Electronic Supplementary Material (ESI) for Chemical Communications.

Supporting Information

Rational linkage of magnetic molecules using click chemistry

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1. Experimental Section

The reactants for the synthesis of H_3eshi were similarly prepared as previously described, starting from 4-iodosalicylate.[1] The intermediate product methyl-4-trimethylsilanylethynyl-2-hydroxybenzoate was chromatographically purified using a mixture of cyclohexane and chloroform (4:1), methyl-4-ethynyl-2-hydroxybenzoate was chromatographically purified using a mixture of cyclohexane and ethyl acetate (9:1). Tetramethylammonium acetate was prepared by reaction of tetramethylammonium hydroxide with acetic acid in MeOH. The complexes [Zn(oda)(aterpy)]·2 H_2O and [Co(oda)(aterpy)]·2 H_2O were prepared following our previously reported procedure.[2] The products **2** - **5** obtained from click reactions were used without further purification due to the difficulty of removing copper iodide and traces of the azide compounds. However, the spectroscopic measurements are not critically affected by the colorless and diamagnetic copper iodide.

4-ethynylsalicylhydroxamic acid (H_3eshi): A solution of hydroxylamine hydrochloride (3.057 g, 44 mmol) in 26 ml of H_2O was stirred at room temperature. NaOH (2.6 g, 65 mmol), dissolved in 13 ml of H_2O and methyl-4-ethynyl-2-hydroxybenzoate (2.553 g, 14.51 mmol), dissolved in 17 ml of dioxane were added dropwise and then the reaction mixture was stirred for a further 24 h. This mixture was concentrated and filtered, then the resulting solution was acidified with 2N HCl to a pH of 5. Immediately a salmon pink precipitate of 4-ethynylsalicylhydroxamic acid was formed, which was collected by filtration, washed with H_2O and dried in vacuum. Yield: 2.275 g (89%); ^{1}H NMR (400 MHz, d^6-DMSO, 298 K): δ=4.34 (s, 1H, C≡CH), 6.95 (m, 2H, 4-H/6-H), 7.66 (d, 1H, 3-H), 9.37 (s, 1H, NH), 11.41 (s, 1H, NOH), 12.24 (s, 1H, COH); ^{13}C NMR (100 MHz, d_6-DMSO, 298 K): δ=79.0 (C≡C), 82.7 (C≡C), 115.2 (Ar), 120.0 (Ar), 122.0 (Ar), 126.2 (Ar), 127.7 (Ar), 158.7 (ArOH), 165.3 ppm (C=O); Selected IR data (KBr): $\tilde{\nu}$=3287 (s, v(C≡C-H)), 3115 (m), 2893 (m), 1616 (s), 1605 (s), 1521 (m), 1496 (m), 1253 (s), 1108 (m), 1042 (m), 966 (m), 626 cm^{-1} (m); MS (FD): m/z (%): 177 (100) [M^+].

1: A suspension of $Cu(OAc)_2 \cdot 5\ H_2O$ (1.101 g, 5.52 mmol) in 60 ml of MeOH was treated with a solution of H_3eshi (0.777 g, 4.39 mmol) and tetramethylammonium acetate (1.171 g, 8.79 mmol) in 30 ml of MeOH. The resulting green solution was stirred for 48 h. A green powder of $(TMA)_2[Cu^{II}(12\text{-}MC_{Cu(II)N(eshi)}\text{-}4)]$ (**1**) was then collected by filtration, washed with MeOH and dried in vacuum. Yield: 1.160 g (83%). The filtrate was left for slowly evaporating at room temperature and after 9 weeks X-ray-quality green crystals were formed which have been identified crystallographically as **1**·2 H_2O. The crystals were collected by filtration, washed with MeOH and dried in vacuum. The powder and the crystals were analytical identified as the same compound. ^1H NMR (400 MHz, d^6-DMSO, 298 K): δ=3.11 (br, 18H, TMA^+), 4.17 (br, 4H, C≡CH), 5.28 (br, 4H, 6-H), 5.70 (br, 4H, 4-H), 7.23 ppm (br, 4H, 3-H); ^{13}C NMR (100 MHz, d^6-DMSO, 298 K): δ=54.4 (TMA^+), 115.8 (4-C), 123.2 (C≡$\underline{C}$H), 123.9 ppm (3-C); $^1H,^1H$ COSY (400 MHz, d_6-DMSO, 298 K): $\delta(^1H/^1H)$=7.23/5.70 (3-H/4-H), 5.70/7.23 ppm (4-H/3-H); $^1H,^{13}C$ HSQC (400 MHz/100 MHz, d^6-DMSO, 298 K): $\delta(^1H/^{13}C)$=3.15/54.2 (TMA^+), 4.16/123.2 (C≡CH), 5.70/115.8 (4-H/4-C) 7.23/123.9 ppm (3-H/3-C); Selected IR data (KBr): $\tilde{\nu}$=3272 (s, v(C≡C-H)), 3115 (m), 1560 (s), 1480 (m), 1406 (s), 1374 (m), 1318 (m), 1259 (s), 1029 (m), 981 (s), 615 cm^{-1} (m); UV/Vis (DMF): λ_{max}=352, 620 nm; MS (ESI): m/z: 506.3 [M^{2-}]; Elemental analysis calcd. for $C_{44}H_{44}Cu_5N_6O_{14}$ (**1**·2 H_2O): C 44.09, H 3.70, N 7.01; found: C 44.16, H 3.70, N 7.02.

