A Difunctional Azido-Cobalt(II) Coordination Polymer Exhibiting Slow Magnetic Relaxation Behaviour and High-Energy Characteristics with Good Thermostability and Insensitivity

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Table S1 Relaxation fitting parameters from least-squares fitting of $\chi(f)$ data under 2000 dc field of **1**

T(K)	χ_T	χ_S	α
2.0	0.411	0.040	0.29
2.1	0.385	0.037	0.26
2.2	0.378	0.039	0.24
2.3	0.358	0.034	0.21
2.4	0.352	0.036	0.19
2.5	0.336	0.025	0.17
2.6	0.335	0.016	0.19

Table S2 Comparison of the experimental (from fitting) and DFT studies

		B3LYP				BP86			
		tzvp	tzv	def2-tzvp	def2-svp	tzvp	tzv	def2-tzvp	def2-svp
J_1(Co1-Co1)	E_{HS}/eV	-135448.15360	-135426.26982	-135451.77322	-135372.32784	-135500.42006	-135480.34189	-135503.88798	-135424.87213
	E_{BS}/eV	-135448.17878	-135426.29696	-135451.79853	-135372.35180	-135500.47077	-135480.39442	-135503.93974	-135424.91790
	J_{DFT}^1/cm^{-1}	-22.56	-24.31	-22.68	-21.47	-45.44	-47.08	-46.38	-41.02
	J_{DFT}^2/cm^{-1}	-16.92	-18.24	-17.01	-16.1	-34.08	-35.31	-34.79	-30.76
	J_{DFT}^3/cm^{-1}	-22.55	-24.3	-22.66	-21.46	-45.14	-46.76	-46.07	-40.78
	J_{Expt}^1/cm^{-1}	-18.36							
J_2(Co1-Co2)	E_{HS}/eV	-135515.94873	-135496.03117	-135519.24859	-135389.00085	-135515.94873	-135496.03117	-135519.24859	-135442.41784
	E_{BS}/eV	-135515.93023	-135496.01142	-135519.22954	-135388.98683	-135515.93023	-135496.01142	-135519.22954	-135442.40296
	J_{DFT}^1/cm^{-1}	16.59	17.7	13.76	12.56	16.59	17.7	17.08	13.34
	J_{DFT}^2/cm^{-1}	12.44	13.27	10.32	9.42	12.44	13.27	12.81	10
	J_{DFT}^3/cm^{-1}	16.52	17.63	13.74	12.55	16.52	17.63	17.01	13.29
	J_{Expt}^1/cm^{-1}	20.87							
J_3(Co2-Co2)	E_{HS}/eV	-135448.41811	-135426.61650	-135452.01439	-135372.49682	-135500.64121	-135480.64594	-135504.09903	-135425.00223
	E_{BS}/eV	-135448.41191	-135426.60910	-135452.00801	-135372.49117	-135500.63756	-135480.64080	-135504.09495	-135425.00063
	J_{DFT}^1/cm^{-1}	5.56	6.63	5.71	5.06	3.27	4.61	3.66	1.44
	J_{DFT}^2/cm^{-1}	4.17	4.97	4.28	3.79	2.46	3.46	2.74	1.08
	J_{DFT}^3/cm^{-1}	5.55	6.62	5.7	5.05	3.26	4.59	3.64	1.43
	J_{Expt}^1/cm^{-1}	2.04							

$J_{DFT}^{1} = -\frac{E_{HS} - E_{BS}}{S_{max}^2}$; $J_{DFT}^{2} = -\frac{E_{HS} - E_{BS}}{S_{max}(S_{max}+1)}$; $J_{DFT}^{3} = -\frac{E_{HS} - E_{BS}}{S_{HS}^2 - S_{BS}^2}$

Table S3 Energy levels (cm^{-1}) of ligand field multiplets in zero field derived from CASSCF/NEVPT2/def2-TZVP CASSCF(7,5) (ORCA) calculations for Co1 ion.

