Supplementary Materials: Reduction of 2,2’-Bipyridine by Quasi-Linear 3d-Metal(I) Silylamides—A Structural and Spectroscopic Study

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1. NMR Spectra



**Figure S1**. 1H NMR spectrum of [K{18c6}][Cr(N(SiMe3)2)2(bipy)] (**1**) in THF-d8 (500.1 MHz).



**Figure S2.** 1H NMR spectrum of [K{18c6}][Mn(N(SiMe3)2)2(bipy)](**2**) in THF-d8 (500.1 MHz).



**Figure S3.** 1H NMR spectrum of [K{18c6}][Fe(N(SiMe3)2)2(bipy)](**3**) in THF-d8 (500.1 MHz).



**Figure S4.** 1H NMR spectrum of [K{18c6}][Co(N(SiMe3)2)2(bipy)] (**4**) in THF-d8 (500.1 MHz).



**Figure S5.** 1H NMR spectrum of [Cr(N(SiMe3)2)2(bipy)](**5**) in THF-d8 (500.1 MHz).



**Figure S6.** 1H NMR spectrum of [Mn(N(SiMe3)2)2(bipy)](**6**) in THF-d8 (500.1 MHz).



**Figure S7.** 1H NMR spectrum of [Fe(N(SiMe3)2)2(bipy)](**7**) in THF-d8 (500.1 MHz).



**Figure S8.** 1H NMR spectrum of [Co(N(SiMe3)2)2(bipy)](**8**) in THF-d8 (500.1 MHz).

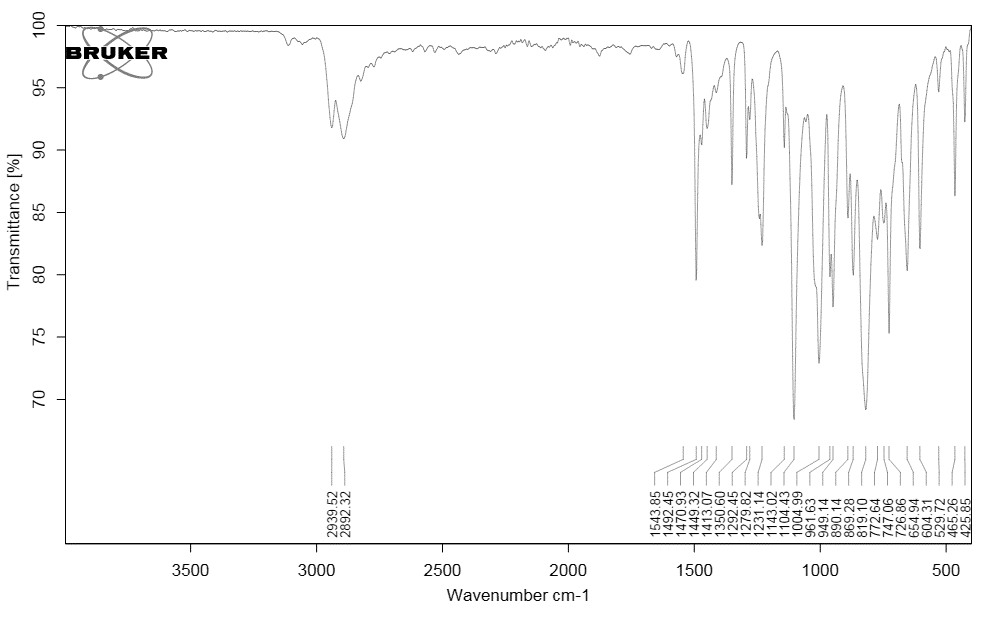


**Figure S9.** 1H NMR spectrum of [Zn(N(SiMe3)2)2(bipy)](**9**) in THF-d8 (500.1 MHz).

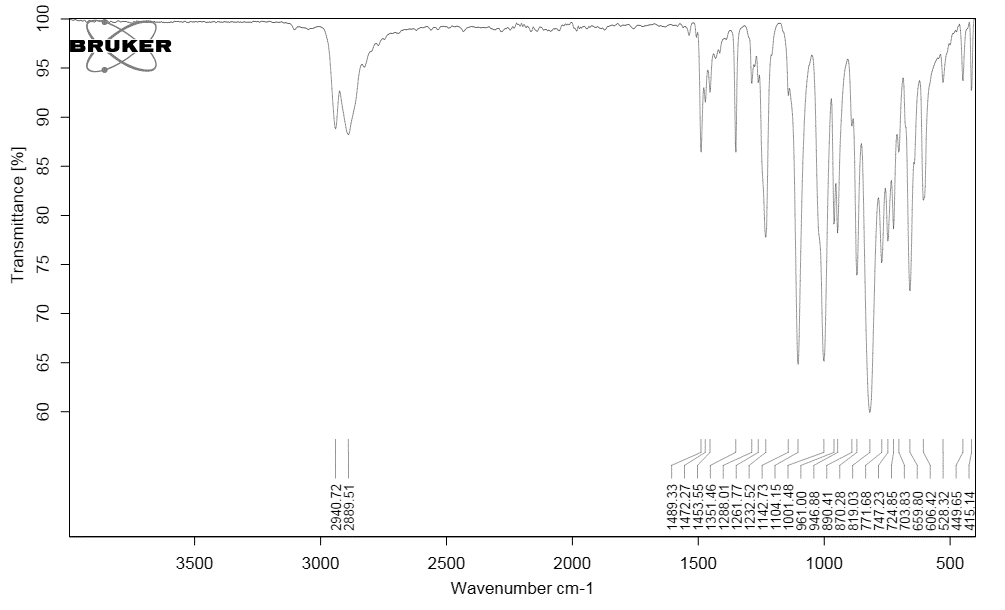


**Figure S10.** 1H NMR spectrum of [K{18c6}][Zn(N(SiMe3)2)2(BiPy)] (**10**) in THF-d8 (500.1 MHz).

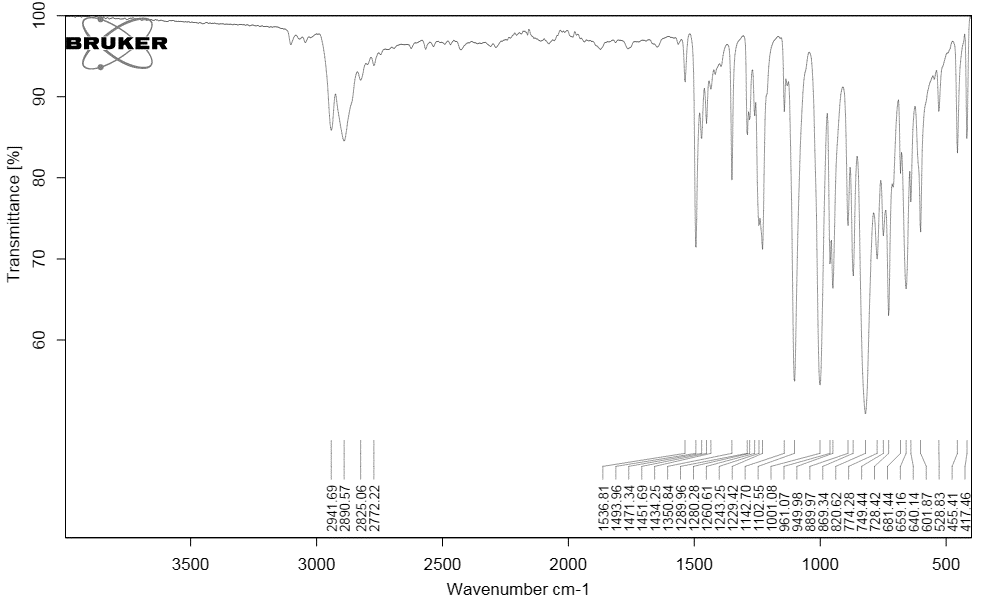
2. IR Spectra



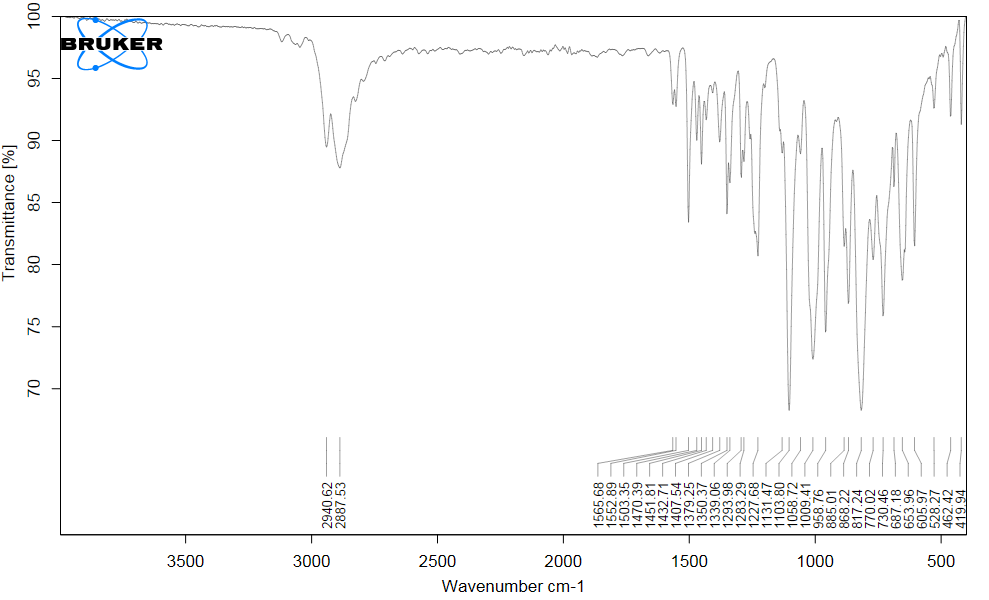
**Figure S11.** IR spectrum of [K{18c6}][Cr(N(SiMe3)2)2(bipy)] (**1**).



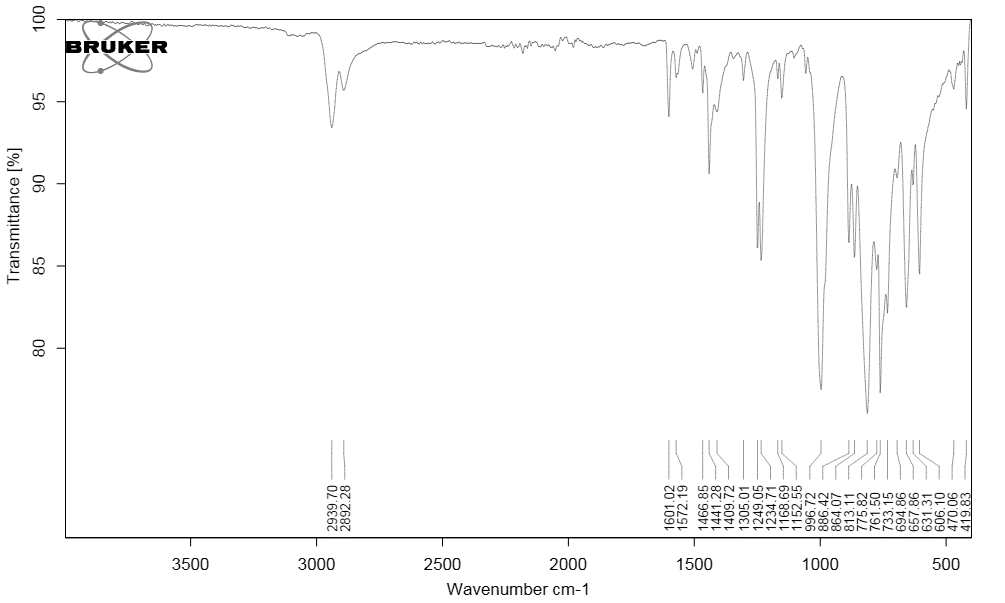
**Figure S12.** IR spectrum of [K{18c6}][Mn(N(SiMe3)2)2(bipy)] (**2**).