2: 1-Azidoadamantane (6.4 mg, 36.1 µmol), **1** (10.3 mg, 8.1 µmol) and CuI (1.6 mg, 8.4 µmol) were dissolved in 1 ml of d_6-DMSO affording a dark green solution, which was heated to 80 °C for 24 h. After filtration of a green precipitate, the solution was used to obtain spectroscopic data. For IR and SQUID measurements, the solvent was removed in vacuo at 100 °C to obtain $(TMA)_2[Cu^{II}(12\text{-}MC_{Cu(II)N(ashi)}\text{-}4)]$ (**2**) as a green solid. ^{1}H NMR (400 MHz, d^6-DMSO, 298 K): δ=1.66 (br, 24H, Ad), 2.10 (br, 24H, Ad) 3.11 (br, 18H, TMA$^+$), 5.96 (br, 4H, 6-H), 6.13 (br, 4H, 4-H), 7.41 (br, 4H, 3-H), 8.35 ppm (br, 4H, Triazole); ^{1}H,^{1}H COSY (400 MHz, d_6-DMSO, 298 K): $\delta(^1H/^1H)$=2.10/1.66 (Ad/Ad), 1.66.2.10 (Ad/Ad), 7.41/6.13 (3-H/4-H), 6.13/7.41 ppm (4-H/3-H); Selected IR data (KBr): $\tilde{\upsilon}$=3008 (w), 2908 (m), 2852 (m), 1608 (m), 1564 (s), 1406 (s), 1376 (m), 1312 (m), 1251 (s), 1129 (m), 1023 (s), 947 (s), 811 (w), 606 cm^{-1} (w); UV/Vis (DMSO): λ_{max}=346, 618 nm; MS (ESI): m/z: 861.7 [M^{2-}].

3: Phenylazide (6.0 mg, 50.4 µmol), **1** (14.7 mg, 11.6 µmol) and CuI (2.3 mg, 12.1 µmol) were dissolved in 1 ml of d_6-DMSO affording a dark green solution, which was heated to 80 °C for 24 h. After filtration of a green precipitate, the solution was used to obtain spectroscopic data. For IR and SQUID measurements, the solvent was removed in vacuo at 100 °C to obtain $(TMA)_2[Cu^{II}(12\text{-}MC_{Cu(II)N(pshi)}\text{-}4)]$ (**3**) as a green solid. ^{1}H NMR (400 MHz, d^6-DMSO, 298 K): δ=3.11 (br, 18H, TMA$^+$), 6.06 (br, 4H, 6-H), 6.23 (br, 4H, 4-H), 7.50 (br, 4H, 3-H), 7.51-7.79 (m, 20H, Ph) 8.99 ppm (br, 4H, Triazole); ^{1}H,^{1}H COSY (400 MHz, d_6-DMSO, 298 K): $\delta(^1H/^1H)$=7.50/6.23 (3-H/4-H), 6.23/7.50 ppm (4-H/3-H); Selected IR data (KBr): $\tilde{\upsilon}$=3008 (w), 2914 (w), 1601 (m), 1566 (s), 1503 (m), 1409 (s), 1378 (m), 1313 (m), 1234 (s), 1022 (s), 945 (s), 811 (w), 601 cm^{-1} (w); UV/Vis (DMSO): λ_{max}=348, 616 nm; MS (ESI): m/z: 745.4 [M^{2-}].

4: The complexes [Zn(oda)(aterpy)] (18.3 mg, 36.1 µmol) and **1** (10.3 mg, 8.1 µmol) as well as CuI (1.7 mg, 8.9 µmol) were dissolved in 5 ml of d$_6$-DMSO affording a dark green solution, which was heated to 80 °C for 48 h. After filtration of a precipitate, the solvent was used to obtain spectroscopic data. For IR and SQUID measurements, the solvent was removed in vacuo at 80 °C to obtain (TMA)$_2$[Cu^{II}(12-MC$_{Cu(II)N([Zn(II)(oda)(ttshi)])}$-4)] (**4**) as a green solid. ^{1}H NMR (400 MHz, d$_6$-DMSO, 298 K): δ=3.11 (br, TMA$^+$), 4.08 (br, oda), 5.06 (d, J=50 Hz, 6-H), 5.72(br, 4-H), 7.22 (m, aterpy 3’,5’-H), 7.27 (d, J=54 Hz, Triazole); 7.68 (br, 3-H), 7.76 (m, aterpy 5,5”-H), 8.27 (m, aterpy 4,4”-H), 8.64 (m, aterpy 6,6”-H), 8.39 ppm (m, aterpy 3,3”-H); ^{1}H,^{1}H COSY (400 MHz, d^6-DMSO, 298 K): δ(^{1}H/^{1}H)=7.76/8.27 (aterpy 5,5”-H/4,4”-H), 7.76/8.64 (aterpy 5,5”-H/6,6”-H), 8.27/8.39 (aterpy 4,4”-H/3,3”-H), 8.27/7.76 (aterpy 4,4”-H/5,5”-H), 8.64/7.76 (aterpy 6,6”-H/5,5”-H), 8.39/8.27 ppm (aterpy 3,3”-H/4,4”-H); Selected IR data (KBr): $\tilde{\upsilon}$=2924 (w), 1604 (s), 1477 (m) 1411 (m), 1313 (m), 1251 (m), 1024 (m), 945 (w), 793 (w), 608 cm^{-1} (w); UV/Vis (DMSO): λ_{max}=282, 615 nm; MS (ESI): m/z: 1481.8 [*(M+TMA)*$^{2-}$], 2947.9 [*(M+2Na)*$^{-}$].

