Supporting Information

Asymmetric tetranuclear nickel chains with unidirectionally ordered 2-(α-(5-phenyl)pyridylamino)-1,8-naphthyridine ligands

Lien-Hung Tsou,[a] Marc Sigrist,[b] Ming-Hsi Chiang,[b] Er-Chien Horng,[a] Chun-hsien Chen,[a] Shou-Ling Huang,[a] Gene-Hsiang Lee[a] and Shie-Ming Peng[a,b,*]

[a]Department of Chemistry, National Taiwan University, No. 1, Sec. 4, Roosevelt Rd., Taipei, Taiwan (R.O.C.).

[b]Institute of Chemistry, Academia Sinica, 128 Academia Road, Section 2, Nankang, Taipei, Taiwan (R.O.C.).

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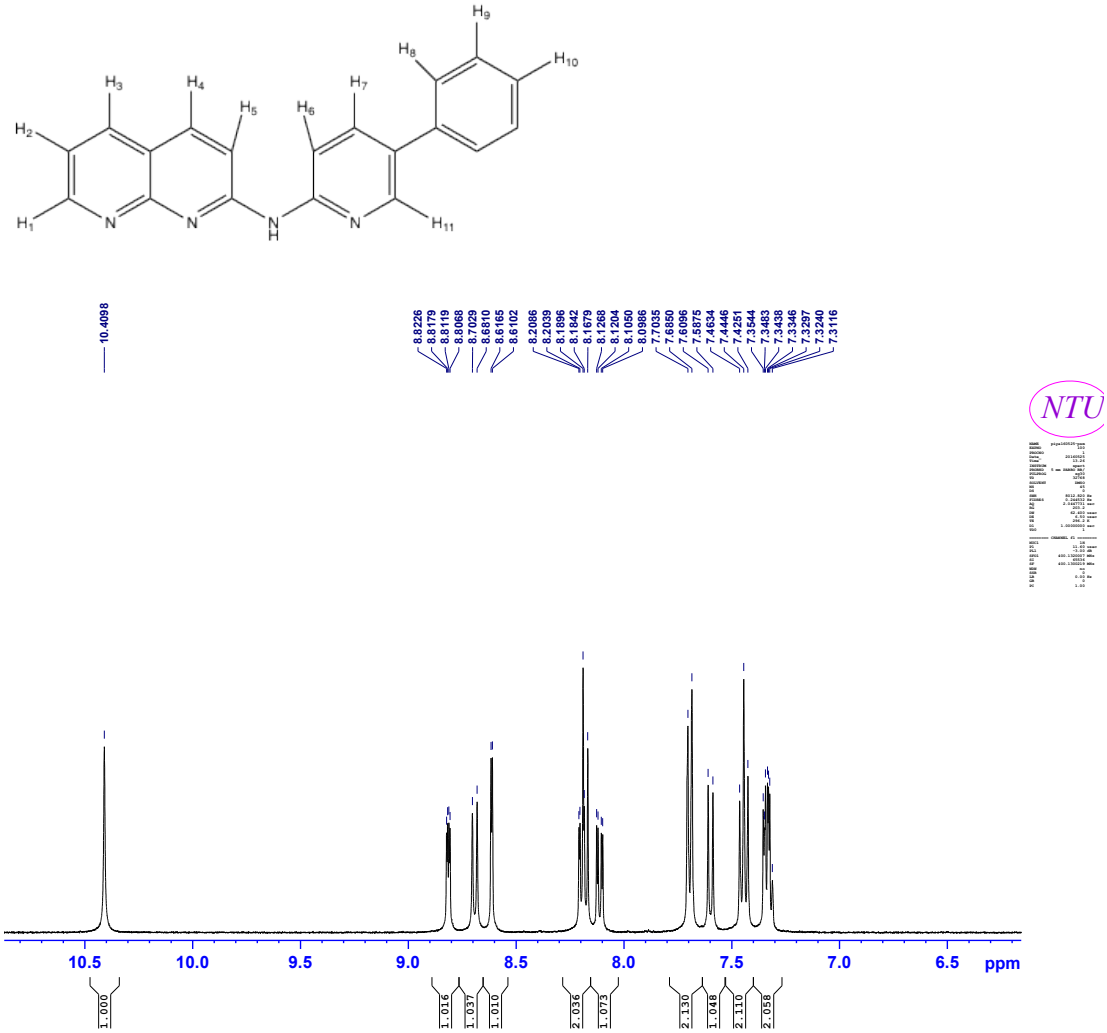

Fig. S1 ^{1}H NMR spectrum of Hphpyany in d_6-DMSO at 400 MHz. δ= 10.41(NH), 8.81(H_1), 8.69(H_7), 8.61(H_{11}), 8.20(H_3), 8.18(H_4), 8.11(H_6), 7.69(2H, H_8), 7.59(H_5), 7.44(2H, H_9), 7.34(H_{10}), 7.32(H_2).