0	0.0	30	16260.9	60	26323.0	90	38383.9
1	0.0	31	16260.9	61	26323.0	91	38383.9
2	147.2	32	17630.8	62	26723.3	92	38578.3
3	147.2	33	17630.8	63	26723.3	93	38578.3
4	1161.5	34	18302.0	64	27215.7	94	39930.3
5	1161.5	35	18302.0	65	27215.7	95	39930.3
6	1361.5	36	19245.5	66	27583.9	96	44307.2
7	1361.5	37	19245.5	67	27583.9	97	44307.2
8	2109.3	38	19317.6	68	28421.3	98	44715.8
9	2109.3	39	19317.6	69	28421.3	99	44715.8
10	2270.3	40	20065.0	70	30416.1	100	45235.0
11	2270.3	41	20065.0	71	30416.1	101	45235.0
12	3461.3	42	20528.0	72	30994.7	102	47779.4
13	3461.3	43	20528.0	73	30994.7	103	47779.4
14	3622.6	44	20628.0	74	31749.7	104	49083.3
15	3622.6	45	20628.0	75	31749.7	105	49083.3
16	4137.9	46	21040.1	76	32111.4	106	49261.2
17	4137.9	47	21040.1	77	32111.4	107	49261.2
18	7900.6	48	21313.0	78	35550.7	108	49603.1
19	7900.6	49	21313.0	79	35550.7	109	49603.1
20	8819.8	50	22244.7	80	36196.1	110	60643.0
21	8819.8	51	22244.7	81	36196.1	111	60643.0
22	9882.8	52	22350.0	82	36495.0	112	64882.3
23	9882.8	53	22350.0	83	36495.0	113	64882.3
24	10111.9	54	22674.7	84	36751.2	114	68342.3
25	10111.9	55	22674.7	85	36751.2	115	68342.3
26	10649.7	56	23337.8	86	37169.1	116	69168.9
27	10649.7	57	23337.8	87	37169.1	117	69168.9
28	10696.1	58	23429.3	88	37613.5	118	71844.4
29	10696.1	59	23429.3	89	37613.5	119	71844.4

Table S4 Individual contributions to D-tonsor for title complex by CASSCF/NEVPT2/def2-TZVP CASSCF(7,5) (ORCA) calculations for Co1 ion.

2*S*+1	Root	*D*	*E*
4	0	0.000	0.000
4	1	-61.493	-4.826
4	2	-1.415	-14.786
4	3	-8.260	-1.033
4	4	3.649	2.134
4	5	-1.429	0.262
4	6	0.119	-0.011

4	7	0.269	0.204
4	8	-0.084	-0.002
4	9	-0.067	-0.007
2	0	-8.740	-4.602
2	1	0.078	0.006
2	2	-1.179	-0.997
2	3	0.803	0.040
2	4	0.659	0.105
2	5	-0.367	0.646
2	6	1.108	-0.030
2	7	-0.452	0.081
2	8	1.085	0.112
2	9	-1.120	1.072
2	10	-0.885	0.174
2	11	0.028	0.015
2	12	0.110	0.043
2	13	-0.262	0.194
2	14	0.390	0.010
2	15	-0.188	0.288
2	16	0.239	0.008
2	17	-0.200	0.045
2	18	0.353	-0.028
2	19	-1.271	-1.253
2	20	-0.234	-0.188
2	21	-0.017	0.011
2	22	-0.044	-0.007
2	23	-0.091	0.056
2	24	-0.166	-0.186
2	25	-0.093	0.032
2	26	0.040	-0.036
2	27	0.026	0.000
2	28	-0.059	-0.083
2	29	0.066	0.004
2	30	0.135	0.009
2	31	-0.031	0.038
2	32	-0.027	0.018
2	33	0.031	-0.002
2	34	0.053	0.003
2	35	-0.009	0.009
2	36	0.000	0.000
2	37	0.005	-0.001
2	38	-0.008	-0.007
2	39	-0.049	-0.022

Table S5 Energy levels (cm^{-1}) of ligand field multiplets in zero field derived from CASSCF/NEVPT2/def2-TZVP CASSCF(7,5) (ORCA) calculations for Co2 ion.

