prolate in shape, are better approximated by a spherical model.

Therefore we calculated a theoretical diffusion coefficient $D_{calc}$ of compound 3a and 8 based on ellipsoid shaped molecules. The size of the ellipsoids we derived from data we obtained from the crystal structure of 3a. The values for 8 were estimated by assuming that 8 has twice the length of 3a but the same width. The diffusion coefficient $D_{calc}$ was calculated by the formula (Table S3):

$$D_{calc} = \frac{k_BT}{6\pi \eta R_{calc}}$$

Where $R_{calc}$ is the calculated effective radius based on ellipsoid shaped models. $R_{calc}$ was computed by the equation:

$$R_{calc} = \frac{s \sqrt[3]{4\pi abc}}{\ln (P + \sqrt{P^2 - 1})}$$

In this equation $a$, $b$ and $c$ represent the ellipsoid axis lengths (given in table S2) and $P$ the ratio between the major and the minor axis of the ellipsoid ($P = a/b$).
**Fig 2** Characteristic axis lengths $a$ and $b$ of the prolate ellipsoid

### Table S3 Diffusion coefficients of 3a and 8

<table>
<thead>
<tr>
<th>Compound</th>
<th>$a$ (m)</th>
<th>$b = c$ (m)</th>
<th>$R_{\text{calc}}$</th>
<th>$D_{\text{calc}}$ (m$^2$s$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>3a</td>
<td>$6.50 \cdot 10^{-10}$</td>
<td>$2.00 \cdot 10^{-10}$</td>
<td>$5.40 \cdot 10^{-10}$</td>
<td>$1.85 \cdot 10^{-10}$</td>
</tr>
<tr>
<td>8</td>
<td>$12.0 \cdot 10^{-10}$</td>
<td>$2.00 \cdot 10^{-10}$</td>
<td>$7.70 \cdot 10^{-10}$</td>
<td>$1.30 \cdot 10^{-10}$</td>
</tr>
</tbody>
</table>

The outcome of these calculations fit well with the values obtained from the experimental data obtained by the DOSY measurements. These findings and the other spectroscopic data for this compound, allow to suggest the molecular structure of 8.