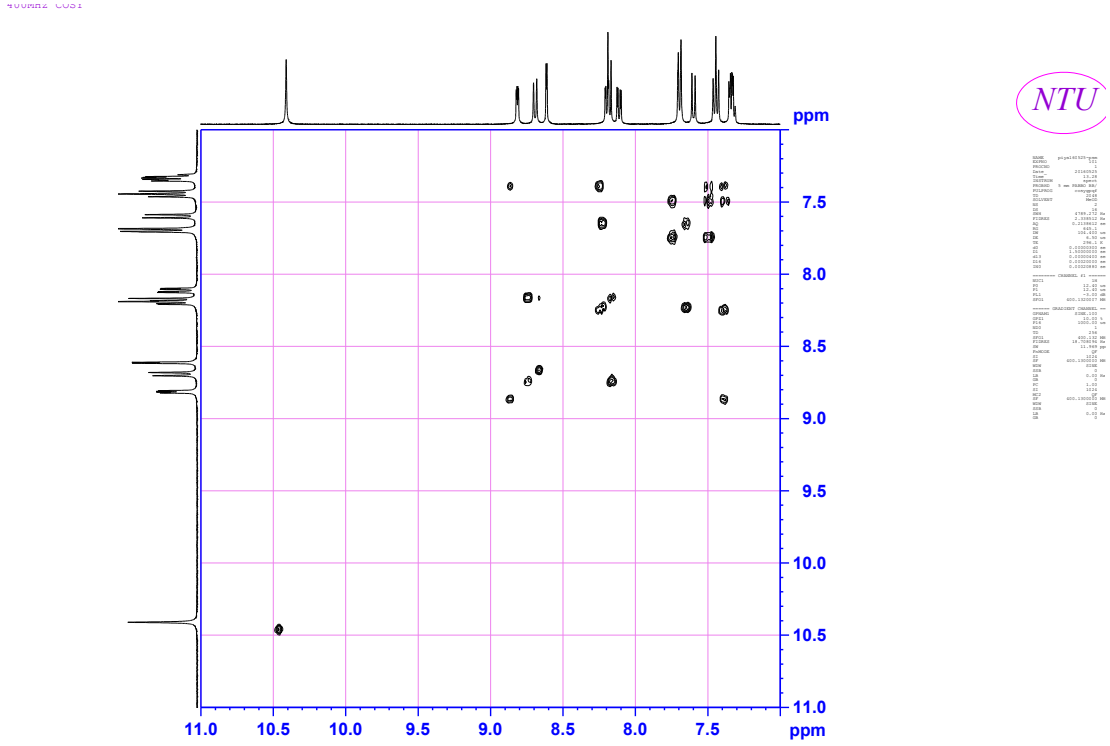

Fig. S2 ^{1}H 2D-COSY spectrum of Hphpyany in D_6-DMSO at 400 MHz.

Table S1 X-ray crystallographic data for **1**-**4**.

Compound	**1**·4CH_2Cl_2	**2**·5$C_2H_4Cl_2$	**3**·3$C_2H_4Cl_2$·0.5CH_2Cl_2	**4**·8$CHCl_3$·1H_2O
Formula	$C_{81}H_{60}Cl_{10}F_3N_{16}Ni_4O_3S$	$C_{86}H_{73}B_2Cl_{12}F_8N_{16}Ni_4$	$C_{84.5}H_{65}Cl_8N_{18}Ni_4O_4S_2$	$C_{88}H_{62}Cl_{24}F_6N_{18}Ni_4O_7S_4$
Formula weight	1983.85	2164.46	1979.10	2811.44
T/K	150(2)	293(2)	150(2)	150(2)
Crystal system	Triclinic	Monoclinic	Monoclinic	Monoclinic
Space group	P-1	P 2_1/n	P 2_1/n	P 2_1/n
a/Å	14.6069(5)	14.6577(9)	14.7684(6)	14.4138(4)
b/Å	17.1511(5)	35.883(2)	21.7310(10)	37.0360(11)
c/Å	17.8766(4)	17.1139(10)	26.4842(11)	21.1405(4)
α (°)	76.392(2)	90	90	90
β (°)	86.344(2)	91.750(2)	99.361(2)	95.6332(16)
γ (°)	69.1391(14)	90	90	90
V/$Å^3$, Z	4066.5(2), 2	8997.1(9), 4	8386.4(6), 4	11230.9(5), 4
Dc/Mg m^{-3}	1.620	1.598	1.567	1.663
Absorption coefficient/mm^{-1}	1.334	1.253	1.253	1.375
Crystal size/mm	0.30 × 0.13 × 0.05	0.40 × 0.10 × 0.10	0.50 × 0.06 × 0.05	0.38 × 0.20 × 0.06
θ range for data collection/°	1.30 - 25.00	1.13 - 25.00	1.22 - 25.00	1.10 - 25.00
Reflection collected	54086	36814	36558	45601
Independent reflections	14281 (R_{int} = 0.0768)	15675 (R_{int} = 0.0823)	14696 (R_{int} = 0.0953)	19695 (R_{int} = 0.0741)
R_1, wR_2 [$I > 2\sigma(I)$]	0.0969, 0.2648	0.1185, 0.2984	0.0791, 0.2038	0.0806, 0.2016
R_1, wR_2 (all data)	0.1874, 0.3369	0.2264, 0.3467	0.1672, 0.2496	0.1762, 0.2595
GOF	1.019	1.410	1.035	1.038