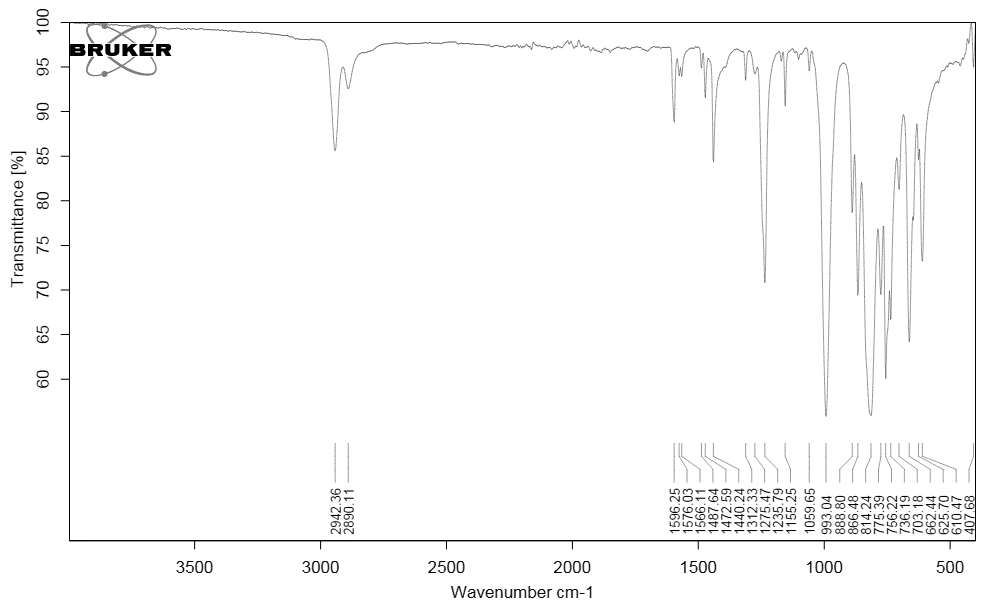
**Figure S13.** IR spectrum of [K{18c6}][Fe(N(SiMe3)2)2(bipy)] (**3**).



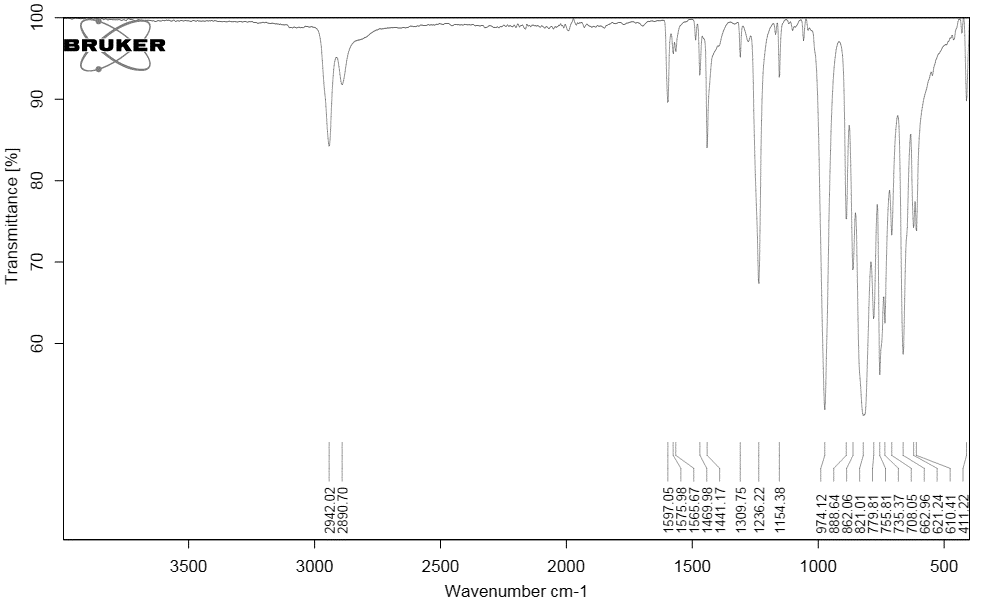
**Figure S14.** IR spectrum of [K{18c6}][Co(N(SiMe3)2)2(bipy)] (**4**).



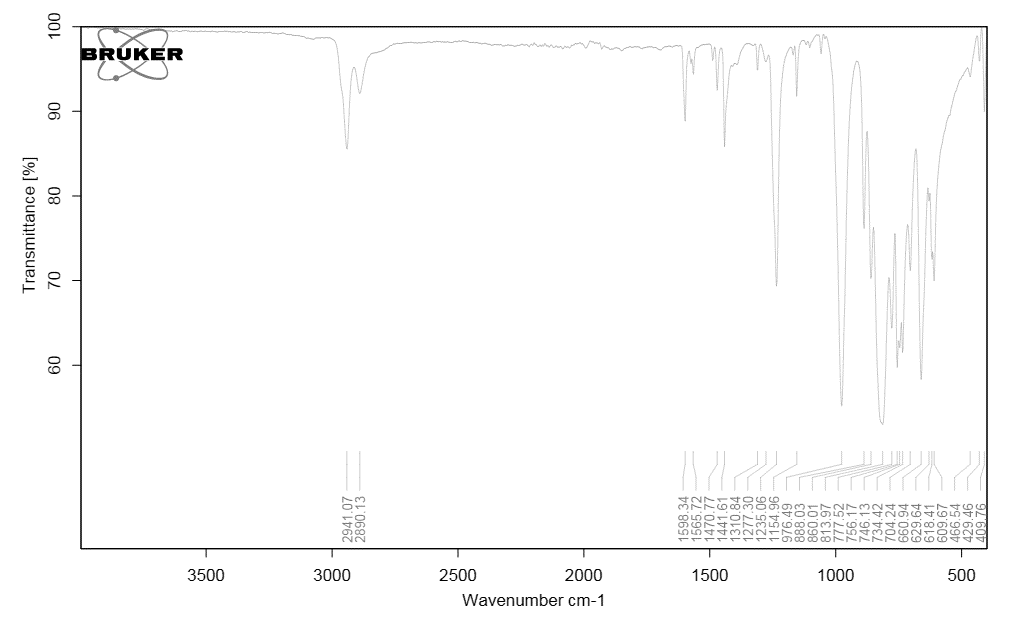
**Figure S15.** IR spectrum of [Cr(N(SiMe3)2)2(bipy)] (**5**).



