Supporting Information

Magnetic Properties of 1:4 Complexes of $CoCl_2$ and Pyridines Carrying Carbenes (S_0 = 4/2, 6/2, and 8/2) in Diluted Frozen Solution; Influence of Carbene Multiplicity on Heterospin Single-molecule Magnets.

Satoru Karasawa, Kimihiro Nakano, Jun-ichi Tanokashira, Noriko Yamamoto, Takahito Yoshizaki, and Noboru Koga*

Graduate School of Pharmaceutical Sciences, Kyushu University, 3-1-1 Maidashi, Higashi-ku, Fukuoka, 812-8582 Japan.

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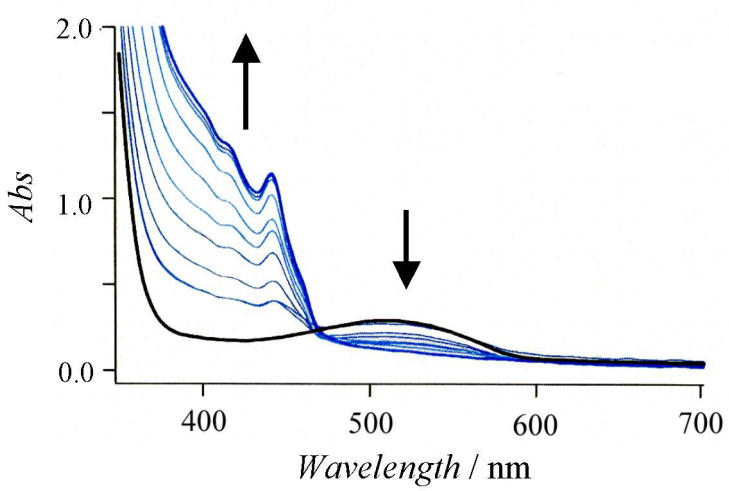


Figure S1. UV-vis spectra changes of **D2bpy** in 2 mM MTHF solution on photolysis at 10 K. Arrows indicate the increasing of the carbene and decreasing of the diazo group by photolysis.

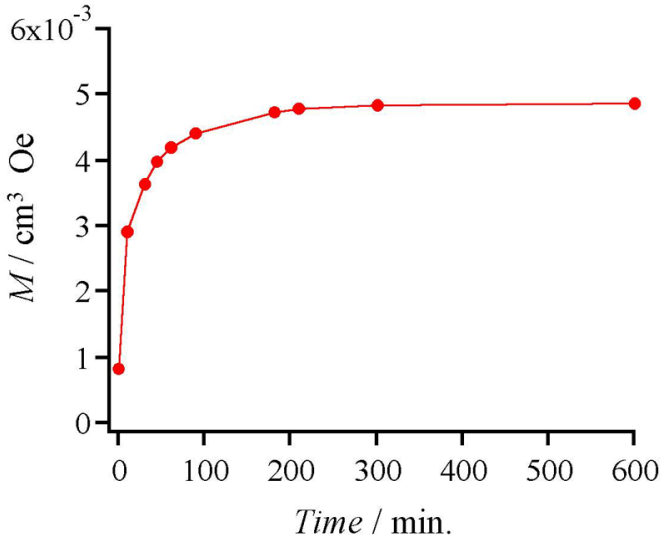


Figure S2-1. *M* vs *irradiation time* plot upon photolysis for **D2py** at 5 K.

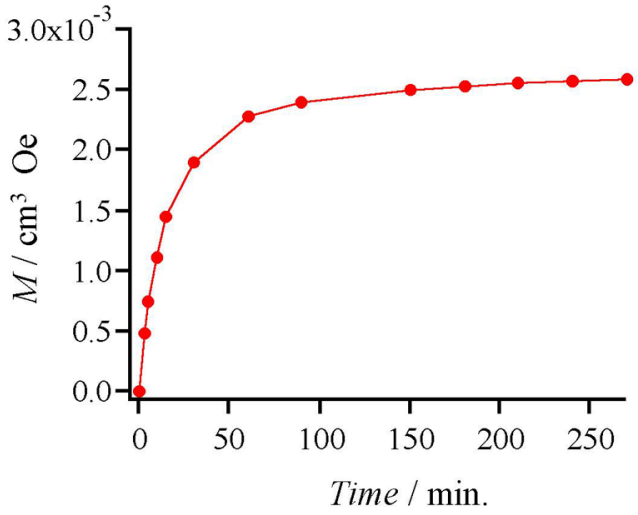


Figure S2-2. *M* vs *irradiation time* plot upon photolysis for $CoCl_2$(**D2py**)$_4$ at 5 K.

