Supporting Information for

Thermally Controlling the Singlet-Triplet Energy Gap of a Diradical in the Solid State

Yuanting Su, Xingyong Wang, Lei Wang, Zaichao Zhang, Xinping Wang,* You Song* and Philip P. Power*

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Table S1. Crystal data and structure refinement for $\mathbf{1}^{2+}$•2[$Al(OR_F)_4$]$^-$

	123 K	200 K
formula	$C_{78}H_{40}Al_2F_{72}N_2O_8$	$C_{78}H_{40}Al_2F_{72}N_2O_8$
Mr [g mol^{-1}]	2555.08	2555.08
crystal system	Monoclinic	Monoclinic
space group	*P*2(1)/c	*P*2(1)/c
Z	2	2
Temp. (K)	123(2)	200(2)
μ(mm^{-1})	0.233	0.226
a (Å)	17.262(3)	17.4037(17)
b (Å)	13.956(2)	14.1343(13)
c (Å)	20.301(3)	20.914(2)
α (°)		
β (°)	109.105(3)	111.7830(15)
γ (°)		
V [Å^3]	4621.4(13)	4777.2(8)
*R*1 ($I>2\sigma(I)$)	0.0489	0.0905
*wR*2 (all data)	0.1394	0.2169

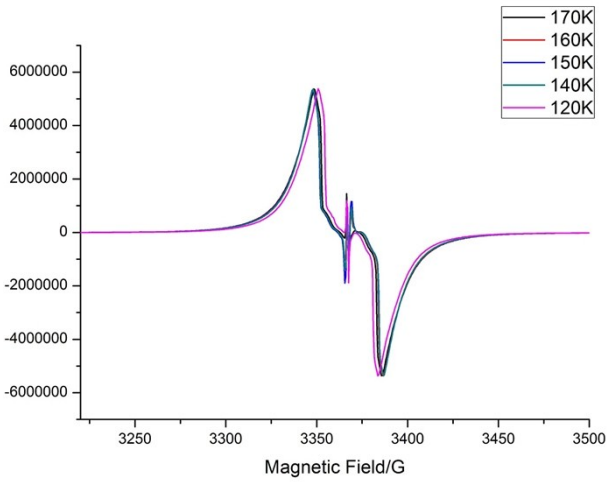

Figure S1. Powder EPR spectra of $\mathbf{1}^{2+}$•2[Al(OR$_F$)$_4$]$^-$ at various temperatures (120 – 170 K). The central peak shows the signal derived from the mono radical impurity.

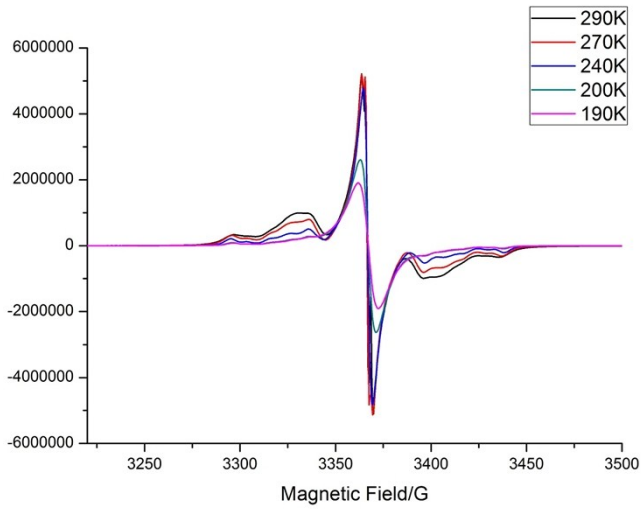

Figure S2. Powder EPR spectra of $\mathbf{1}^{2+}\bullet 2[Al(OR_F)_4]^-$ at various temperatures (190 – 290 K). The central peak shows the signal derived from the mono radical impurity.