0	0.0	30	16490.7	60	25672.7	90	35981.5
1	0.0	31	16490.7	61	25672.7	91	35981.5
2	213.7	32	17021.3	62	26250.4	92	36387.9
3	213.7	33	17021.3	63	26250.4	93	36387.9
4	549.0	34	17284.5	64	26674.7	94	37620.4
5	549.0	35	17284.5	65	26674.7	95	37620.4
6	812.4	36	17691.7	66	27523.0	96	42483.8
7	812.4	37	17691.7	67	27523.0	97	42483.8
8	1500.6	38	17967.3	68	27831.2	98	43059.3
9	1500.6	39	17967.3	69	27831.2	99	43059.3
10	1552.8	40	19499.7	70	28963.7	100	43523.8
11	1552.8	41	19499.7	71	28963.7	101	43523.8
12	2344.2	42	19974.0	72	29057.3	102	46142.9
13	2344.2	43	19974.0	73	29057.3	103	46142.9
14	2518.6	44	20188.4	74	30268.4	104	46940.3
15	2518.6	45	20188.4	75	30268.4	105	46940.3
16	5449.3	46	20405.4	76	31001.6	106	47146.6
17	5449.3	47	20405.4	77	31001.6	107	47146.6
18	8714.0	48	20606.6	78	34161.8	108	47372.0
19	8714.0	49	20606.6	79	34161.8	109	47372.0
20	9034.5	50	20893.1	80	34377.8	110	59766.1
21	9034.5	51	20893.1	81	34377.8	111	59766.1
22	9264.1	52	21169.9	82	34798.5	112	63108.0
23	9264.1	53	21169.9	83	34798.5	113	63108.0
24	9692.5	54	21484.9	84	35013.3	114	66758.3
25	9692.5	55	21484.9	85	35013.3	115	66758.3
26	9848.6	56	21810.6	86	35219.3	116	67168.5
27	9848.6	57	21810.6	87	35219.3	117	67168.5
28	10338.8	58	22044.9	88	35675.9	118	69639.6
29	10338.8	59	22044.9	89	35675.9	119	69639.6

Table S6 Individual contributions to D-tonsor for title complex by CASSCF/NEVPT2/def2-TZVP CASSCF(7,5) (ORCA) calculations for Co2 ion.

2*S*+1	Root	*D*	*E*
4	0	0.000	0.000
4	1	-76.656	-3.728
4	2	-21.903	-10.021
4	3	-45.439	1.139
4	4	4.937	4.014
4	5	-0.581	-0.023
4	6	0.152	-0.050

4	7	0.293	0.227
4	8	-0.025	0.001
4	9	-0.109	-0.008
2	0	-3.768	4.483
2	1	-0.029	0.007
2	2	-1.471	-0.156
2	3	1.429	-0.023
2	4	1.136	0.043
2	5	-1.604	0.671
2	6	0.399	-0.001
2	7	-0.611	0.330
2	8	-0.471	-0.358
2	9	-0.080	0.214
2	10	-1.263	-0.078
2	11	0.025	-0.002
2	12	0.202	-0.015
2	13	-0.055	-0.052
2	14	0.090	0.003
2	15	-0.515	0.229
2	16	0.275	-0.015
2	17	-0.175	-0.173
2	18	0.131	0.005
2	19	-0.335	-0.128
2	20	-0.058	-0.022
2	21	-0.596	-0.012
2	22	-0.045	0.046
2	23	-0.042	0.003
2	24	-0.549	-0.098
2	25	-0.152	0.133
2	26	0.000	-0.067
2	27	0.066	0.011
2	28	0.217	0.013
2	29	0.047	-0.022
2	30	0.015	-0.022
2	31	-0.045	0.008
2	32	-0.012	-0.016
2	33	0.031	0.001
2	34	0.097	0.006
2	35	-0.022	0.007
2	36	0.000	0.000
2	37	0.002	0.000
2	38	-0.015	-0.013
2	39	-0.038	0.045