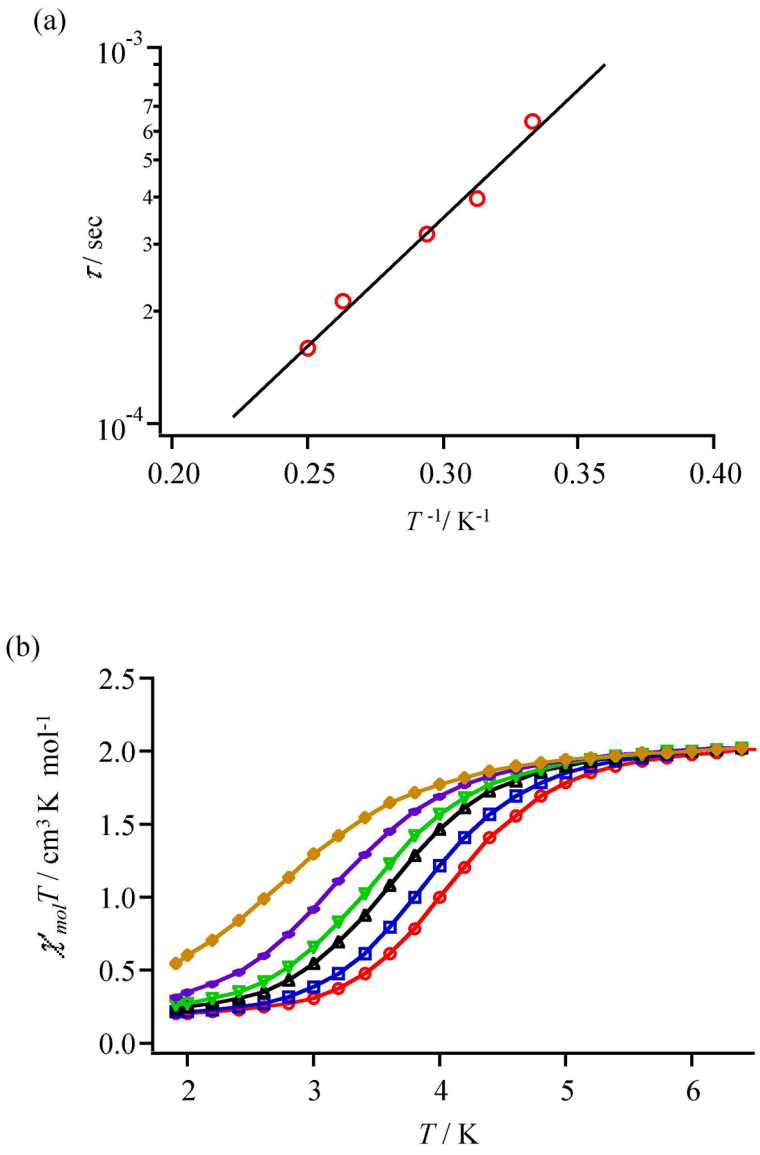
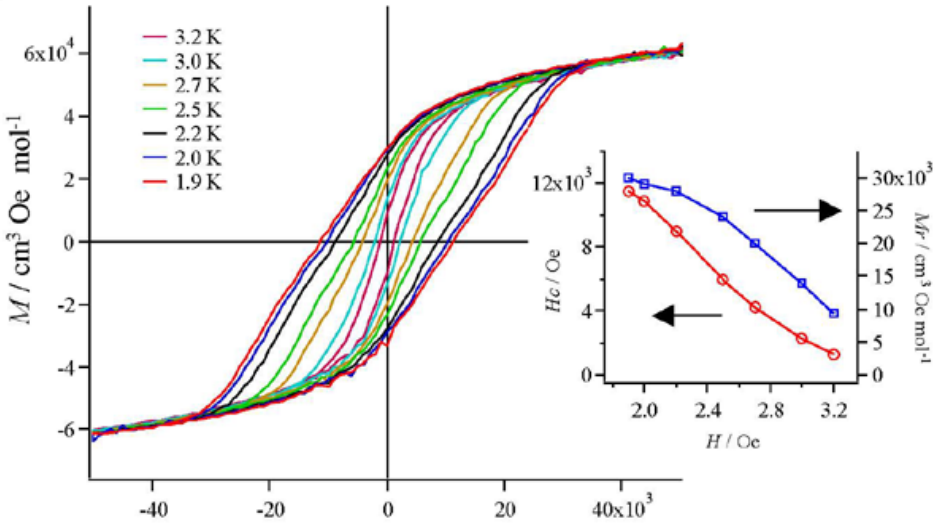
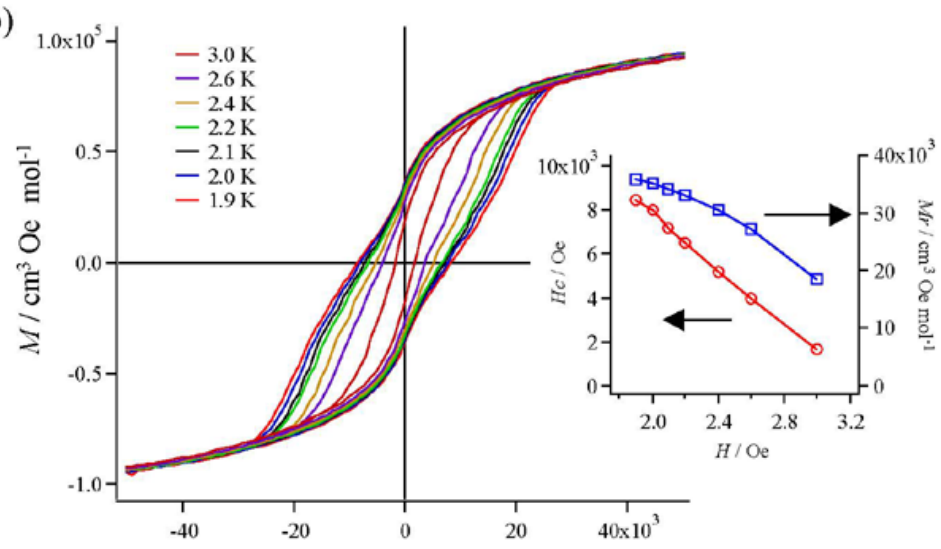


