Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information

Gadolinium Based Endohedral Metallofullerene $Gd_2@C_{79}N$ as a Relaxation Boosting Agent for Dissolution DNP at High Fields

Xiaoling Wang,[a*] Johannes E. McKay,[a] Bimala Lama,[b] Johan Van Tol,[a] Tinghui Li,[c] Kyle Kirkpatrick,[c] Zhehong Gan,[a] Stephen Hill,[a,d] Joanna R. Long,[b] and Harry C. Dorn[c]

[a.] National High Magnetic Field Laboratory, Tallahassee, FL 32310, USA
[b.] Department of Biochemistry and Molecular Biology, University of Florida, Gainesville, FL 32603, USA
[c.] Department of Chemistry, Virginia Tech, Blacksburg, VA 24061, USA
[d.] Department of Physics, Florida State University, FL 32306, USA

The synthesis and purification of $Gd_2@C_{79}N$ is as reported in Reference 15 '$Gd_2@C_{79}N$: Isolation, Characterization, and Monoadduct Formation of a Very Stable Heterofullerene with a Magnetic Spin State of S = 15/2'.

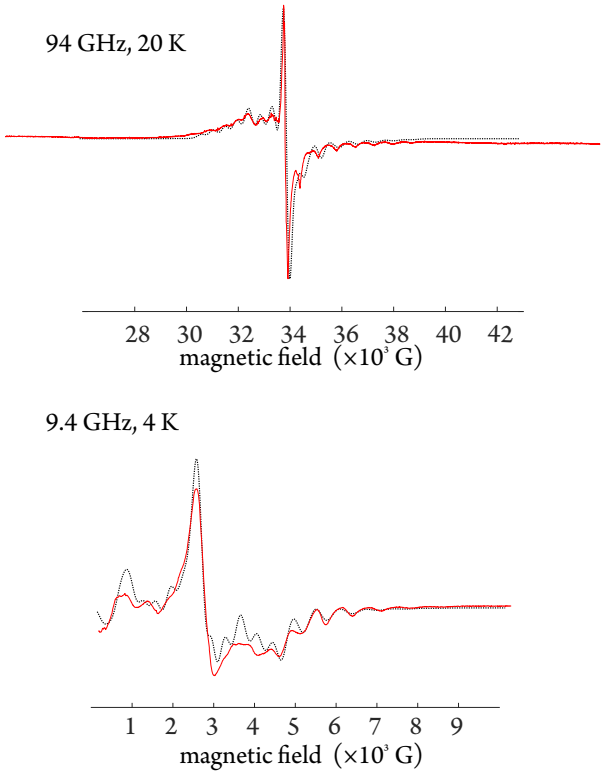

Figure S1. Experimental cw EPR spectra of $Gd_2@C_{79}N$ at measured at 94 GHz and 20 K, and at 9.4 GHz and 4 K (red solid) cited from ref. 15 and simulated spectra at both conditions (black dash) using EasySpin[1]. Input parameters based on reported values in ref. 15 are shown in Table S1.

Table S1 Input parameters for cw EPR spectra simulation of $Gd_2@C_{79}N$ at 94 GHz and 20 K, and at 9.4 GHz and 4 K using EasySpin.

S	*g*-factor	*D* / MHz	*E* / MHz	*D*-Strain / MHz	isotropic broadening (Gaussian) / mT
15/2	1.978	966	112	112	22