5: The complexes [Co(oda)(aterpy)] (18.1 mg, 36.1 µmol) and **1** (10.3 mg, 8.1 µmol) as well as CuI (1.6 mg, 8.1 µmol) were dissolved in 5 ml of d$_6$-DMSO affording a reddish brown solution, which was heated to 80 °C for 48 h. After filtration of a precipitate, the solution was used to obtain spectroscopic data. For IR and SQUID measurements, the solvent was removed in vacuo at 80 °C to obtain (TMA)$_2$[Cu^{II}(12-MC$_{Cu(II)N([Co(II)(oda)(ttshi)])}$-4)] (**5**) as a brown solid. Selected IR data (KBr): $\tilde{\upsilon}$=2925 (w), 2120 (w), 1602 (s), 1479 (w) 1411 (s), 1315 (m), 1254 (m), 1027 (m), 979 (w), 724 (w), 607 cm^{-1} (w); UV/Vis (DMSO): λ_{max}=266, 546, 626 nm; MS (ESI): m/z: 2916.0 [*(M+2Na)*$^{-}$].

2. X-Ray Structure Determination

The Single crystal was coated with perfluoropolyether, picked up with nylon loops and mounted in the nitrogen cold stream of the diffractometer. Mo-Kα radiation (λ = 0.71073 Å) from a Mo-target rotating-anode X-ray source was used. Final cell constants were obtained from least squares fits of several thousand strong reflections. Intensity data were corrected for absorption using PLATON.[3] SIR-97[4] was used for crystal structure solution, SHELXL-97[5] was used for the refinement. All non-hydrogen atoms were anisotropically refined and hydrogen atoms were placed at calculated positions and refined as riding atoms with isotropic displacement parameters. The tetramethylammonium ion is disordered and was modeled as two split positions with a refined occupation factor ratio.

Table S1: Selected bond lengths (Å) and M-O-M angles (deg) for complex **1**.

O3—Cu1	1.881 (2)	N2—Cu3	1.940 (3)
O6—Cu1	1.880 (2)	O1—Cu2	1.886 (2)
O2—Cu3	1.969 (2)	O5—Cu2	1.964 (2)
O3—Cu3	1.905 (2)	O6—Cu2	1.897 (2)
O4—Cu3	1.889 (2)	N1—Cu2	1.948 (3)
Cu1—O3—Cu3	120.96 (12)	Cu1—O6—Cu2	119.57 (12)

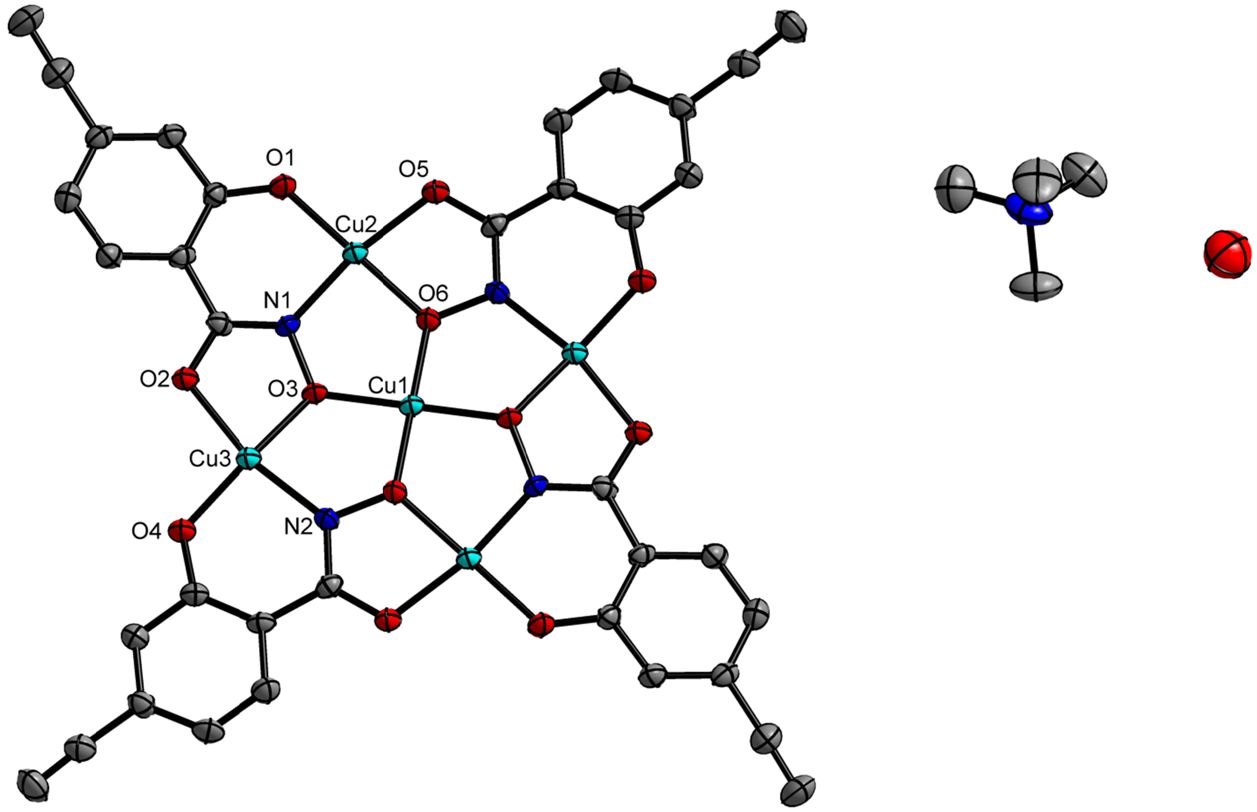

Figure S1. Representation of thermal ellipsoids (at 50% probability level) of **1**$\cdot 2H_2O$. Hydrogen atoms and symmetry-equivalent tetramethylammonium and water molecules are omitted for clarity. Light blue (Cu), Grey (C), Red (O), Dark blue (N).