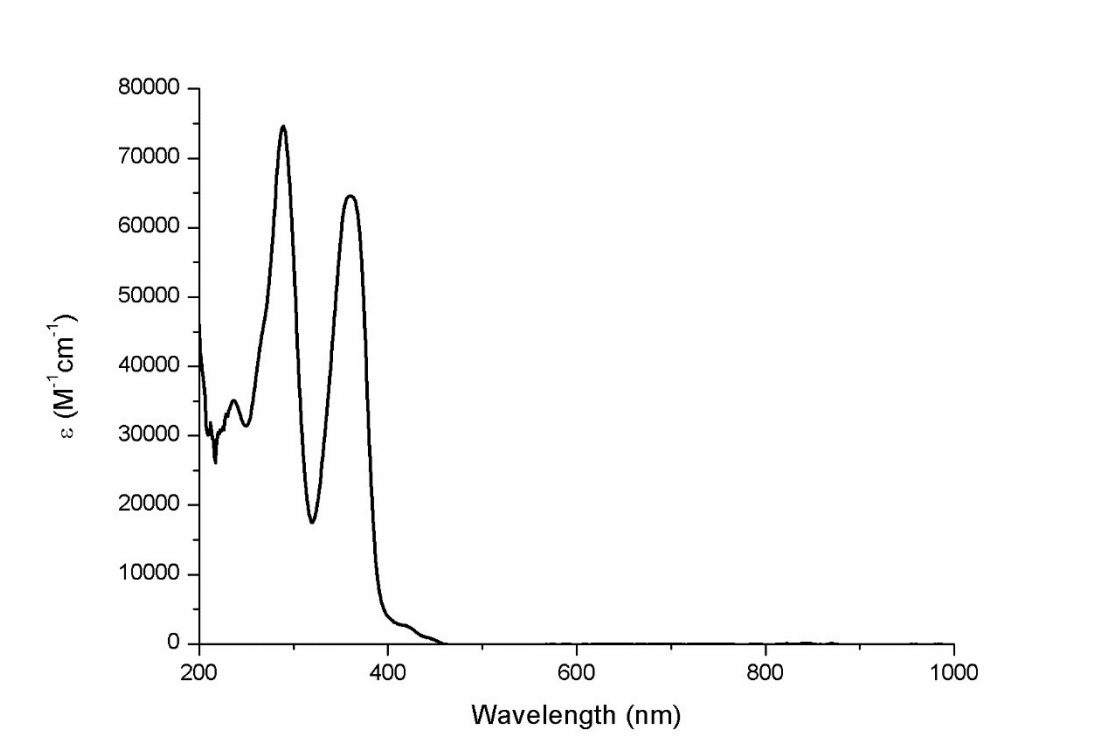

Fig. S3 Absorption spectrum of ligand in CH_2Cl_2 (1×10^{-5} M).