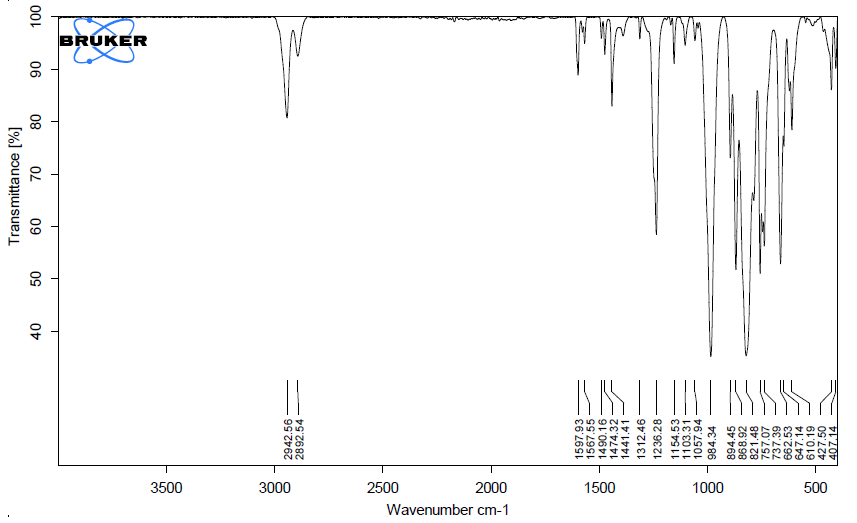
**Figure S16.** IR spectrum of [Mn(N(SiMe3)2)2(bipy)] (**6**).



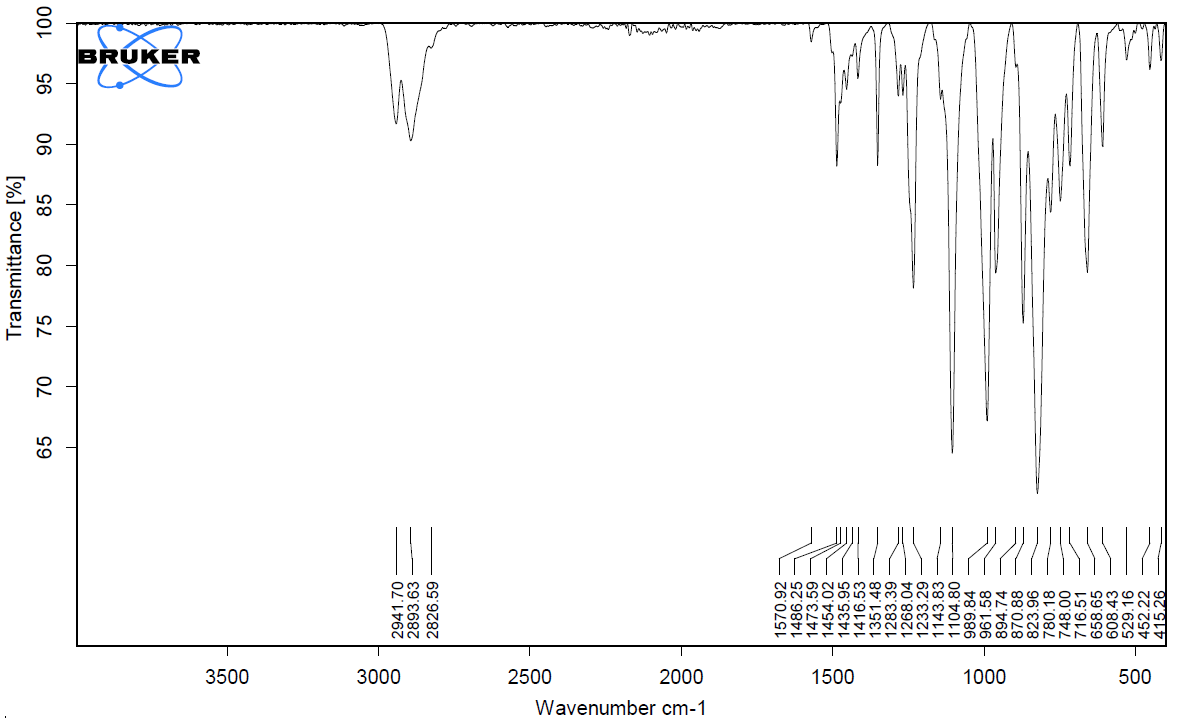
**Figure S17.** IR spectrum of [Fe(N(SiMe3)2)2(bipy)] (**7**).



**Figure S18.** IR spectrum of [Co(N(SiMe3)2)2(bipy)] (**8**).



**Figure S19.** IR spectrum of [Zn(N(SiMe3)2)2(bipy)] (**9**).



**Figure S20.** IR spectrum of [K{18c6}][Zn(N(SiMe3)2)2(bipy)] (**10**).

3. UV/Vis Spectra

**Figure S21.** UV/Vis spectrum of [K{18c6}][Cr(N(SiMe3)2)2(bipy)] (**1**) in Et2O.

**Figure S22.** UV/Vis spectrum of [K{18c6}][Mn(N(SiMe3)2)2(bipy)] (**2**) in Et2O.

**Figure S23.** UV/Vis spectrum of [K{18c6}][Fe(N(SiMe3)2)2(bipy)] (**3**) in Et2O.

**Figure S24.** UV/Vis spectrum of [K{18c6}][Co(N(SiMe3)2)2(bipy)] (**4**) in Et2O.

**Figure S25.** UV/Vis spectrum of [Cr(N(SiMe3)2)2(bipy)] (**5**) in Et2O.

**Figure S26.** UV/Vis spectrum of [Mn(N(SiMe3)2)2(bipy)] (**6**) in Et2O.

**Figure S27**. UV/Vis spectrum of [Fe(N(SiMe3)2)2(bipy)] (**7**) in Et2O.

**Figure S28.** UV/Vis spectrum of [Co(N(SiMe3)2)2(bipy)] (**8**) in Et2O.

**Figure S29.** UV/Vis spectrum of [Zn(N(SiMe3)2)2(bipy)] (**9**) in Et2O.

**Figure S30.** UV/Vis spectrum of [K{18c6}][Zn(N(SiMe3)2)2(bipy)] (**10**) in Et2O.

**Figure S31.** UV/Vis spectrum of [K{18c6}][(bipy)]in Et2O. [K{18c6}][(bipy)]was obtained in-situ from a reaction of 2,2´-bipyridine with KC8 in the presence of 18-crown-6 in Et2O.

**Figure S32.** Time-dependent UV/Vis spectra of in-situ synthesized [K{18c6}][(bipy)]in Et2O.

**Figure S33.** Overlay of UV/Vis spectra of [K{18c6}][Cr(N(SiMe3)2)2(bipy)] (**1**) and [Cr(N(SiMe3)2)2(bipy)] (**5**) in Et2O.

**Figure S34.** Overlay of UV/Vis spectra of [K{18c6}][Mn(N(SiMe3)2)2(bipy)] (**2**) and [Mn(N(SiMe3)2)2(bipy)] (6) in Et2O.