3. ESI-MS Spectra

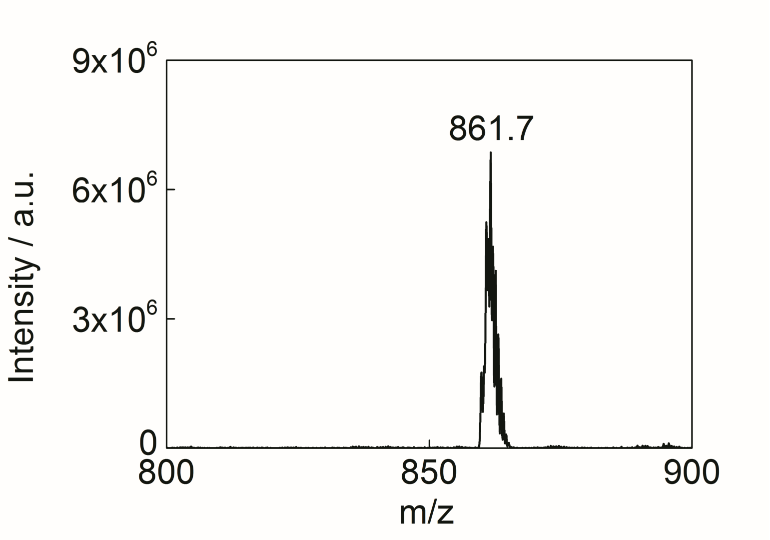

Figure S2. ESI-MS spectrum of **2**.

4. NMR Spectra

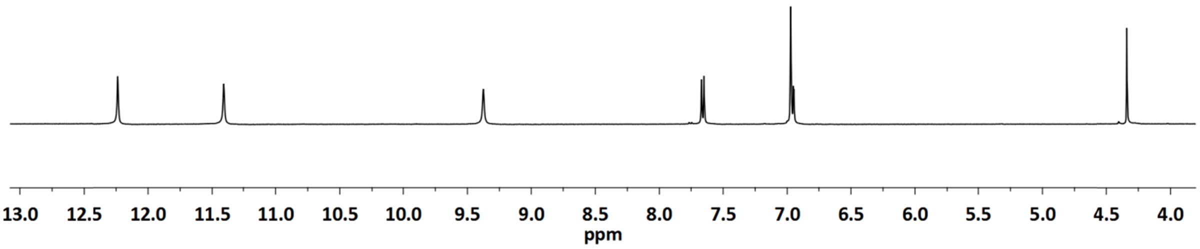

Figure S3. ^{1}H NMR spectrum of H_3eshi in d^6-DMSO.

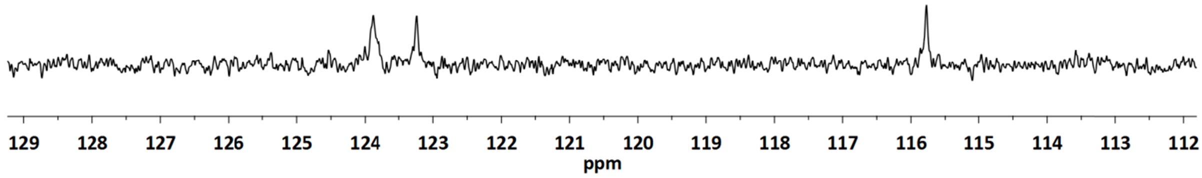

Figure S4. ^{13}C NMR spectrum of **1** in d^6-DMSO.

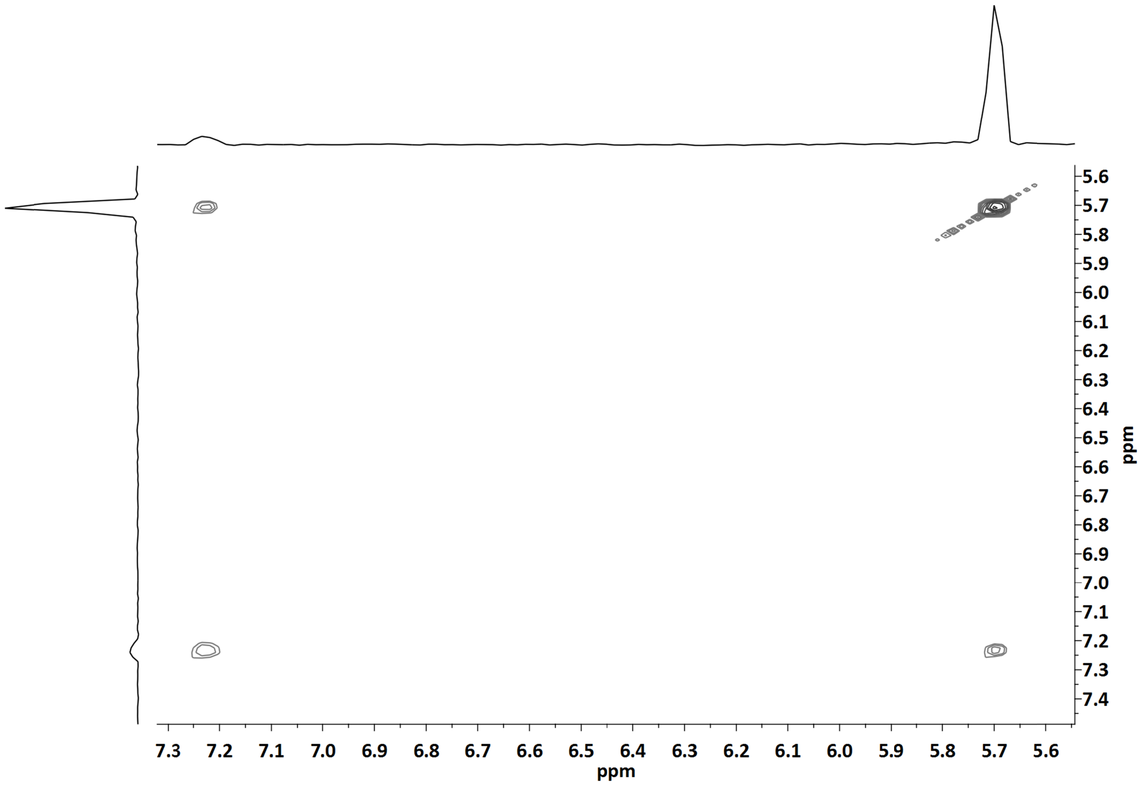

Figure S5. ^{1}H-^{1}H COSY NMR spectrum of **1** in d^6-DMSO.