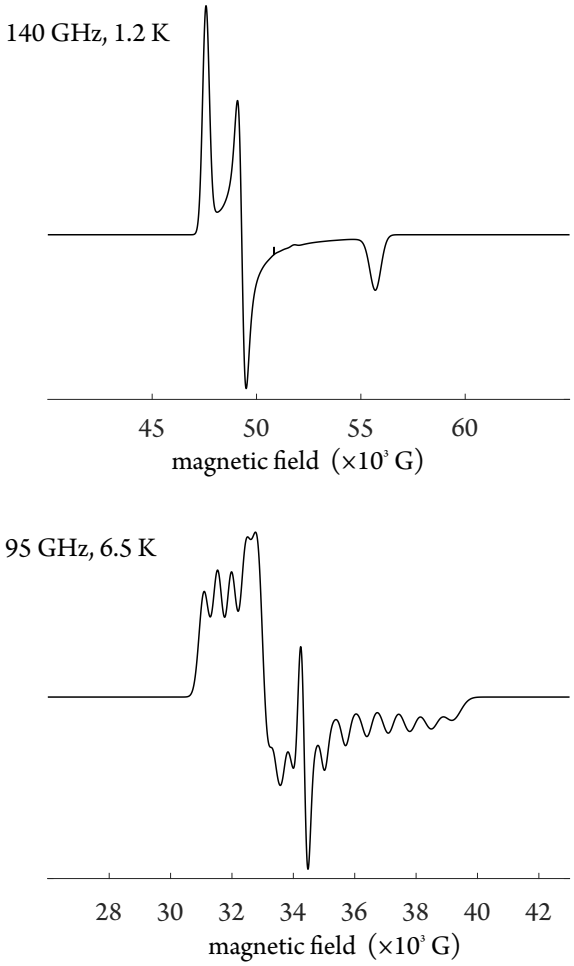

Figure S2. Simulated cw EPR spectra of $Gd_2@C_{79}N$ at measured at 140 GHz and 1.2 K (top), and 95 GHz and 6.5 K (bottom), using EasySpin[1]. Input parameters based on reported values in ref. 15 are shown in Table S1. The figure shows that only the maximum spin projection states are populated under the conditions used in the DNP experiment (140GHz, 5T and 1.2K).

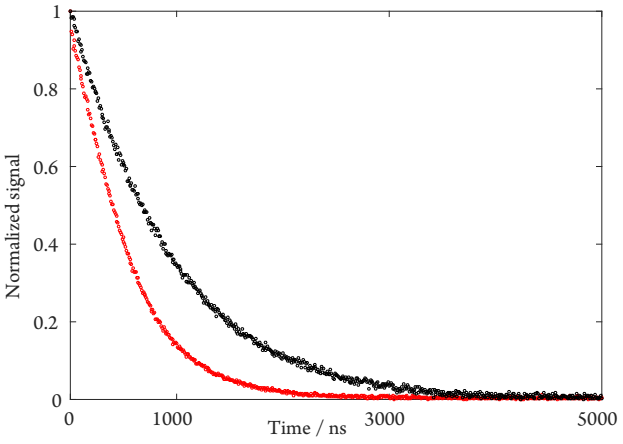

Figure S3. T_M echo signal decay curves at 3.35 T and 6.5 K for the samples of 40 mM TEMPO with (red) and without (black) 60 μM $Gd_2@C_{79}N$.

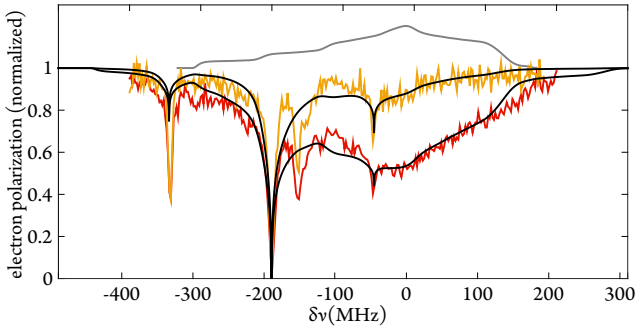

Figure S4. Experimental ELDOR spectra measured at t_{excite} value of 3.9 ms (yellow line) and 23 ms (red line) and fits (black lines) using parameters in Table 1 with detection frequencies at δ=−189 MHz for the sample of 40 mM TEMPO + 60 μM $Gd_2@C_{79}N$.