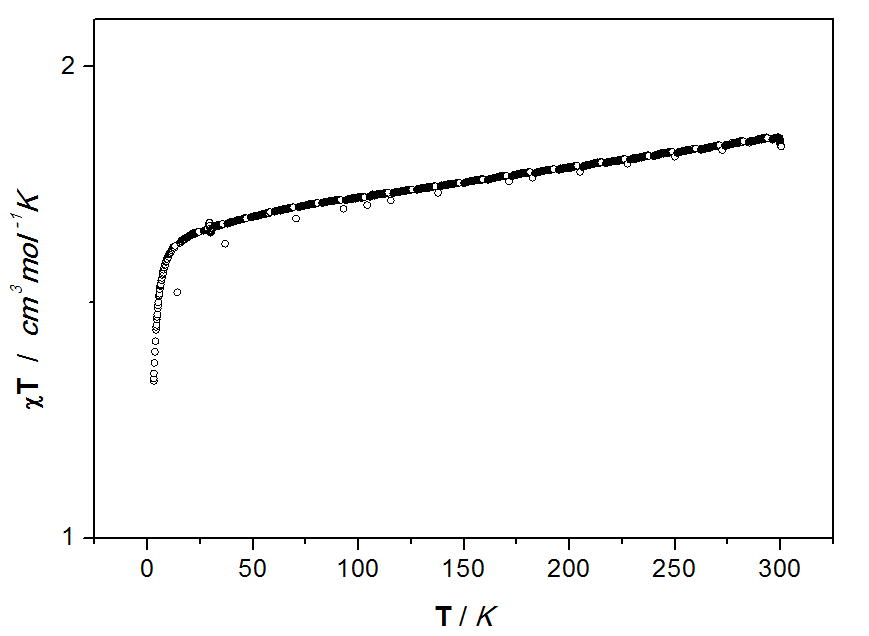
**Figure S35.** Overlay of UV/Vis spectra of [K{18c6}][Fe(N(SiMe3)2)2(bipy)] (**3**) and [Fe(N(SiMe3)2)2(bipy)](**7**) in Et2O.

**Figure S36.** Overlay of UV/Vis spectra of [K{18c6}][Co(N(SiMe3)2)2(bipy)] (**4**) [Co(N(SiMe3)2)2(bipy)] (**8**) in Et2O.

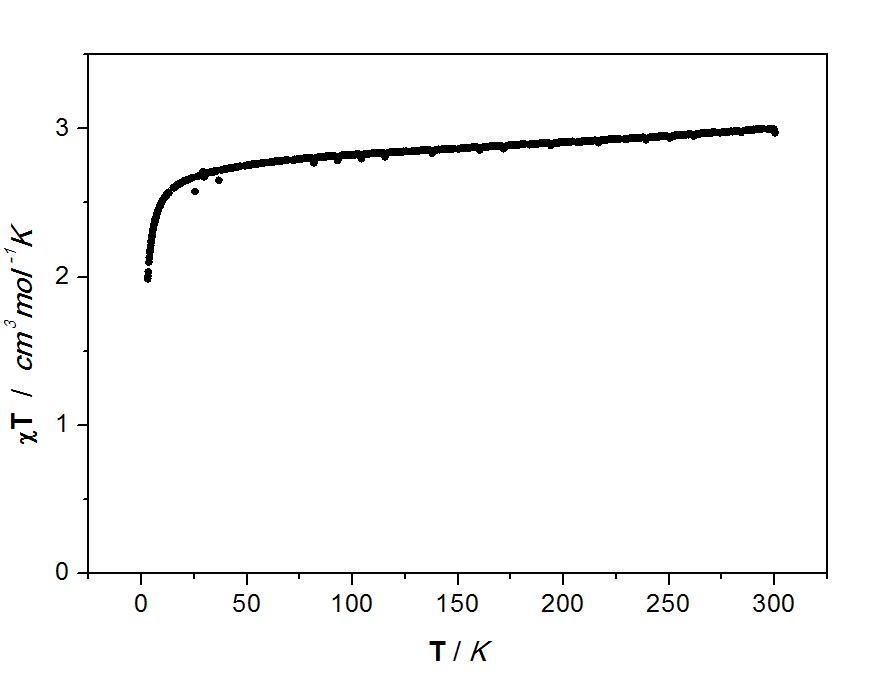
**Figure S37.** Overlay of UV/Vis spectra of [Zn(N(SiMe3)2)2(bipy)] (**9**) and [K{18c6}][Zn(N(SiMe3)2)2(bipy)] (**10**) in Et2O.

4. Magnetic Data

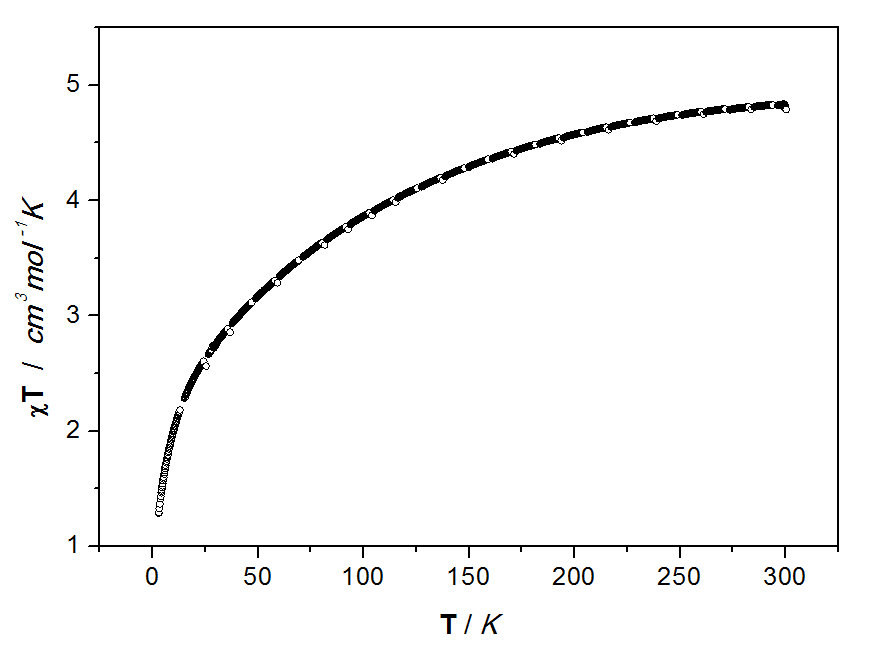
Magnetic data of compounds **1**–**4** and **10** were recorded on dried crystalline samples and were corrected for diamagnetic contributions from the sample holder and the diamagnetic susceptibility of the respective compound using Pascal constants. Obtained paramagnetic susceptibility *χ*para was fit using the Curie-Weiss-law (*n*eff = effective magnetic moment in Bohr’s magnetons per formula unit, *Θ* = Weiss temperature) with contributions from a temperature independent paramagnetism *χ*TIP using the overall equation *χ*paraT = (*χ*TIP + *χ*CW)T.



