Paramagnetic spherical nanoparticles by self-assembly of persistent trityl radicals.

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Supplementary information

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Figure S1. UV-Vis spectra of Finland radical in phosphate buffer pH 7. a) 5 mM (l = 0.01 cm); b) 500 μ M (l = 0.01 cm); c) 5 μ M (l = 1 cm).



Figure S2.

(a) Effect of cooling rate in the magnetization curves of 20 mM Finland in 1:1 Glycerol water at 2K.. The two samples had identical composition but were cooled at different rates. Slow cooling was at a controlled rate of 10K per minute. The quenched sample was directly immersed in the liquid helium bath and The different response indicates substantial deviations from the model of non-interacting S=1/2 radicals when samples are cooled slowly.

(b) Temperature dependence of the magnetic susceptibility measured under a magnetic field H = 1000 Oe (solid symbols). The lines give the expected susceptibility of N_A spins s = 1/2 (i.e., the case of noninteracting radicals), of $N_A/2$ spins S = 1, and of $N_A/4$ spins S = 2.



Figure S3. X-band continuous wave EPR spectra of Finland radical at concentrations of 1.5 mM (blue) and 15 mM (red) in glycerol:water (1:1) at 20K measured with a microwave power of 250 nW. Spectra are normalized with respect to the intensity of the central band. An expansion of the side-bands is shown in the bottom pannel. The arrows indicate the concentration-dependent features. The sides of the 15mM radical EPR spectrum is also shown 5x enhanced. The inset shows the half-field signal recorded at 2.5 K with a microwave power of 200 μ W.



Figure S4 A. Overlay of the experimental (blue) and simulated (green) ESE-detected EPR spectra for a frozen H₂O/glycerol solution of 30mM Finland radical. This includes the simulation of contributions of the S=1/2 system taking into account the ¹³C hyperfine couplings derived in [M. K. Bowman et al., J. Magn. Reson., 172 (2005) 254-267] and additional S=1 systems as shown in B. B. Detailed zoom of graph A (top) and the simulated spectra of the individual *S*=1 systems with *D*=-75 MHz (magenta), *D*=-58 MHz (black) and *D*=-32 MHz (red) used for the simulation. Assuming isolated spin pairs, the larger observed couplings would correspond to interspin distances of 10.1 and 11.0 Å. The peaks of the less intense Pake pattern overlap with spin-flip satellites and, therefore, this particular assignment is ambiguous. The relative contributions of the *S*=1 systems in the simulation are 18%, 16% and 3% but may not reflect the actual populations of the corresponding species as the spectral intensities may be affected by different relaxation.



Figure S5: Comparison of the PEANUT experiments taken at the observer positions marked in the inset. The spectra were recorded of frozen $H_2O/glycerol$ solutions of 30 mM Finland radical at 7K. The shift of the nutation peak is indicated.

For S=1/2 systems, the nutation frequency observed in this experiment should coincide with the microwave field strength $v_1 = \beta_e gB_1/h$ (set to 3.5 MHz in this experiment). This is indeed the case for the PEANUT spectrum taken at the central line. However, the nutation peak shifts to higher frequency for observer positions in the side band (shift to 4.95 MHz, with a tail to even higher frequencies). For an *S*=1 system, the expect shift is $\sqrt{2} (= \sqrt{S(S+1)} - m_S(m_S+1))$. For higher spin systems, the nutation frequency shifts even further to higher values. This confirms again the presence of *S*=1 and possibly higher spin systems.

An extended study of the temperature and concentration dependence of the T_1 and T_2 relaxation times falls outside the scope of the current work. Nevertheless, at 7K, two-pulse echo decay measurements were performed for 1.5 mM and 30 mM Finland solutions without TMA. Accurate determination of the T_m values was hampered by the presence of the nuclear modulation and the multi-exponential decay. However, the longest T_m values were found to be ~600 ns for the 1.5 mM solution and ~380 ns for the 30 mM solution. The multi-exponential decay agrees with the fact that Finland solutions contain various types of supramolecular structures (fibers, spheres, sheets, as seen by electron microscopy). Presumably there are smaller aggregates (dimers, trimer, as suggested by mass-spectrometry). The choice of the repetition rate (indicative of T_1) for the ESE-detected EPR spectra was empirically optimized by determining the repetition rate at which the echo intensity did not diminish in the second shot. This was found to be ~400 ms for the 1.5 mM Finland solutions and ~100 ms for the 30 mM Finland solutions at 7K.