Figure S3. (a) τ vs T^1 plot of the data collected by ac magnetic susceptibility. (b) $\chi'_{\mathrm{mol}}T$ vs. T with a 5 Oe ac field oscillating at 1000 (red), 750 (blue), 500 (black), 400 (green), 250 (purple) and 100 (brown) Hz in the presence of 3 kOe dc field for a microcrystalline sample of $[CoCl_2(\mathbf{py})_4]$.The solid line indicates least squares fitting data for (a) and visual guides for (b).

(a)


3.2 K
3.0 K
2.7 K
2.5 K
2.2 K
2.0 K
1.9 K
M / cm3 Oe mol-1
6x10^4
4
2
0
-2
-4
-6
-40
-20
0
20
40x10^3
12x10^3
8
4
0
Hc / Oe
30x10^3
25
20
15
10
5
0
Mr / cm3 Oe mol-1
2.0
2.4
2.8
3.2
H / Oe

(b)


3.0 K
2.6 K
2.4 K
2.2 K
2.1 K
2.0 K
1.9 K
M / cm3 Oe mol-1
1.0x10^5
0.5
0.0
-0.5
-1.0
-40
-20
0
20
40x10^3
10x10^3
8
6
4
2
0
Hc / Oe
40x10^3
30
20
10
0
Mr / cm3 Oe mol-1
2.0
2.4
2.8
3.2
H / Oe