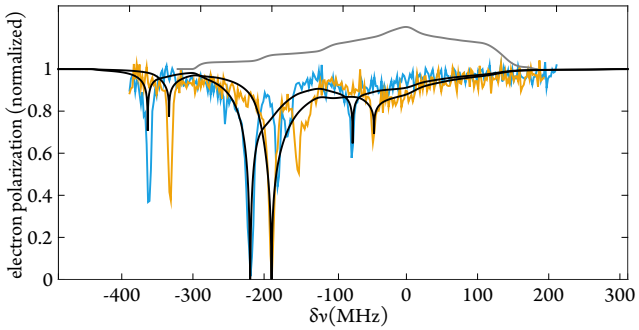

Figure S5. Experimental ELDOR spectra measured at t_{excite} value of 3.9 ms with detection frequencies at δ=−189 MHz (yellow line) and δ=−219 MHz (blue line), and fits (black lines) using parameters in Table 1 for the sample of 40 mM TEMPO + 60 μM $Gd_2@C_{79}N$.

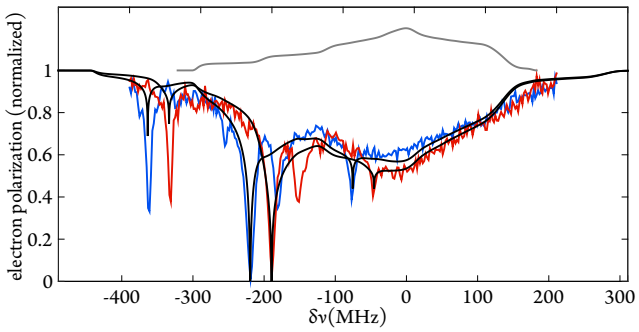

Figure S6. Experimental ELDOR spectra measured at t_{excite} value of 23 ms with detection frequencies at δ=−189 MHz (red line) and δ=−219 MHz (blue line), and fits (black lines) using parameters in Table 1 for the sample of 40 mM TEMPO + 60 μM $Gd_2@C_{79}N$.

DNP experiment parameters:

The DNP polarizer consisted of a Bruker 89 mm bore 5 T NMR magnet and a continuous-flow cryostat. Continuous wave microwave irradiation at 140.71 GHz using 120 mW of power was used to create DNP polarization. The steady state DNP enhancements were measured after approximately 3 hours' build up time to ensure full polarization of the samples and ^{1}H spin signal decay rates after polarization were monitored by small flip angle pulses at 212 MHz. ^{1}H DNP and NMR experiments were performed with same sample volume. For ^{13}C DNP and NMR, different volumes were used for samples of 40 mM 4-oxo-TEMPO with and without $Gd_2@C_{79}N$. For each sample, the on/off DNP enhancement factor was calculated using steady-state NMR signals by turning MW on and off during signal buildup and acquisition.

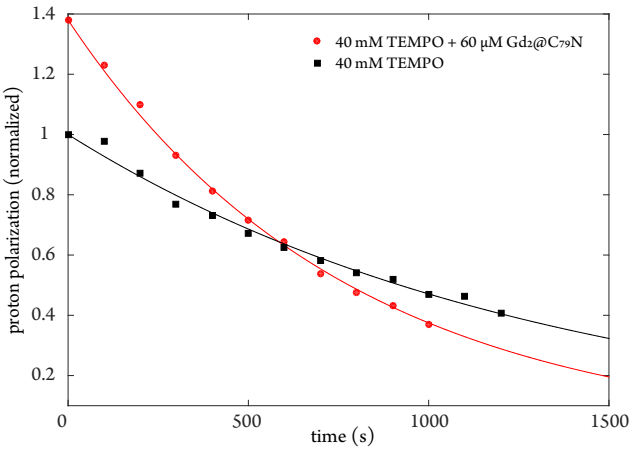

Figure S7. Decay curves of hyperpolarized proton signal of toluene mixed with 40 mM 4-oxo-TEMPO (black square) and 40 mM 4-oxo-TEMPO doped with 60 uM $Gd_2@C_{79}N$ (red dot).