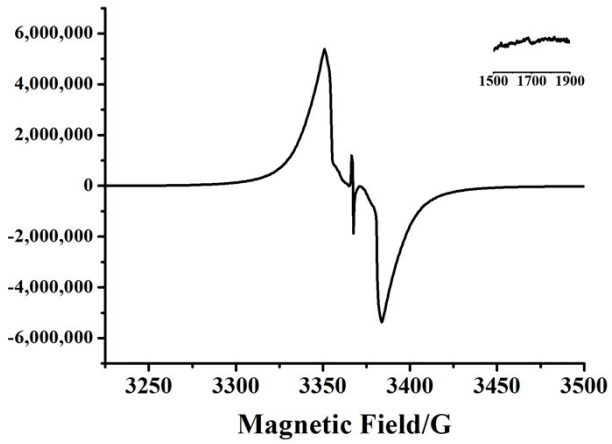

Figure S3. Powder EPR spectra of $\mathbf{1}^{2+}\bullet 2[Al(OR_F)_4]^-$ at 123K. The central peak shows the signal derived from the mono radical impurity.

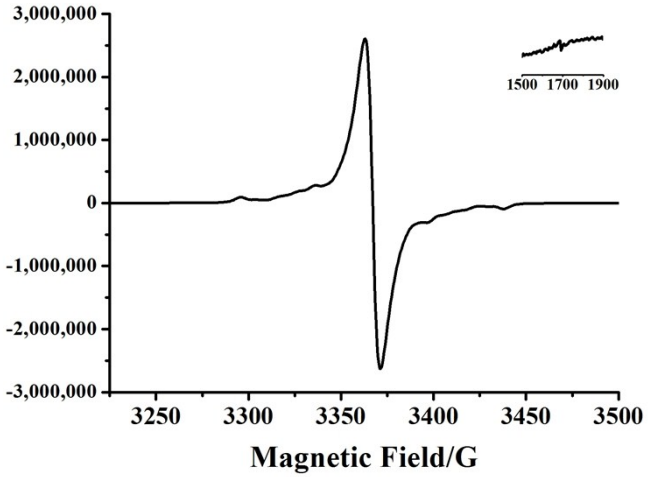

Figure S4. Powder EPR spectra of $\mathbf{1}^{2+}$•2$[Al(OR_F)_4]^-$ at 200K.

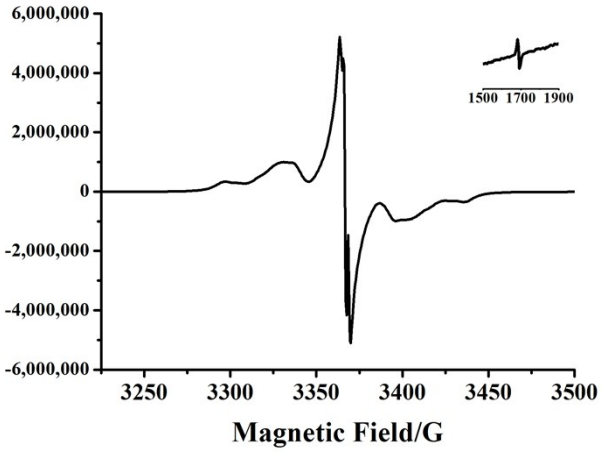

Figure S5. Powder EPR spectra of $\mathbf{1}^{2+}$•2[Al(OR$_F$)$_4$]$^-$ at 290K.

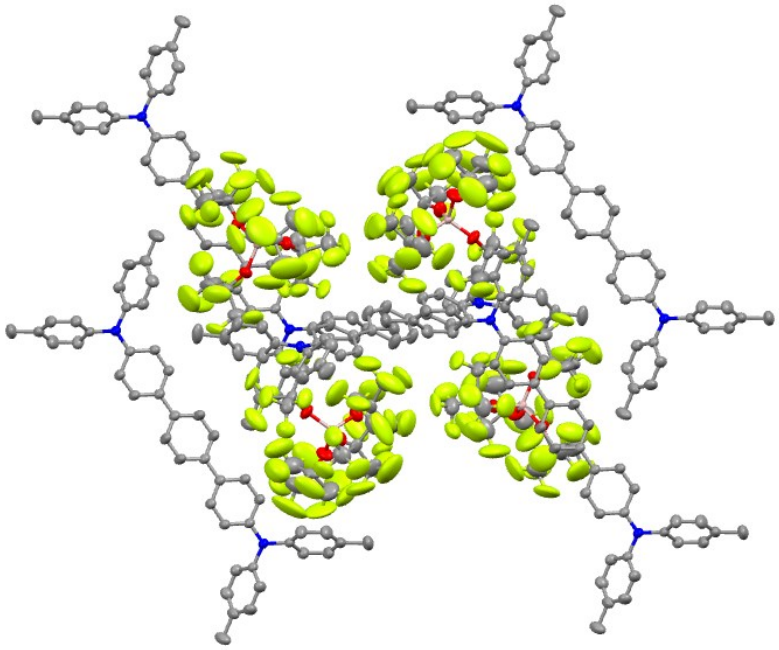

Figure S6. Packing diagram of $\mathbf{1}^{2+}$•2[Al(OR$_F$)$_4$]$^-$ at 200 K.