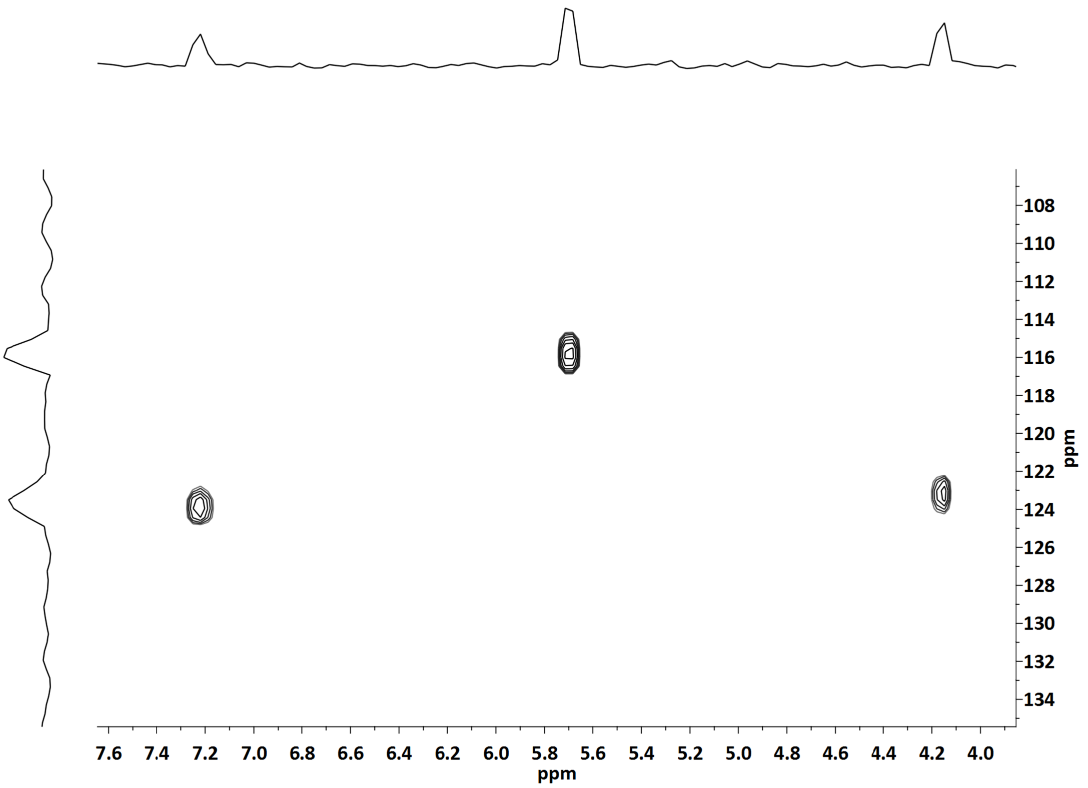

Figure S6. ^{1}H-^{13}C HSQC NMR spectrum of **1** in d^6-DMSO.