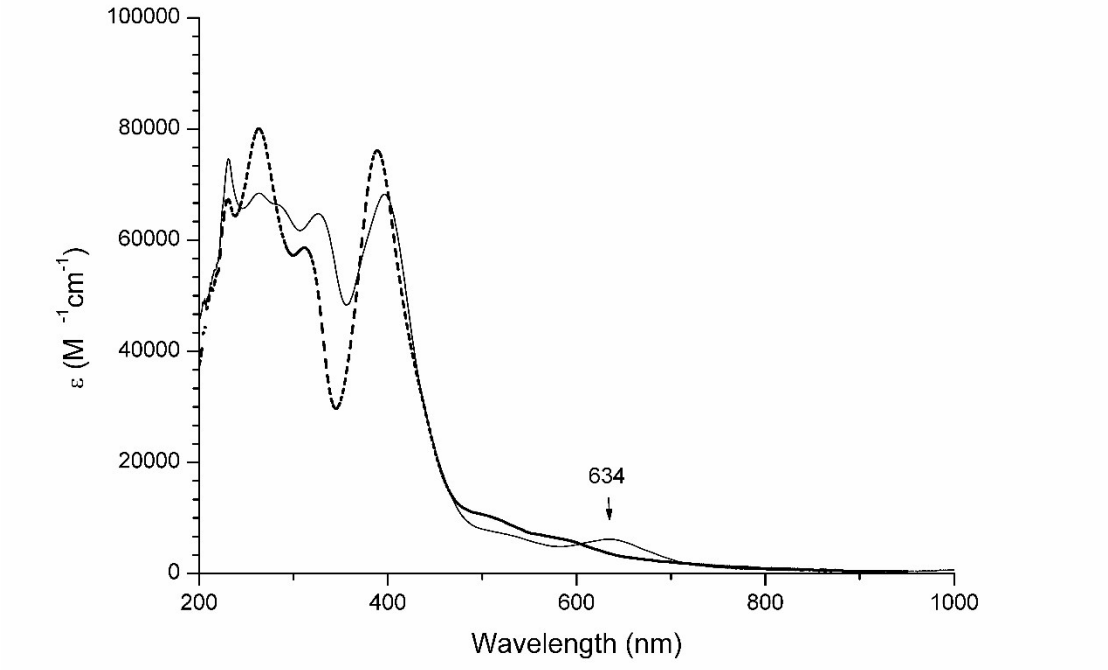

Fig. S4 Absorption spectrum of **1** (solid line) and **2** (dashed line) in CH_2Cl_2 (1×10^{-5} M).

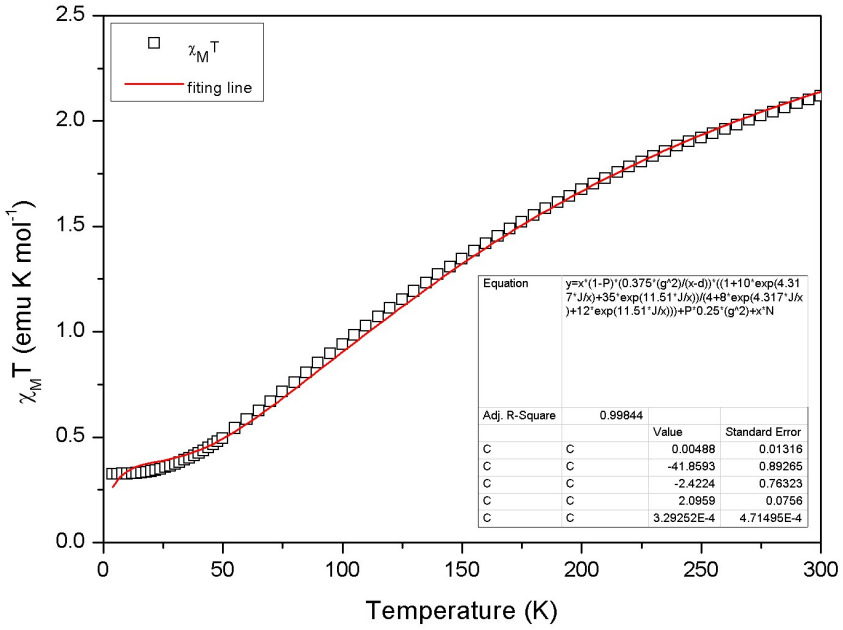

Fig. S5 Plot of $\chi_M T$ vs. T with fitting line for **1**.

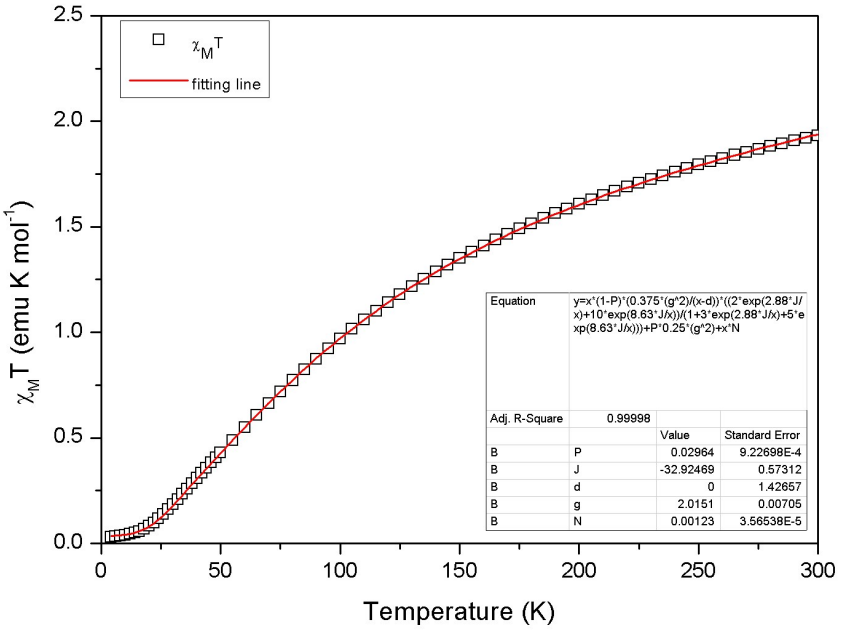

Fig. S6 Plot of $\chi_M T$ vs. T with fitting line for **2**.