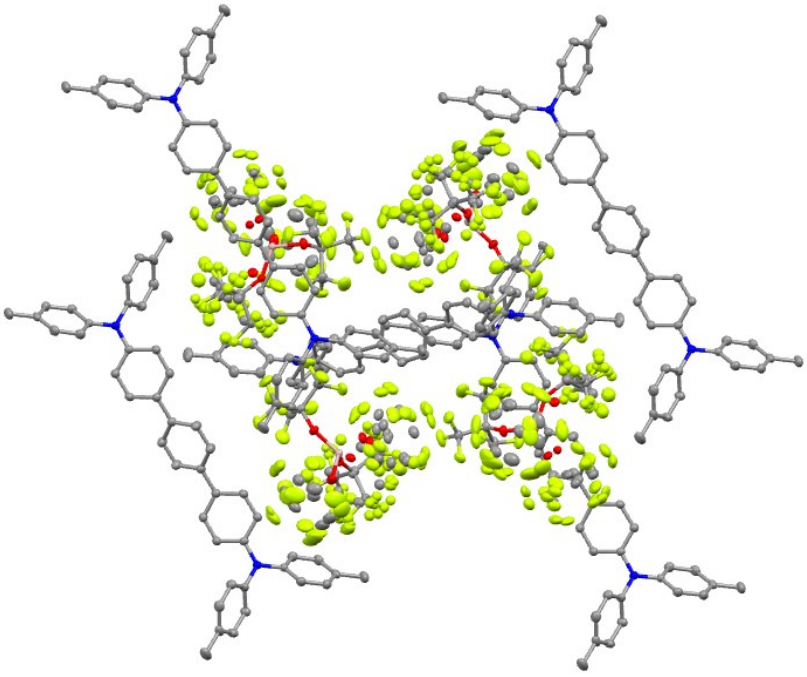

Figure S7. Packing diagram of $\mathbf{1}^{2+}$•2[Al(OR$_F$)$_4$]$^-$ at 123 K.

Coordinates for calculated geometries:

1^{2+}-CS

C	-1.437688000	0.000040000	0.000246000
C	-0.688524000	-0.834357000	-0.874442000
H	-1.199005000	-1.457558000	-1.599616000
C	0.688108000	-0.834411000	-0.874681000
H	1.198288000	-1.457657000	-1.600027000
C	-5.742726000	0.000159000	0.000966000
C	-5.012218000	-1.071003000	-0.583277000
H	-5.545986000	-1.887754000	-1.054426000
C	-3.637104000	-1.055587000	-0.592243000
H	-3.123536000	-1.890520000	-1.054472000
C	-2.888662000	0.000086000	0.000501000
C	-3.636858000	1.055794000	0.593498000
H	-3.123114000	1.890673000	1.055629000
C	-5.011979000	1.071303000	0.584964000
H	-5.545527000	1.888023000	1.056437000
C	-7.857783000	1.221521000	-0.002897000
C	-8.977196000	1.370130000	0.836472000
H	-9.258791000	0.567403000	1.509856000
C	-9.692735000	2.558491000	0.822243000
H	-10.543508000	2.672087000	1.488177000
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C	-8.980098000	-1.369188000	-0.829423000
H	-9.265466000	-0.564813000	-1.499211000
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H	-9.880746000	-5.501799000	-0.856253000
H	-11.197791000	-4.714459000	0.010509000
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C	0.688466000	0.834327000	0.874441000
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C	-0.688166000	0.834385000	0.874676000
H	-1.198354000	1.457628000	1.600021000
C	5.742691000	-0.000189000	-0.000962000
C	5.012168000	1.070900000	0.583409000
H	5.545928000	1.887591000	1.054670000
C	3.637059000	1.055483000	0.592369000
H	3.123503000	1.890361000	1.054707000
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C	3.636814000	-1.055743000	-0.593634000
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C	5.011930000	-1.071253000	-0.585104000
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C	7.857784000	-1.221522000	0.002697000
C	8.977128000	-1.369983000	-0.836786000
H	9.258625000	-0.567172000	-1.510110000
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H	9.562543000	-5.730831000	0.449148000
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H	6.645352000	2.143844000	-1.542488000
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H	7.936306000	4.245415000	-1.554190000
C	9.335924000	3.620221000	-0.035935000
C	9.698209000	2.555345000	0.811012000
H	10.555233000	2.665561000	1.469633000
C	8.979985000	1.369079000	0.829734000
H	9.265296000	0.564629000	1.499457000