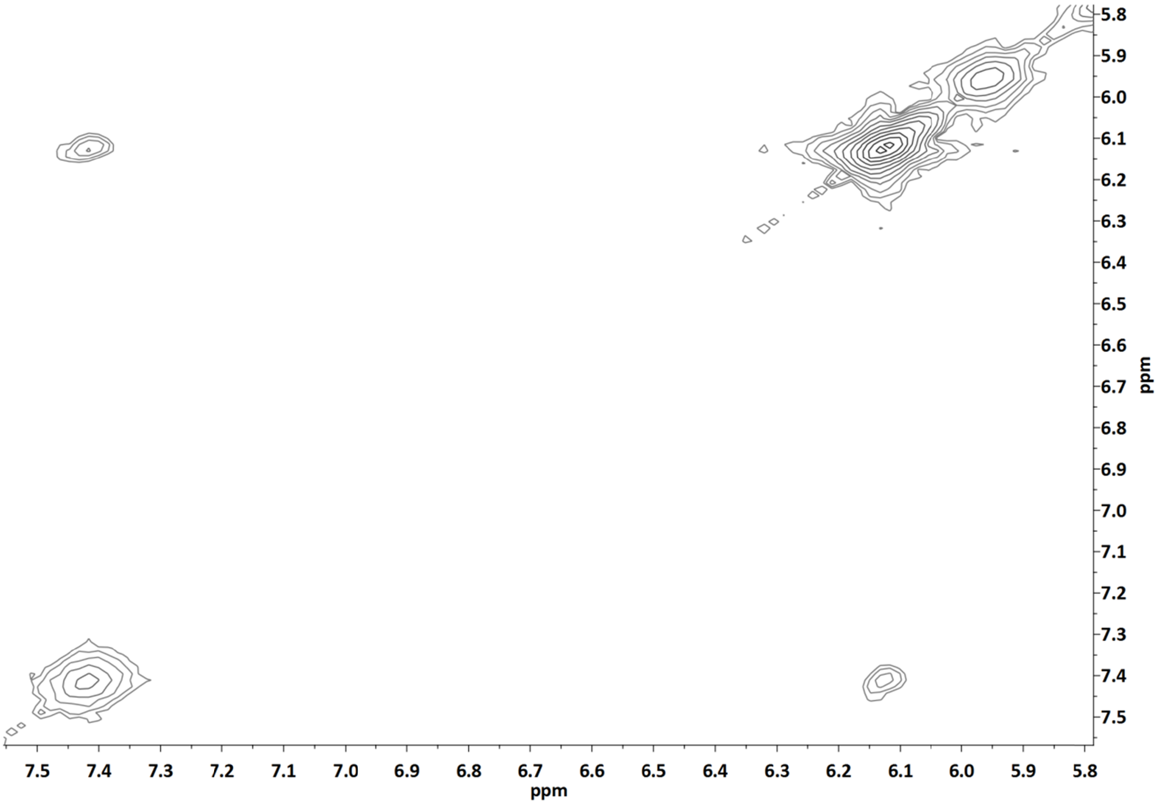

Figure S7. ^{1}H-^{1}H COSY NMR spectrum of **2** in d^6-DMSO.

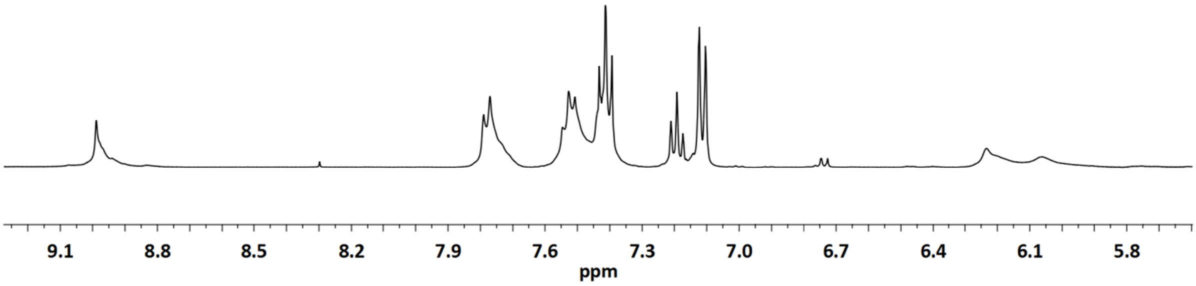

Figure S8. ^{1}H NMR spectrum of **3** in d^6-DMSO.

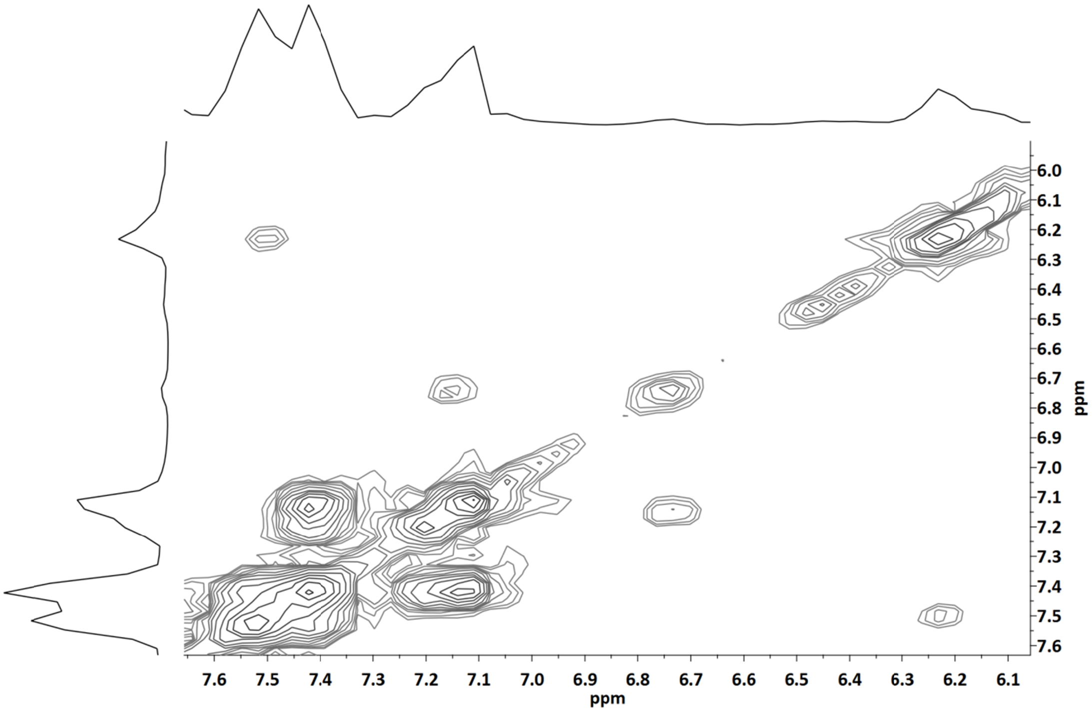

Figure S9. ^{1}H-^{1}H COSY NMR spectrum of **3** in d^6-DMSO.