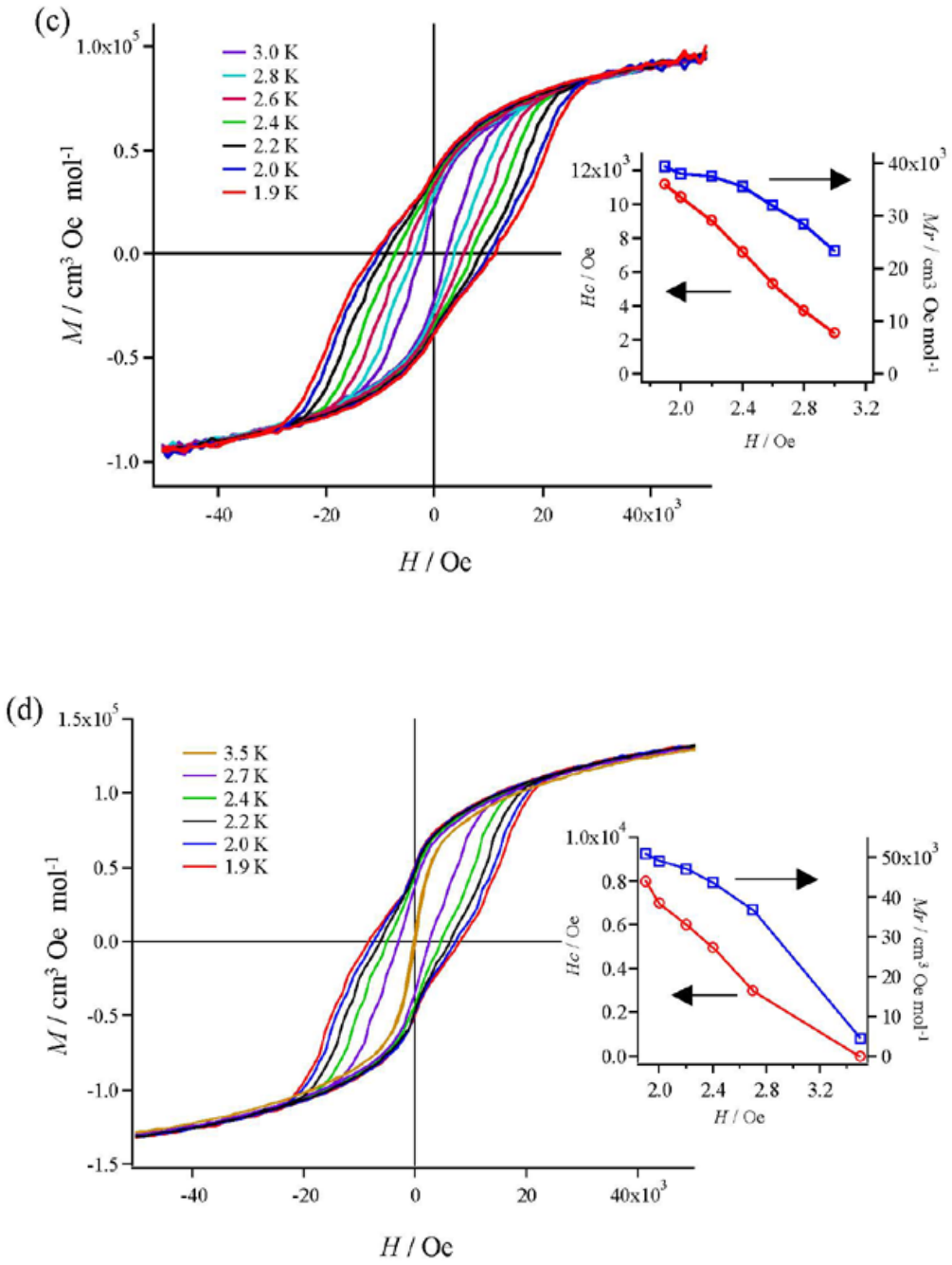


Figure S4. Plots of hysteresis loops at given temperature after irradiation of 1:4 mixtures of $CoCl_2$ and **CYpy**; **Y** = **2** (a), **3l** (b), **3b** (b), and **4** (d) in frozen MTHF solution with a sweeping rate of 0.36 kOe/sec. Individual inset indicate *Hc* vs *T* (left axis) and *Mr* vs *T* (right axis) plots, respectively.