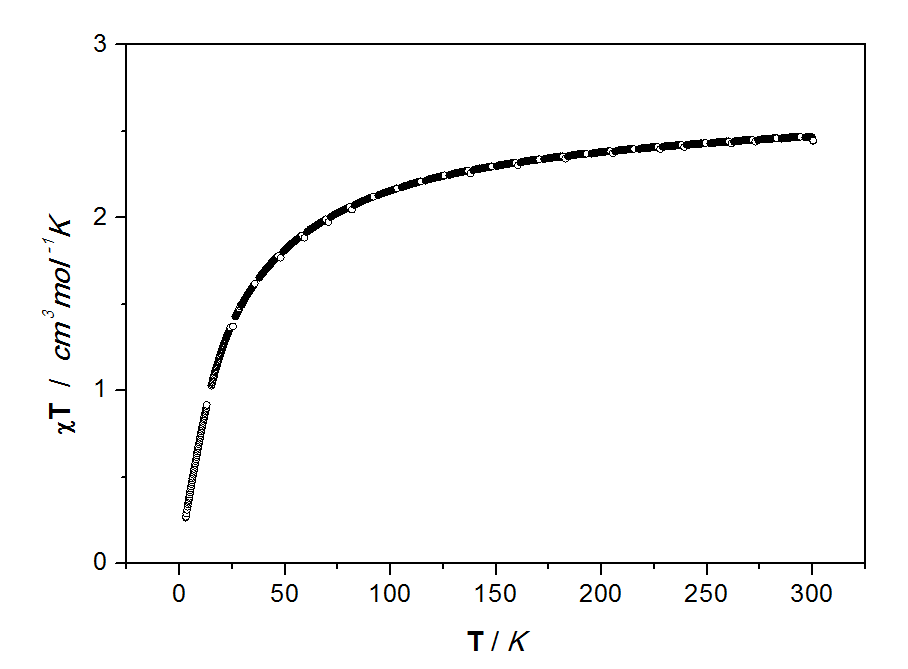
**Figure S38.** Temperature dependence of the molar magnetic susceptibility times temperature product (χT vs. T) for compound K{18c6}][Cr(N(SiMe3)2)2(bipy)](**1**). Data were collected under an applied dc field of 1 T in a temperature range of 3 to 300 K.



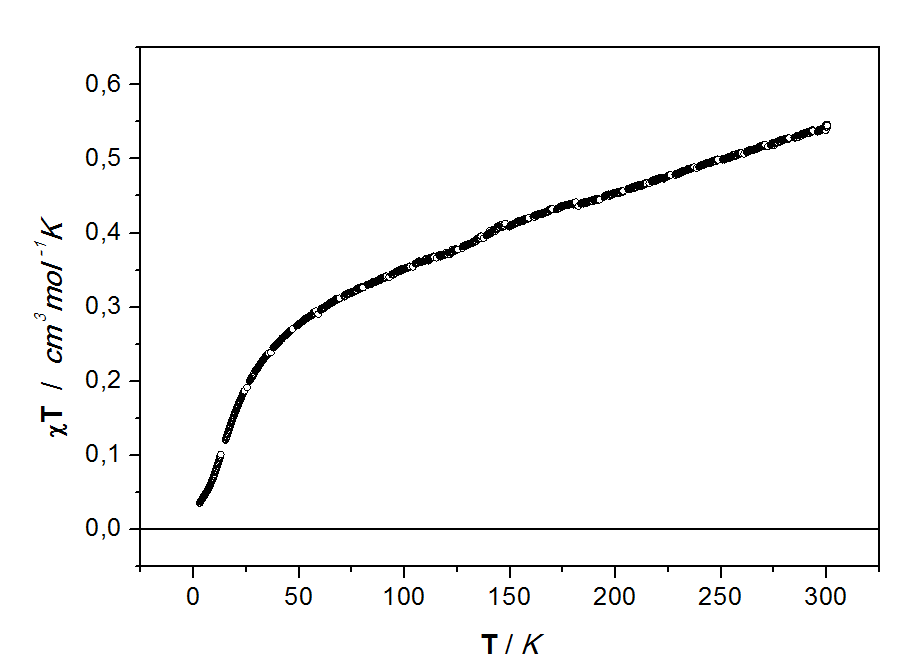
**Figure S39.** Temperature dependence of the molar magnetic susceptibility times temperature product (χT vs. T) for compound K{18c6}][Mn(N(SiMe3)2)2(bipy)](**2**). Data was collected under an applied dc field of 1 T in a temperature range of 3 to 300 K.



**Figure S40.** Temperature dependence of the molar magnetic susceptibility times temperature product (χT vs. T) for compound K{18c6}][Fe(N(SiMe3)2)2(bipy)] (**3**). Data was collected under an applied dc field of 1 T in a temperature range of 3 to 300 K.



**Figure S41.** Temperature dependence of the molar magnetic susceptibility times temperature product (χT vs. T) for compound K{18c6}][Co(N(SiMe3)2)2(bipy)] (**4**). Data was collected under an applied dc field of 1 T in a temperature range of 3 to 300 K.



**Figure S42.** Temperature dependence of the molar magnetic susceptibility times temperature product (χT vs. T) for compound K{18c6}][Zn(N(SiMe3)2)2(bipy)](**10**). Data was collected under an applied dc field of 1 T in a temperature range of 3 to 300 K.