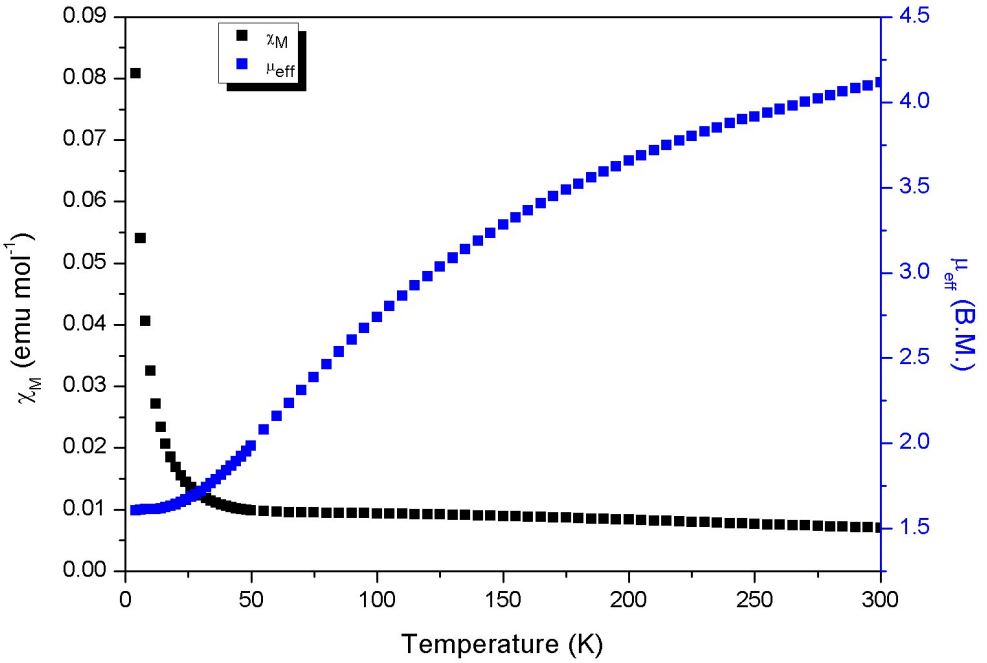

Fig. S7 Plot of χ_M vs. T and μ_{eff} vs. T for **1**.

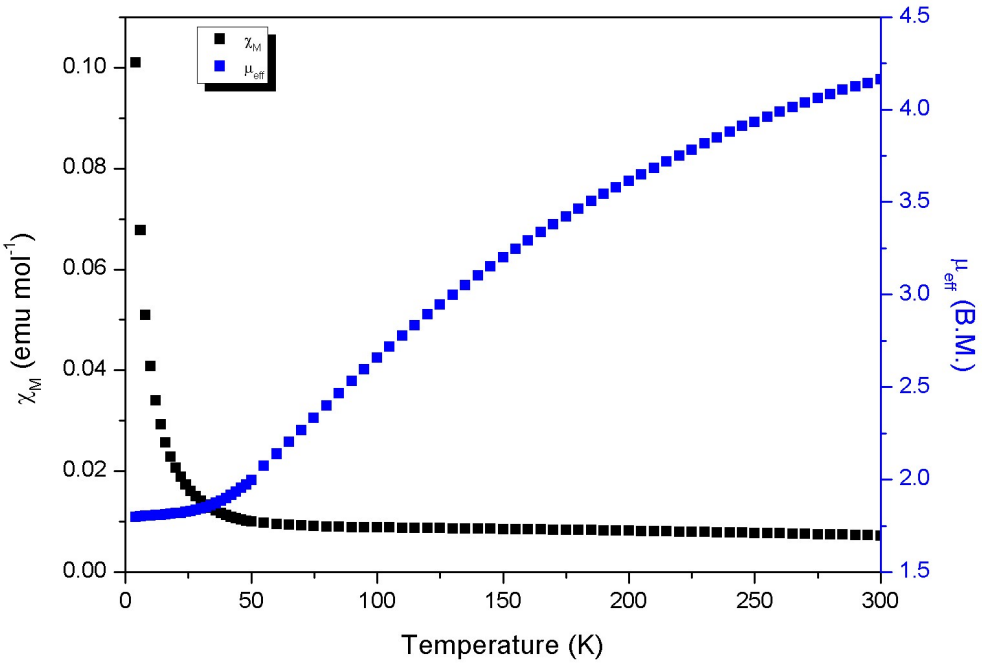

Fig. S8 Plot of χ_M vs. T and μ_{eff} vs. T for **3**.