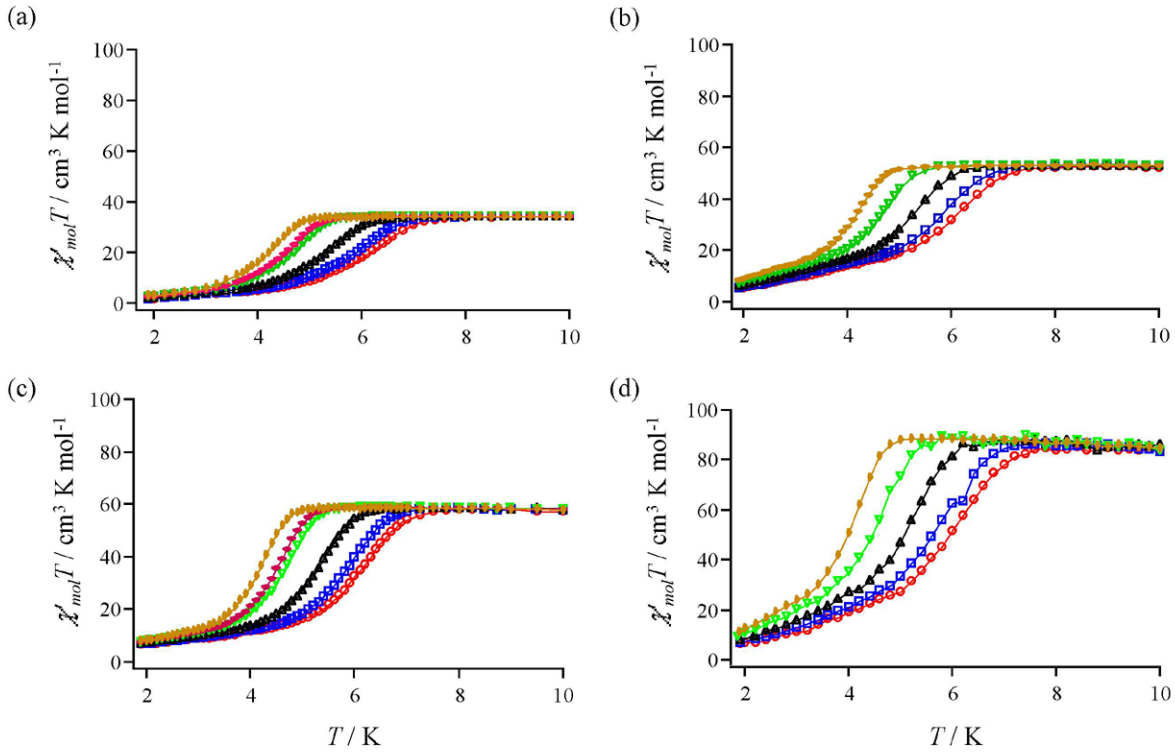


Figure S5. Plots of $\chi'_{\mathrm{mol}}T$ vs. T obtained after irradiation of a 1:4 mixture (5.0 −1.5 mM) of $CoCl_2$ (**CYpy**)$_4$; **Y** = (a) **2**, (b) **3l**, (c) **3b**, and (d) **4**, in frozen MTHF solution with a 5 Oe ac field oscillating at 1000 (red), 500 (blue), 100 (black), 10 (green), 5 (deep red) and 1(brown) Hz. The solid lines are visual guides.