Table S5 Peak temperatures of exothermic stage at different heating rates and kinetic parameters

β(°C·min^{-1})	Peaks temperatures T_p(°C)
	Compound **1**
2	167
5	182
8	190
10	201
The calculation results by Kissinger's method E_k (kJ·mol^{-1})	77.244
Log A (s^{-1})	6.407
Linear correlation coefficient (R_k)	0.9988
The calculation results by Ozawa-Doyle's method E_o (kJ·mol^{-1})	80.6695
Linear correlation coefficient (R_o)	0.9990

Table S6 Selected bond lengths [Å] and bond angles [°] for **1**

Co(1)-N(1)	1.978(3)	N(5)#1-Co(1)-N(4)	92.45(14)
Co (1)- N(3)	2.021(3)	N(5)#1-Co(1)-N(7)	95.72(14)
Co (1)-N(4)	1.994(3)	N(5)#1-Co(1)-N(3)	169.52(14)
Co (1)-N(5) #1	1.978(4)	N(8)-Co(2)-N(3)	94.35(12)
Co (1)-N(7)	2.408(4)	N(8)-Co(2)-N(4)	97.94(13)
Co (2)-N(2)	1.974(3)	N(8)#2-Co(2)-N(3)	92.69(14)
Co (2)-N(3)	2.015(3)	N(8)#2-Co(2)-N(7)	85.24(14)
Co (2)-N(4)	2.032(3)	N(8)-Co(2)-N(2)	97.38(12)
Co (2)-N(8)	2.432(3)	Co(1)-N(3)-Co(2)	100.24(14)
Co (2)-N(8)#2	1.982(3)	Co(2)-N(8)-Co(2)	94.76(14)

Symmetry transformations used to generate equivalent atoms:

#1 –x+1, -y+1 ,-z #2 -x+1, -y+1, -z+1

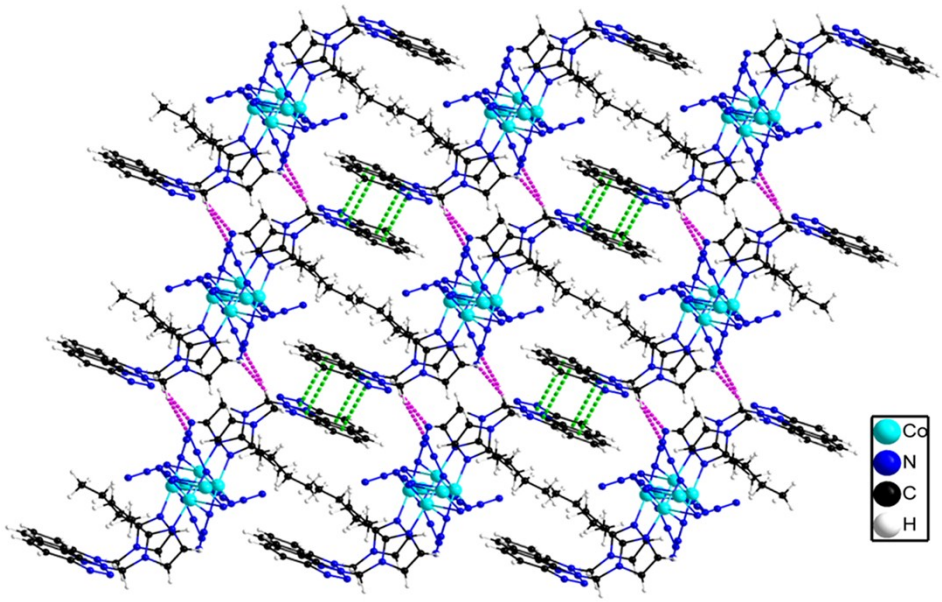

Fig. S1 3D networks through inter-molecular interactions in **1**

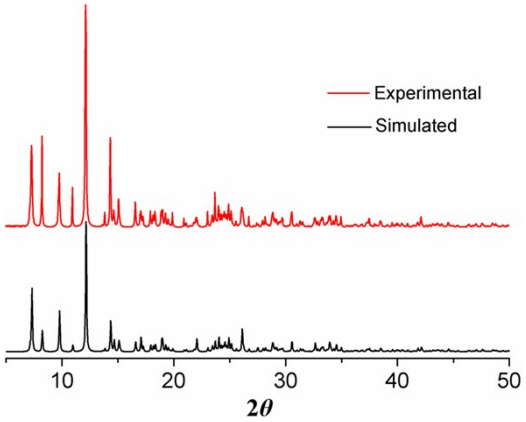

Fig. S2 PXRD patterns for compound **1**

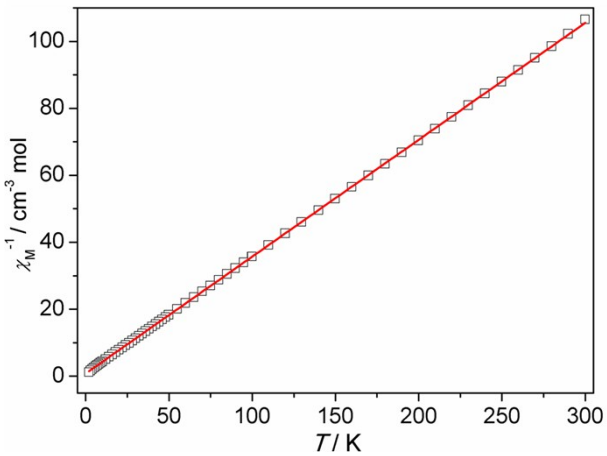

Fig. S3 $1/\chi_M$ *vs.* *T* plots, the red solid line is the best fit to the Curie–Weiss law

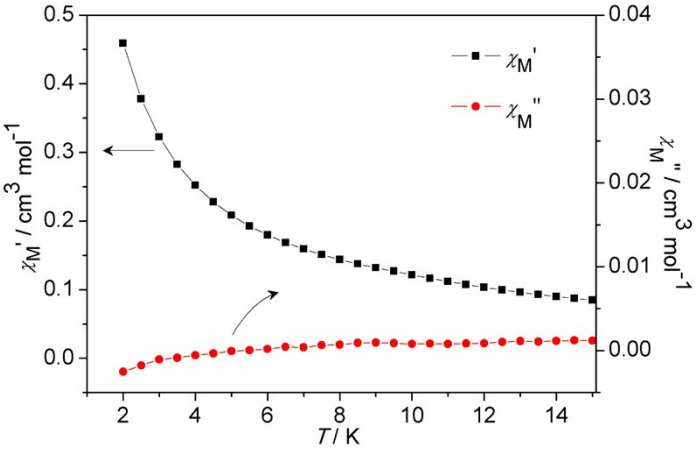

Fig. S4 The in-phase and out-of phase ac susceptibility signals under 0 Oe dc field for **1**

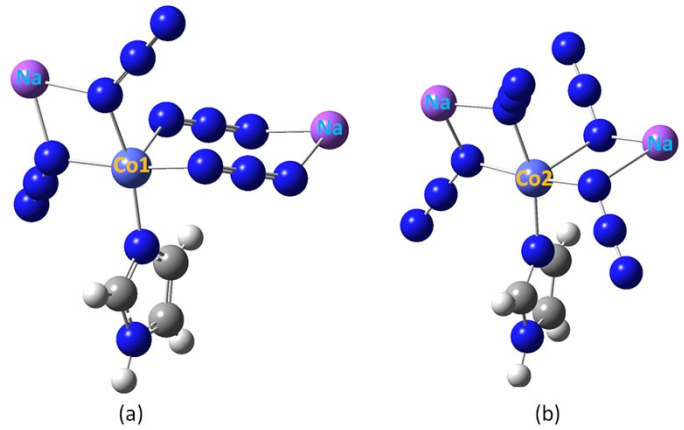

Fig. S5 *Ab initio* computational models for Co1 centre (a) and Co2 centre (b). The pink spheres designate Na(I) ions to compensate the charges of the dianionic fragments.