5. Cyclic Voltammetry

**Figure S33**. Cyclic voltammogram for complex **1** in THF (1 mM, 500 mV/s, 0.1 M [NBu4][PF6]).

**Figure S44.** Cyclic voltammogram for complex **2** in THF (1 mM, 500 mV/s, 0.1 M [NBu4][PF6]).

**Figure S44.** Cyclic voltammogram for complex **3** in THF (1 mM, 500 mV/s, 0.1 M [NBu4][PF6]).

**Figure S46.** Cyclic voltammogram for complex **4** in THF (1 mM, 500 mV/s, 0.1 M [NBu4][PF6]).

**Figure S47.** Cyclic voltammogram for complex **5** in THF (1 mM, 500 mV/s, 0.1 M [NBu4][PF6]).

**Figure S48.** Cyclic voltammogram for complex **6** in THF (1 mM, 500 mV/s, 0.1 M [NBu4][PF6]).

**Figure S49.** Cyclic voltammogram for complex **7** in THF (1 mM, 500 mV/s, 0.1 M [NBu4][PF6]).

**Figure S50.** Cyclic voltammogram for complex **8** in THF (1 mM, 500 mV/s, 0.1 M [NBu4][PF6]).

**Figure S51.** Cyclic voltammogram for complex **9** in THF (1 mM, 500 mV/s, 0.1 M [NBu4][PF6]).

**Figure S52.** Cyclic voltammogram for complex **10** in THF (1 mM, 500 mV/s, 0.1 M [NBu4][PF6]).

**Figure S53.** Cyclic voltammogram for 2,2´-bipyridine in THF (1 mM, 500 mV/s, 0.1 M [NBu4][PF6]).

6. X-Ray Diffraction Analysis and Molecular Structures

Data for **3** (CCDC 1918204), **4** (CCDC 1918205), **10** (CCDC 1918207) were collected at 100 K on a Bruker Quest D8 diffractometer using a graphite-monochromated Mo-Kα radiation and equipped with an Oxford Instrument Cooler Device. Data for **8** (CCDC 1918202), **1** (CCDC 1918208), **9** (CCDC 1918206) was collected at 100 K a STOE IPDS2 diffractometer and data for **2** (CCDC 1918203) were collected at 100 K a STOE IPDS2T diffractometer using a graphite-monochromated Mo-Kα radiation (λ = 0.71073 Å) and equipped with an Oxford Cryosystems Cryostream Cooler Device. The structures have been solved using either OLEX SHELXT V2014/1 [1] and refined by means of least-squares procedures on a *F*2 with the aid of the program SHELXL-2016/6 [2] included in the software package WinGX version 1.63 [3] or using CRYSTALS [4].

The Atomic Scattering Factors were taken from International Tables for X-Ray Crystallography [5]. All non-hydrogen atoms were refined anisotropically. All hydrogens atoms were refined by using a riding model. Absorption corrections were introduced by using the MULTISCAN and X-Red program [6,7]. Drawings of molecules are performed with the program DIAMOND with 50% probability displacement ellipsoids for non-H atoms. Depiction of H atoms is omitted for clarity.

**Table S1.** Crystal data and structure refinement for **1**.

|  |  |
| --- | --- |
| **Identification Code** | **K(18c6)Cr5** |
| Empirical formula | C42H84CrKN4O8Si4 |
| Formula weight | 976.59 |
| Temperature/K | 100.0 |
| Crystal system | triclinic |
| Space group | P−1 |
| *a*/Å | 11.6269(2) |
| *b*/Å | 21.5546(4) |
| *c*/Å | 21.8560(4) |
| *α*/° | 95.633(2) |
| *β*/° | 89.8920(10) |
| *γ*/° | 90.377(2) |
| Volume/Å3 | 5450.83(17) |
| *Z* | 4 |
| *ρ*calc g/cm3 | 1.190 |
| *μ*/mm−1 | 0.422 |
| *F*(000) | 2108.0 |
| Crystal size/mm3 | 0.3494 × 0.2903 × 0.2027 |
| Radiation | Mo-Kα (*λ* = 0.71073) |
| *2Θ* range for data collection/° | 3.504 to 50 |
| Index ranges | −13 ≤ h ≤ 13, −25 ≤ k ≤ 25, −25 ≤ l ≤ 25 |
| Reflections collected | 88325 |
| Independent reflections | 19148 [*R*int = 0.0630, *R*sigma = 0.0368] |
| Data/restraints/parameters | 19148/0/1112 |
| Goodness-of-fit on *F*2 | 1.073 |
| Final *R* indexes [*I*>=2σ (*I*)] | *R*1 = 0.0512, *wR*2 = 0.1293 |
| Final *R* indexes [all data] | *R*1 = 0.0571, *wR*2 = 0.1323 |
| Largest diff. peak/hole/e Å−3 | 0.79/−0.47 |

**Table S2.** Crystal data and structure refinement for **2**. The structure was refined as an inversion twin, twin ratio refined to 0.085(13).

|  |  |
| --- | --- |
| **Identification Code** | **K(18c6)Mn6** |
| Empirical formula | C34H68KMnN4O6Si4 |
| Formula weight | 835.32 |
| Temperature/K | 100.0 |
| Crystal system | monoclinic |
| Space group | C2 |
| *a*/Å | 34.8403(17) |
| *b*/Å | 18.4715(11) |
| *c*/Å | 14.5302(8) |
| *α*/° | 90 |
| *β*/° | 96.555(4) |
| *γ*/° | 90 |
| Volume/Å3 | 9289.8(9) |
| *Z* | 8 |
| *ρ*calc g/cm3 | 1.194 |
| *μ*/mm−1 | 0.518 |
| *F*(000) | 3584.0 |
| Crystal size/mm3 | 0.27 × 0.18 × 0.07 |
| Radiation | Mo-Kα (*λ* = 0.71073) |
| *2Θ* range for data collection/° | 3.668 to 54.998 |
| Index ranges | −45 ≤ h ≤ 43, −24 ≤ k ≤ 24, −18 ≤ l ≤ 18 |
| Reflections collected | 52126 |
| Independent reflections | 21354 [*R*int = 0.0285, *R*sigma = 0.0488] |
| Data/restraints/parameters | 21354/1546/1264 |
| Goodness-of-fit on *F*2 | 0.917 |
| Final *R* indexes [*I*>=2σ (*I*)] | *R*1 = 0.0376, *wR*2 = 0.0780 |
| Final *R* indexes [all data] | *R*1 = 0.0521, *wR*2 = 0.0815 |
| Largest diff. peak/hole / e Å−3 | 0.81/−0.39 |