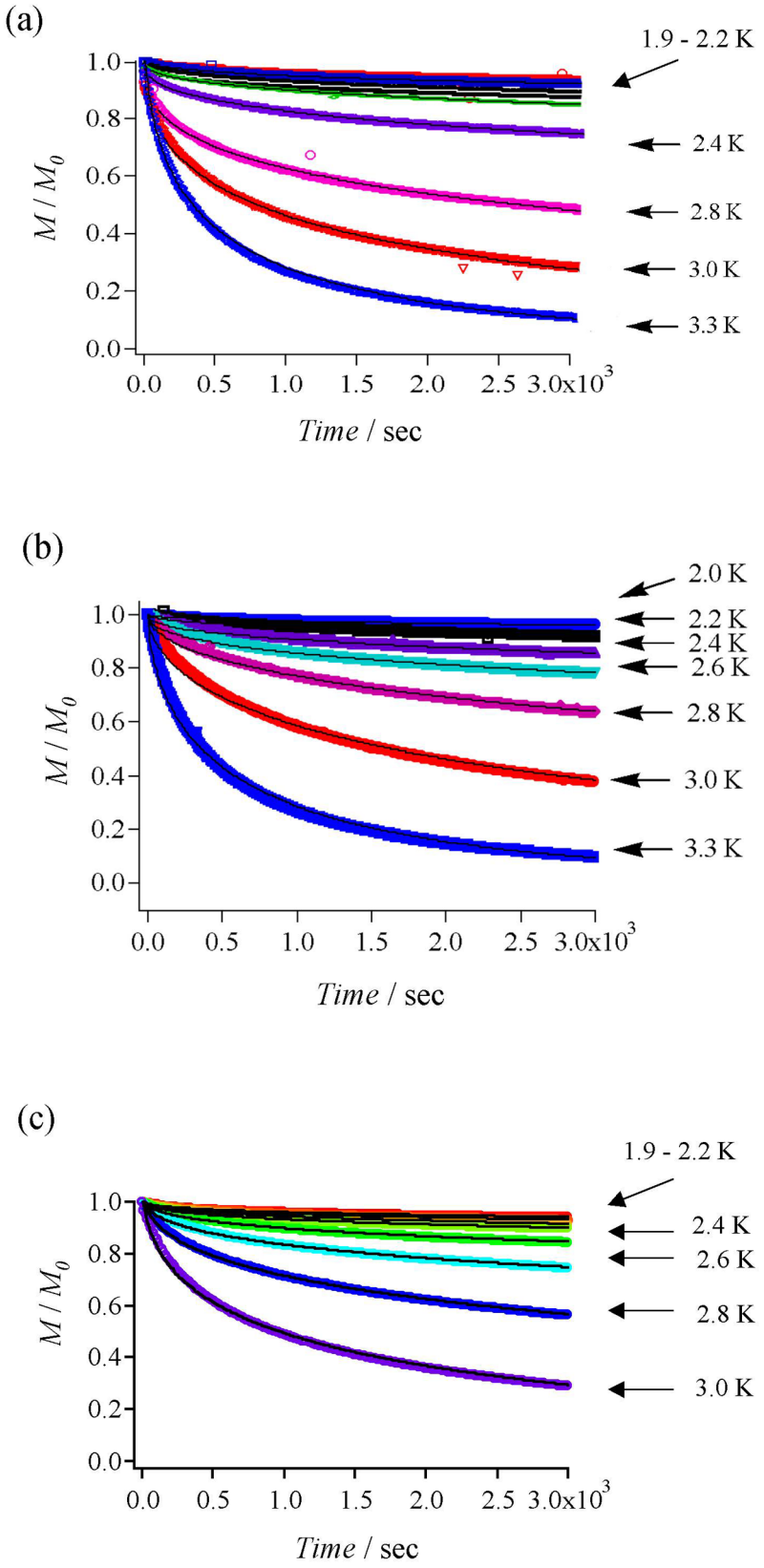


Figure S6. Dc magnetization decays at the indicated temperatures after irradiation of 1:4 mixtures of $CoCl_2$ and **CYpy**; **Y** = **3l**(a), **3b**(b), and **4**(c) in frozen solution. Solid lines show fittings by the

stretched exponential equation.

Table S1.

List of τ values (sec) estimated by stretch exponential at given temperature.