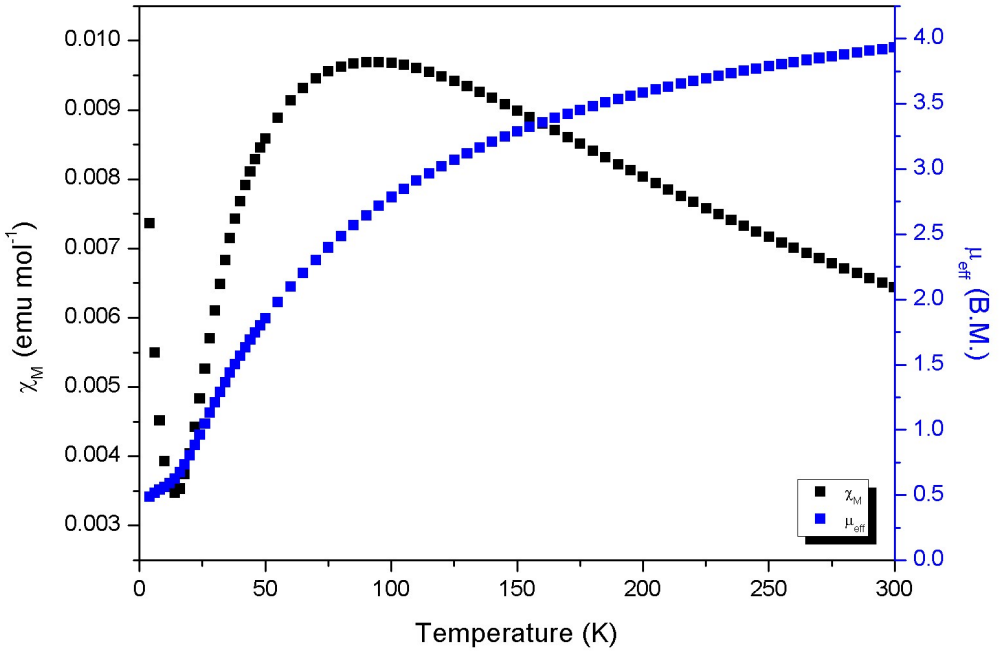

Fig. S9 Plot of χ_M vs. T and μ_{eff} vs. T for **2**.

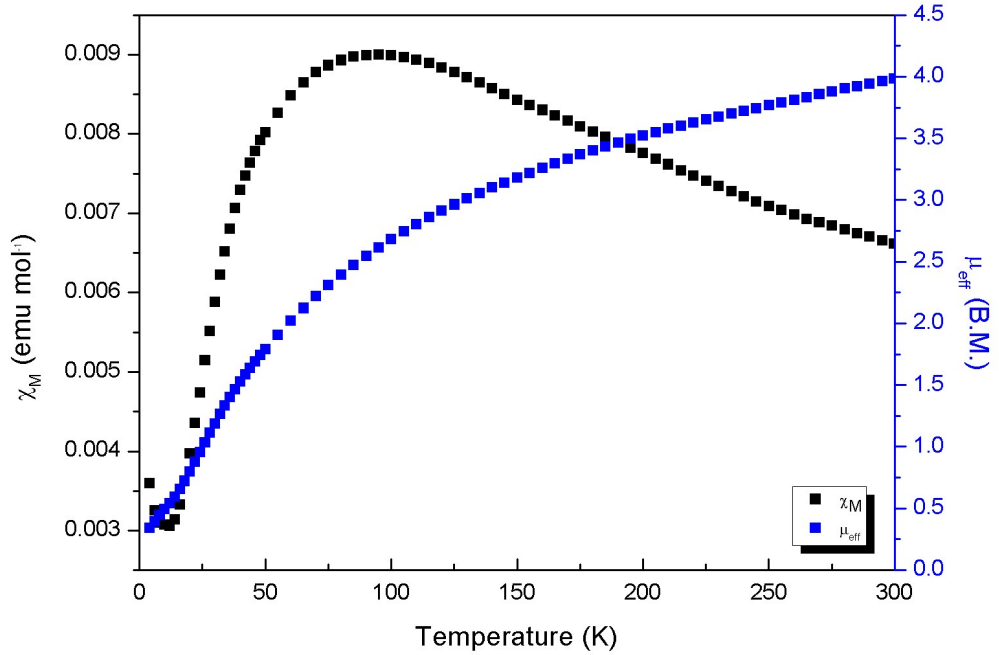

Fig. S10 Plot of χ_M vs. T and μ_{eff} vs. T for **4**.

The ^{1}H NMR spectrum of **2** is not presented here as impurities complicated the analysis. We assume that the NMR samples contained a small trace of a different isomer that was not eliminated during the recrystallization. ^{1}H NMR spectra of **3** (top) and **4** (bottom) in CD_2Cl_2. For Fig. S11-S13, the peaks are greatly broadened in the lower downfield region rendering the exact integration of the signals impossible and leading to small integrals. The Integration of neighboring peaks in the downfield region with similar half-width, however yielded comparable values supporting the assumption that each of these highly shifted peaks represents one single hydrogen atom (see Table S2).