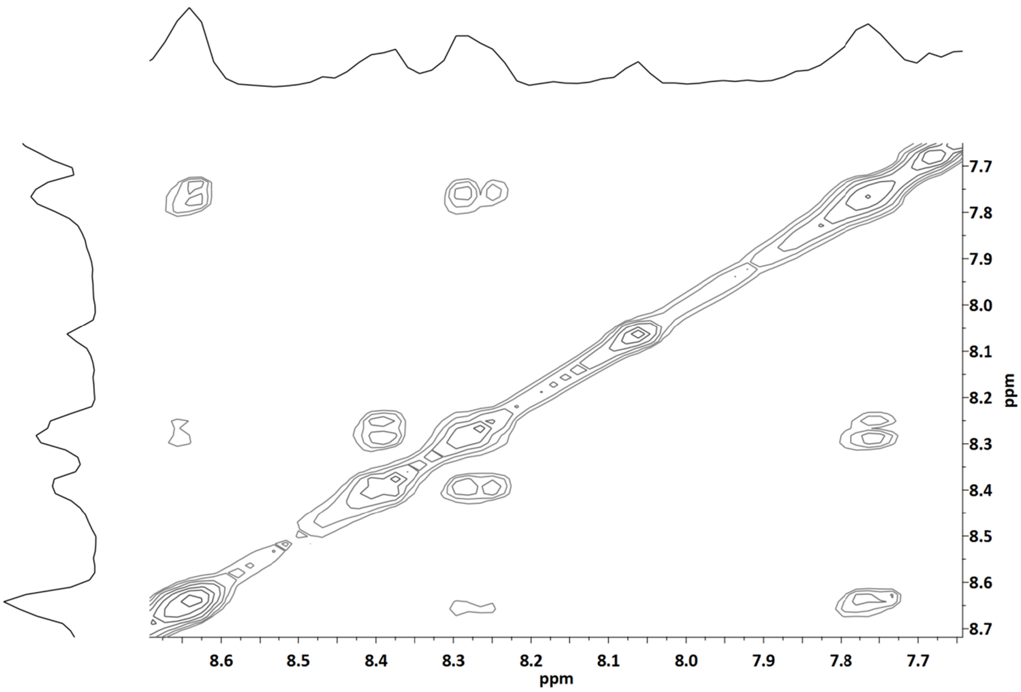

Figure S10. ^{1}H-^{1}H COSY NMR spectrum of **4** in d^6-DMSO.

5. Magnetism

The magnetic susceptibility measurements were performed on polycrystalline samples with the use of a Quantum Design SQUID magnetometer MPMS-7. The magnetic data were corrected for the sample holder, the diamagnetic contributions (Pascal's constants) and especially for the known diamagnetic impurity of copper iodide in compounds **2** – **5**.

Due to an assumed D_{4h} symmetry of the complexes **1** - **3** the $\chi_m T$ data (Figure S12) at 1 T have been fitted to Hamiltonian of equation (1) in the temperature range 2-300 K with two different exchange interaction parameters J_1 and J_2 (Figure S11) using the PHI program.[6] The best-fit parameters with fixed g values are given in Table S2.

$$\hat{H} = -J_1(\hat{S}_1\hat{S}_5 + \hat{S}_2\hat{S}_5 + \hat{S}_3\hat{S}_5 + \hat{S}_4\hat{S}_5) - J_2(\hat{S}_1\hat{S}_2 + \hat{S}_2\hat{S}_3 + \hat{S}_3\hat{S}_4 + \hat{S}_4\hat{S}_1) \qquad (1)$$

Table S2: Fitted magnetic data for compounds **1** - **3**.

Compound	J_1 [cm^{-1}]	J_2 [cm^{-1}]	g	*PI* [mol%]	*R*
1	-157.7	-65.1	2.13	4.0	1.7×10^{-3}
2	-137.9	-71.8	2.05	2.0	2.9×10^{-2}
3	-140.3	-72.3	2.10	-	1.7×10^{-2}

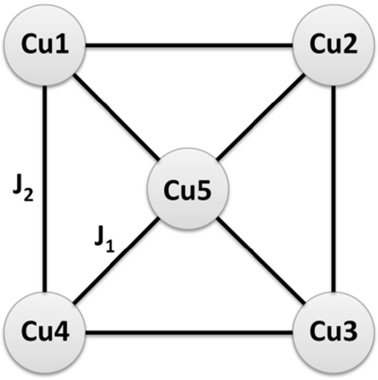

Figure S11. Schematic topologie of exchange interactions for **1** - **3**.