	$CoCl_2$(**C2py**)$_4$	$CoCl_2$(**C3lpy**)$_4$	$CoCl_2$(**C3bpy**)$_4$	$CoCl_2$(**C4py**)$_4$
1.9 K	$> 5 \times 10^5$	$> 5 \times 10^5$	–	$> 5 \times 10^5$
2.0 K	$> 5 \times 10^5$	$> 5 \times 10^5$	$> 5 \times 10^5$	$> 5 \times 10^5$
2.1 K	3.9×10^5	$> 5 \times 10^5$	–	$> 5 \times 10^5$
2.2 K	1.9×10^5	3.8×10^5	$> 5 \times 10^5$	$> 5 \times 10^5$
2.4 K	8.0×10^4	8.9×10^4	$> 5 \times 10^5$	4.7×10^5
2.6 K	5.7×10^4	2.5×10^4	1.2×10^5	6.0×10^4
2.8 K	1.2×10^4	6.0×10^3	1.4×10^4	8.9×10^3
3.0 K	2.7×10^3	1.6×10^3	2.3×10^3	1.6×10^3
3.25 K	–	4.6×10^2	3.3×10^2	–

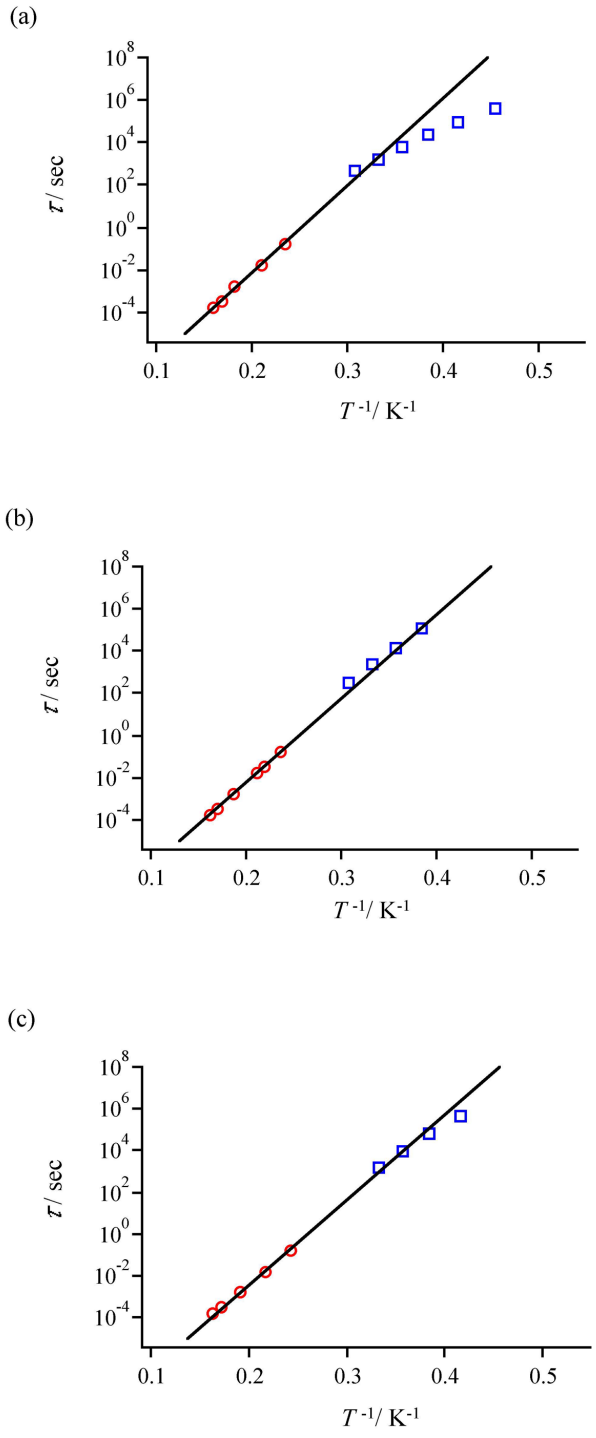


Figure S7. τ vs T^{1} pots of the data collected by ac magnetic susceptibility technique (red circle) and dc magnetization decay (blue square) after irradiation of 1:4 mixture of $CoCl_2$ and **CYpy**; **Y** = **3l** (a), **3b** (b), and **4** (c) in MTHF frozen solution. The solid lines are the least-squares fits of the ac data according to the Arrhenius equation.