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H	9.881087000	5.501463000	0.857302000
H	11.197805000	4.714368000	-0.010169000
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1^{2+}-OS

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C	0.694107000	0.416656000	1.131160000
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H	9.804620000	-5.557608000	0.917907000

1^{2+}-T

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H	-1.220535000	0.588763000	-2.072479000
C	5.726359000	-0.000664000	-0.000702000
C	5.015538000	0.945106000	-0.765814000
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C	3.629477000	0.935043000	-0.764171000
H	3.100734000	1.677231000	-1.353287000
C	2.900509000	-0.000611000	-0.000656000
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C	5.015532000	-0.946544000	0.764298000
H	5.554597000	-1.666772000	1.370008000
C	7.848803000	-1.222672000	-0.004199000
C	9.028178000	-1.360541000	0.758014000
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H	10.608546000	-2.667538000	1.359381000
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C	7.380410000	2.310953000	0.772734000
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C	8.091007000	3.501232000	0.781059000
H	7.738291000	4.323965000	1.396341000
C	9.270298000	3.658866000	0.028124000
C	9.719544000	2.564000000	-0.735371000
H	10.620004000	2.665517000	-1.334476000
C	9.030415000	1.361893000	-0.750876000
H	9.378214000	0.538799000	-1.365646000
C	10.017669000	4.964022000	0.019823000
H	9.712142000	5.575701000	-0.840059000
H	11.097559000	4.807822000	-0.064076000
H	9.819690000	5.548154000	0.922979000
N	7.140927000	-0.000154000	-0.000079000
C	-1.421470000	0.000380000	0.000440000
C	-0.694497000	-0.351253000	1.153056000
H	-1.219713000	-0.588121000	2.073244000
C	0.694757000	-0.351549000	1.152690000
H	1.220297000	-0.588573000	2.072646000
C	-5.726405000	0.000666000	0.000804000
C	-5.015639000	-0.946484000	0.764218000
H	-5.554793000	-1.667894000	1.368435000
C	-3.629562000	-0.936347000	0.762677000
H	-3.100736000	-1.679504000	1.350501000
C	-2.900667000	0.000642000	0.000766000
C	-3.629576000	0.937780000	-0.760956000
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C	-5.015651000	0.947955000	-0.762475000
H	-5.554768000	1.669288000	-1.366827000
C	-7.848832000	1.222634000	0.007768000
C	-9.028376000	1.362738000	-0.753789000
H	-9.371448000	0.542036000	-1.374414000
C	-9.715190000	2.566502000	-0.742586000
H	-10.608767000	2.671546000	-1.351138000
C	-9.269801000	3.659382000	0.025458000
C	-8.090772000	3.501997000	0.779420000
H	-7.734982000	4.327362000	1.389466000
C	-7.382675000	2.310528000	0.775363000
H	-6.492751000	2.199949000	1.385635000

C	-10.044569000	4.948100000	0.059021000
H	-10.799421000	4.920002000	0.856756000
H	-9.394413000	5.805141000	0.257593000
H	-10.575079000	5.123008000	-0.881660000
C	-7.847217000	-1.223363000	-0.009281000
C	-7.379854000	-2.308782000	-0.779033000
H	-6.491058000	-2.195187000	-1.390395000
C	-8.090262000	-3.499270000	-0.790904000
H	-7.737019000	-4.320279000	-1.408146000
C	-9.269813000	-3.659125000	-0.039122000
C	-9.719590000	-2.566352000	0.727341000
H	-10.620223000	-2.669743000	1.325903000
C	-9.030755000	-1.364271000	0.746450000
H	-9.378858000	-0.542947000	1.363412000
C	-10.018127000	-4.963759000	-0.034823000
H	-9.738513000	-5.563880000	0.841798000
H	-11.099905000	-4.805346000	0.016520000
H	-9.795847000	-5.559841000	-0.924270000
N	-7.141040000	0.000116000	0.000139000