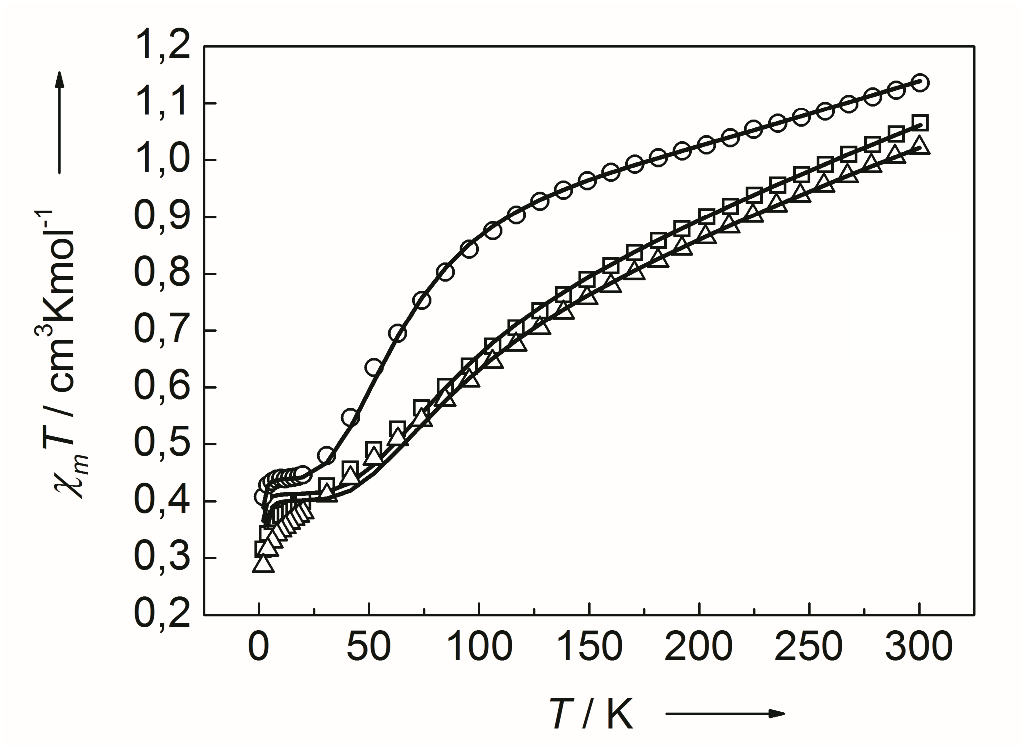

Figure S12. $\chi_m T$ vs. T plots at 1 T of **1** (○), **2** (Δ) and **3** (□); solid lines: best fittings.

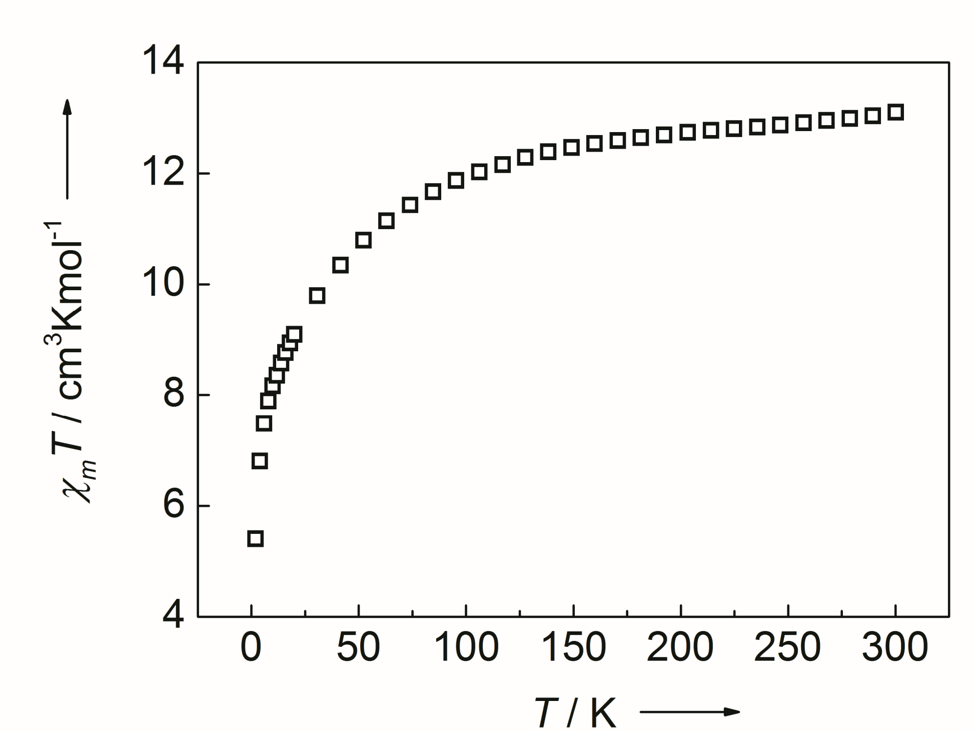

Figure S13. $\chi_m T$ vs. T plot at 1 T of **5**.

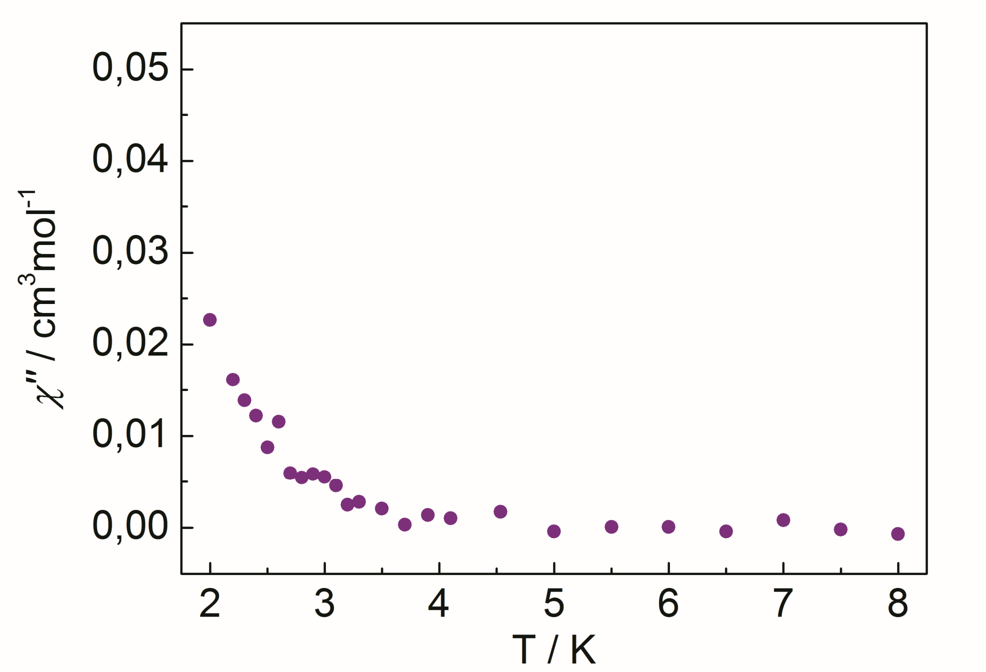

Figure S14. *χ''* vs. *T* plot under a static applied dc field of 0.15 T with an alternating ac field of 0.3 mT of **5** at a frequency of 1 Hz.

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