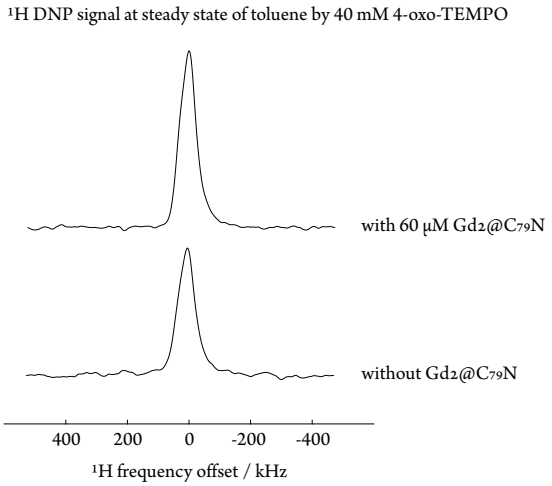

Figure S8. ^{1}H DNP spectra of toluene by 40 mM 4-oxo-TEMPO with and without 60 uM $Gd_2@C_{79}N$.

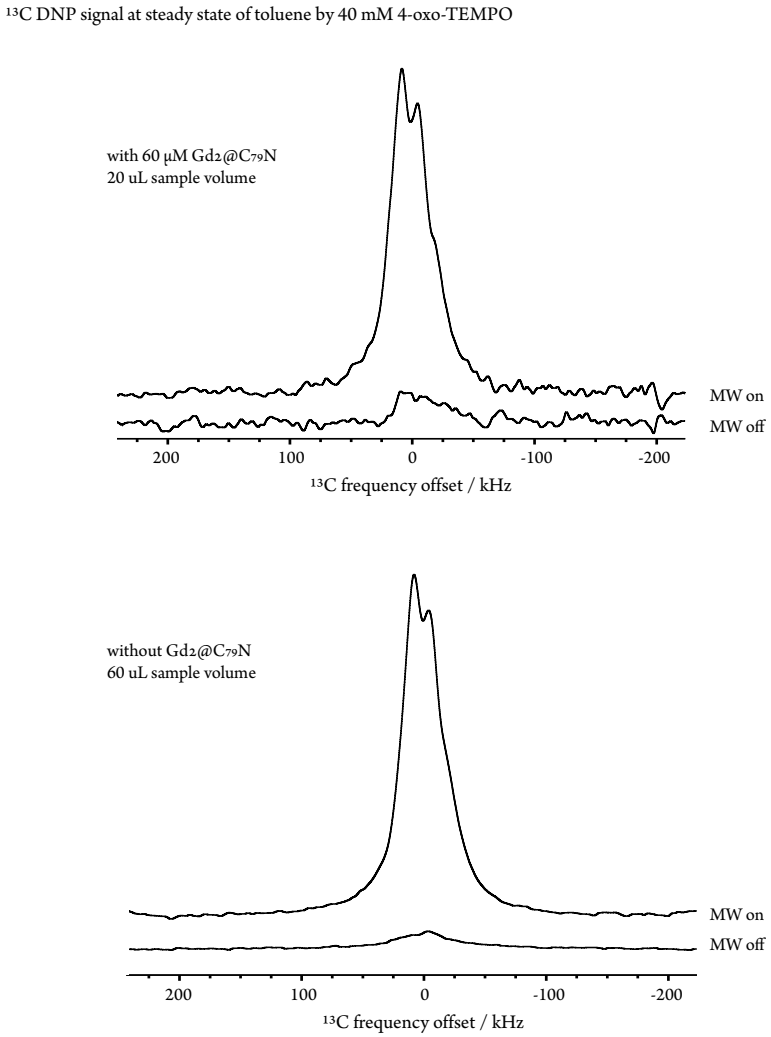

Figure S9. ^{13}C NMR and DNP spectra of 67% ^{13}C isotope enriched toluene by 40 mM 4-oxo-TEMPO with and without 60 uM $Gd_2@C_{79}N$.

Reference:

1. S. Stoll and A. Schweiger, *Journal of Magnetic Resonance*, 2006, **178**, 42 – 55.