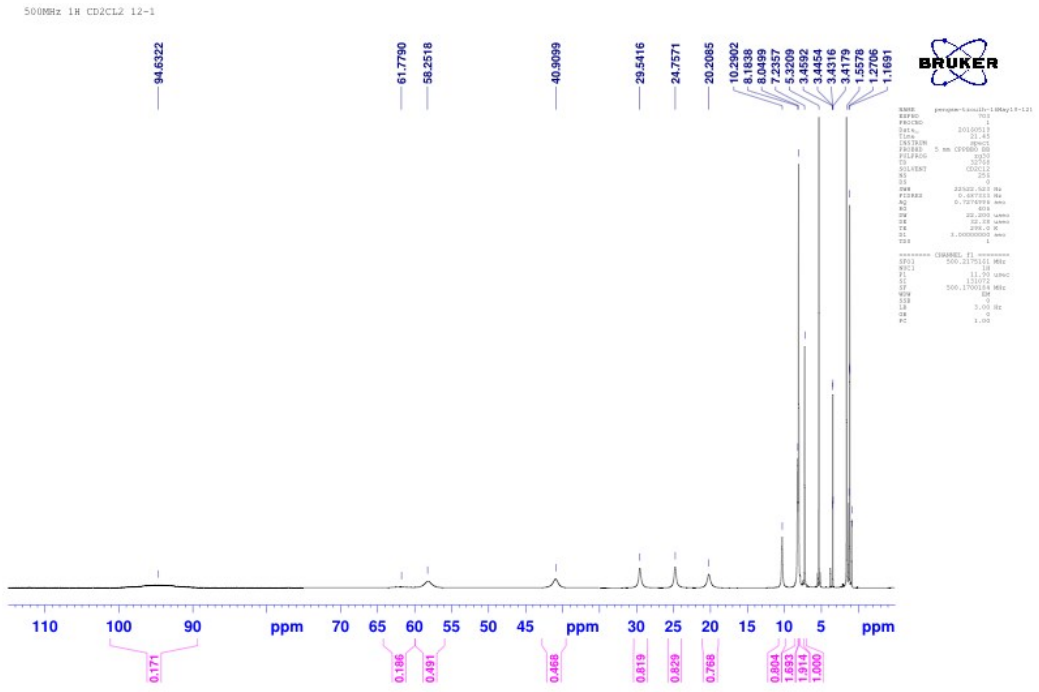

Fig. S11 ^{1}H NMR spectrum of **1** in CD_2Cl_2.

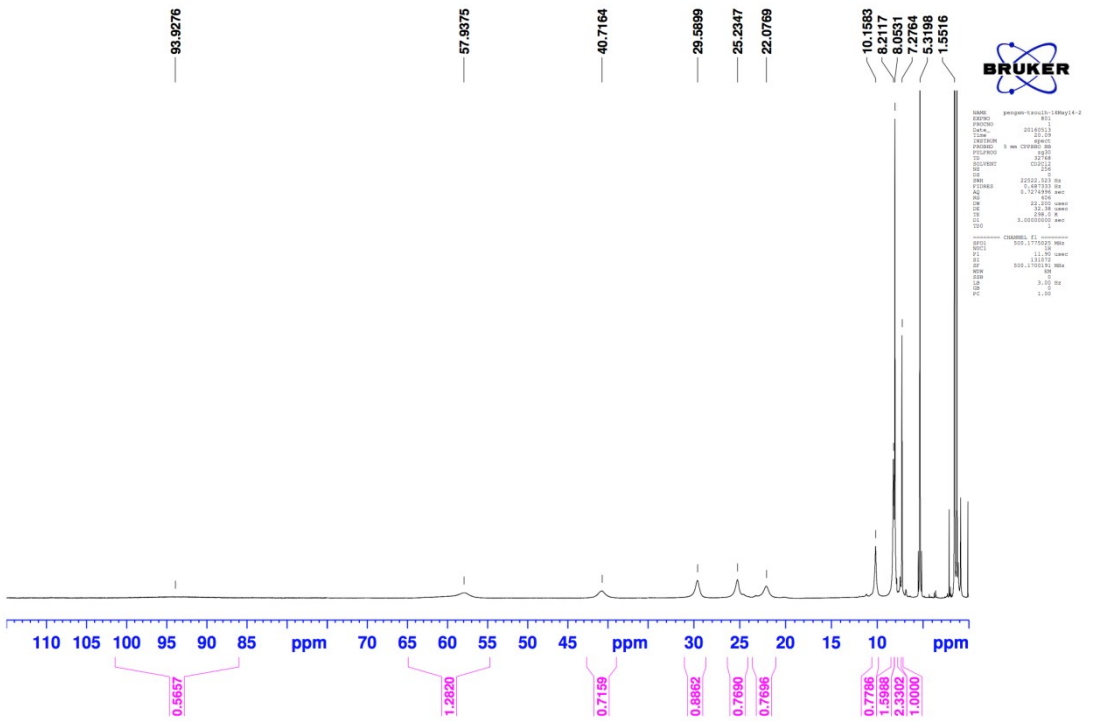

Fig. S12 ^{1}H NMR spectrum of **3** in CD_2Cl_2.