PinPin

PoutMin



Fig. S6. Alternative structures of Finland radical dimers (see Table 1 of main text)



Figure S7. MS spectrum of Finland radical in H_2O . Expansion from m/z 1050-1110



Figure S8.

Concentration dependence of ESI- MS spectra of Finland in $\rm H_2O$ at (a) 1200 μM , (b) 120 μM , (c) 12 μM



Figure S9.

- A. 2D ion-mobility spectra of Finland radical showing the presence of various species with identical m/z but showing different drift-times.
- B. Projection MS obtained by merging spectra of species with all mobilities. In the following supplementary figures, MS spectra from species separated by their mobility are presented and analyzed.





A. Theoretical isotopic distribution for monomer $(F+H)^+$ B. Compiled MS spectra from ions within arrival drift time peak with maximum at 8.84 ms

(monomers). Expansion of the m/z 1062-1074 region.





A. Theoretical isotopic distributions for dimers: (a) $(F_2-2Na+2H+2H_2O+2H)^{2+}$, (b) $(F_2-3Na+3H+3H_2O+2H)^{2+}$, (c) $(F_2-4Na+4H+4H_2O+2H)^{2+}$

B. Compiled MS spectra from ions within arrival drift time peak with maximum at 4.87 ms (dimers). Expansion of the m/z 1062-1074 region.



Figure S12.

- A. Theoretical isotopic distributions for dimers: (a) $(F_2+Na+H)^{2+}$, (b) $(F_2-Na+H+2H_2O+2H)^{2+}$
- B. Compiled MS spectra from ions with arrival drift time peak with maximum at 4.87 ms (dimers). Expansion of the m/z 1073-1085 region.



Figure S13.

A. Theoretical isotopic distributions for trimers: (a) $(F_3-2Na+2H+3H_2O+3H)^{3+}$, (b) $(F_3-3Na+3H+4H_2O+3H)^{3+}$, (c) $(F_3+3H)^{3+}$, (d) $(F3-2Na+2H+2H_2O+3H)^{3+}$, (e) $F_3-4Na+4H+4H_2O+3H)^{3+}$ B. Compiled MS spectra from ions within arrival drift time peak with maximum at 4.07 ms (trimers). Expansion of the m/z 1060-1077 region.



Figure S14.

- A. Theoretical isotopic distributions for trimers: (a) $(F_3 + Na + H_2O + 2H)^{3+}$, (b) $(F_3 + 2H_2O + 3H)^{3+}$
- B. Compiled MS spectra from ions with arrival drift time peak with maximum at 4.07 ms (trimers). Expansion of the m/z 1077-1085 region.



Figure S15. Size distribution of compact nanoparticles in 10 mM citrate (a,b) or 10 mM MES (c,d) observed in Finland samples of 30 mM (a,c) or 15 mM (b,d) Finland. pH was 6.0.



Figure S16. Electron microscopy of 30 mM Finland in 10 mM MES buffer pH 6 obtained by negative staining with uranyl acetate after drying the sample at room temperature. Notice that the bead string structure is formed by spheres of a similar size than those observed by cryo-electron microscopy. The interaction between nanospheres and their less regular appearance are probably the result of drying and staining. The milder conditions of cryo-electron microscopy probably provide a more realistic picture.



Figure S17. Cryo-EM image of 30 mM Finland in MES (10mM) adjusted to pH 7.5.



Figure S18. Comparison of the intensity of the half-field signal of 150μ L of a 15mM solution of Finland radical (red) and OX63 (blue) in glycerol:water (1:1) measured at 2.8K and 200 μ W microwave power. The signals are depicted with their relative intensity. Finland: R=CH₃ OX63: R= CH₂CH₂OH



Figure S19. Comparison of the side-bands of the CW-EPR spectrum of a 15mM Finland radical solution (red) and a 15mM OX63 radical solution (blue). The signals are normalized to the central line and shifted to the same central position as to allow facile comparison of the side-band patterns. Both spectra were taken with a microwave power of 250 nW. Red spectrum was taken at 20K, blue spectrum at 40K.