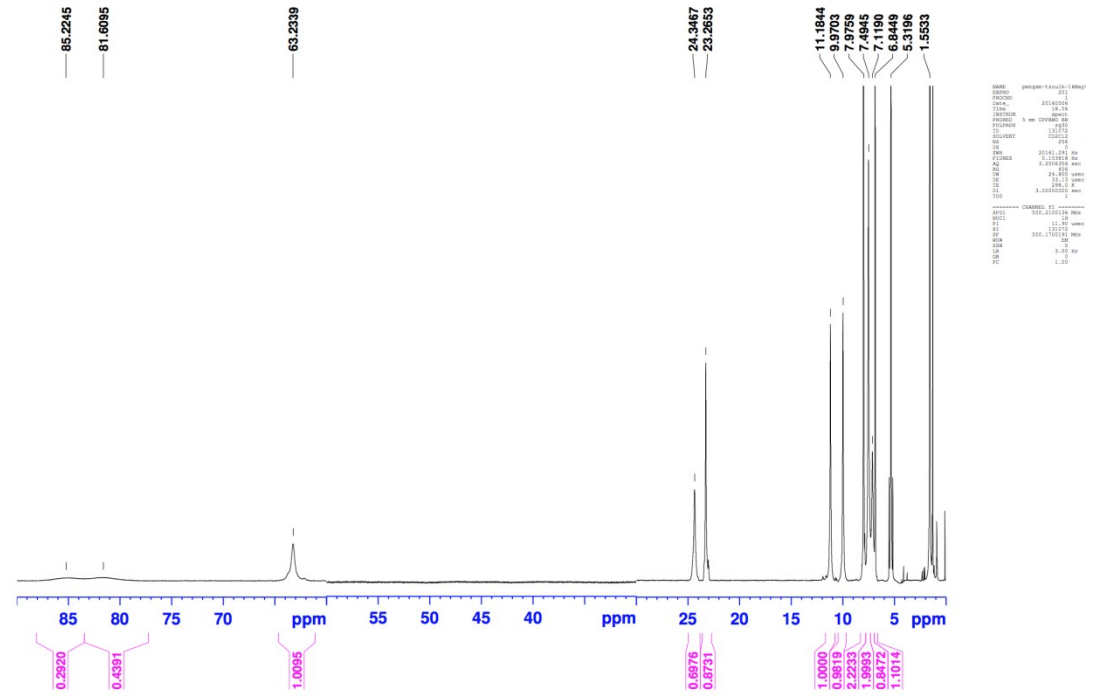

Fig. S13 ^{1}H NMR spectrum of **4** in CD_2Cl_2.

Table S2 ^{1}H NMR spectra peaks for **1**, **3** and **4**.

compound 1

	ppm	peakw(Hz)	integral	
1	7.2357	17.351	1.0000	1
2	8.0499	20.218	1.9136	2
3	8.1838	72.631	1.6930	2
4	10.2903	69.937	0.8043	1
5	20.2085	244.853	0.7678	1
6	24.7571	163.537	0.8289	1
7	29.5416	173.383	0.8190	1
8	40.9099	362.802	0.4676	1
9	58.2518	534.510	0.4910	1
10	61.779	1747.885	0.1864	1
11	94.6322	2917.147	0.1711	1
total				13

compound 3

	ppm	peakw(Hz)	integral	
1	7.2764	19.306	1.0000	1
2	8.0531	20.930	2.3302	2
3	8.2117	70.390	1.5988	2
4	10.1583	88.860	0.7786	1
5	22.0769	312.715	0.7696	1
6	25.2347	225.027	0.7690	1
7	29.5899	247.414	0.8862	1
8	40.7164	512.771	0.7159	1
9	57.9375	863.779	1.2820	2
10	93.9276	3431.000	0.5657	1
total				13

compound 4

	ppm	peakw(Hz)	integral	
1	6.8449	18.129	1.1014	1
2	7.1119	76.064	0.8472	1
3	7.4945	52.086	1.9993	2
4	7.9759	19.179	2.2230	2
5	9.9703	36.451	0.9818	1
6	11.1844	38.713	1.0000	1
7	23.2653	38.749	0.8731	1
8	24.3467	85.041	0.6976	1
9	63.2339	187.267	0.6762	1
10	81.6095	1581.024	0.2941	1
11	85.2245	1536.032	0.1956	1
total				13