**Table 3.** Crystal data and structure refinement for **3**.

|  |  |
| --- | --- |
| **Identification Code** | **K(18c6)Fe7** |
| Empirical formula | C42H83FeKN4O8Si4 |
| Formula weight | 978.61 |
| Temperature/K | 100.0 |
| Crystal system | triclinic |
| Space group | P−1 |
| *a*/Å | 10.8613(5) |
| *b*/Å | 13.2627(6) |
| *c*/Å | 19.8669(9) |
| *α*/° | 77.5970(10) |
| *β*/° | 80.062(2) |
| *γ*/° | 83.452(2) |
| Volume/Å3 | 2744.3(2) |
| *Z* | 2 |
| *ρ*calc g/cm3 | 1.184 |
| *μ*/mm−1 | 0.485 |
| *F*(000) | 1055.0 |
| Crystal size/mm3 | 0.21 × 0.2 × 0.11 |
| Radiation | Mo-Kα (*λ* = 0.71073) |
| *2Θ* range for data collection/° | 4.646 to 55.124 |
| Index ranges | −14 ≤ h ≤ 14, −17 ≤ k ≤ 17, −25 ≤ l ≤ 25 |
| Reflections collected | 103782 |
| Independent reflections | 12642 [*R*int = 0.0332, *R*sigma = 0.0201] |
| Data/restraints/parameters | 12642/276/683 |
| Goodness-of-fit on *F*2 | 1.054 |
| Final *R* indexes [*I*>=2σ (*I*)] | *R*1 = 0.0279, *wR*2 = 0.0618 |
| Final *R* indexes [all data] | *R*1 = 0.0383, *wR*2 = 0.0658 |
| Largest diff. peak/hole/e Å−3 | 0.34/−0.24 |

**Table S4.** Crystal data and structure refinement for **4**.

|  |  |
| --- | --- |
| **Identification Code** | **K(18c6)Co8** |
| Empirical formula | C42H84CoKN4O8Si4 |
| Formula weight | 983.52 |
| Temperature/K | 100.0 |
| Crystal system | triclinic |
| Space group | P−1 |
| *a*/Å | 10.8097(5) |
| *b*/Å | 13.2648(6) |
| *c*/Å | 19.9051(10) |
| *α*/° | 77.712(2) |
| *β*/° | 80.199(2) |
| *γ*/° | 83.606(2) |
| Volume/Å3 | 2739.7(2) |
| *Z* | 2 |
| *ρ*calc g/cm3 | 1.192 |
| *μ*/mm−1 | 0.524 |
| *F*(000) | 1060.0 |
| Crystal size / mm3 | 0.23 × 0.14 × 0.07 |
| Radiation | Mo-Kα (*λ* = 0.71073) |
| *2Θ* range for data collection/° | 4.238 to 55.058 |
| Index ranges | −14 ≤ h ≤ 14, −16 ≤ k ≤ 17, −25 ≤ l ≤ 25 |
| Reflections collected | 89930 |
| Independent reflections | 12549 [*R*int = 0.0853, *R*sigma = 0.0565] |
| Data/restraints/parameters | 12549/57/584 |
| Goodness-of-fit on *F*2 | 1.017 |
| Final *R* indexes [*I*>=2σ (*I*)] | *R*1 = 0.0420, *wR*2 = 0.0739 |
| Final *R* indexes [all data] | *R*1 = 0.0780, *wR*2 = 0.0831 |
| Largest diff. peak/hole/e Å−3 | 0.29/−0.49 |

**Table S5.** Crystal data and structure refinement for **8**. The structure was refined as an inversion twin, twin ratio refined to 0.495(10).

|  |  |
| --- | --- |
| **Identification Code** | **Co4** |
| Empirical formula | C44H88Co2N8Si8 |
| Formula weight | 1071.80 |
| Temperature/K | 100 |
| Crystal system | orthorhombic |
| Space group | P*ca*21 |
| *a*/Å | 18.7674(9) |
| *b*/Å | 18.1030(8) |
| *c*/Å | 17.5930(7) |
| *α*/° | 90 |
| *β*/° | 90 |
| *γ*/° | 90 |
| Volume/Å3 | 5977.2(5) |
| *Z* | 4 |
| *ρ*calc g/cm3 | 1.191 |
| *μ*/mm−1 | 0.751 |
| *F*(000) | 2296.0 |
| Crystal size/mm3 | 0.31 × 0.2 × 0.2 |
| Radiation | Mo Kα (*λ* = 0.71073) |
| *2Θ* range for data collection/° | 3.89 to 51.998 |
| Index ranges | −23 ≤ h ≤ 21, −19 ≤ k ≤ 22, −19 ≤ l ≤ 21 |
| Reflections collected | 20518 |
| Independent reflections | 10939 [*R*int = 0.0219, *R*sigma = 0.0228] |
| Data/restraints/parameters | 10939/1/588 |
| Goodness-of-fit on *F*2 | 1.014 |
| Final *R* indexes [*I*>=2σ (*I*)] | *R*1 = 0.0280, *wR*2 = 0.0670 |
| Final *R* indexes [all data] | *R*1 = 0.0307, *wR*2 = 0.0679 |
| Largest diff. peak/hole/e Å−3 | 0.45/−0.25 |

**Table S6.** Crystal data and structure refinement for **9**. The structure was refined as an inversion twin, twin ratio refined to 0.292(9).

|  |  |
| --- | --- |
| **Identification Code** | **Zn9** |
| Empirical formula | C44H88N8Si8Zn2 |
| Formula weight | 1084.68 |
| Temperature/K | 100 |
| Crystal system | orthorhombic |
| Space group | P*ca*21 |
| *a*/Å | 18.8806(12) |
| *b*/Å | 18.0560(13) |
| *c*/Å | 17.6133(17) |
| *α*/° | 90 |
| *β*/° | 90 |
| *γ*/° | 90 |
| Volume / Å3 | 6004.5(8) |
| *Z* | 4 |
| *ρ*calc g/cm3 | 1.200 |
| *μ*/mm−1 | 0.994 |
| *F*(000) | 2320.0 |
| Crystal size/mm3 | 0.254 × 0.189 × 0.085 |
| Radiation | Mo-Kα (*λ* = 0.71073) |
| *2Θ* range for data collection/° | 4.314 to 51.996 |
| Index ranges | −23 ≤ h ≤ 23, −21 ≤ k ≤ 22, −21 ≤ l ≤ 21 |
| Reflections collected | 52603 |
| Independent reflections | 11789 [*R*int = 0.0737, *R*sigma = 0.0589] |
| Data/restraints/parameters | 11789/1/584 |
| Goodness-of-fit on *F*2 | 0.969 |
| Final *R* indexes [*I*>=2σ (*I*)] | *R*1 = 0.0340, *wR*2 = 0.0700 |
| Final *R* indexes [all data] | *R*1 = 0.0445, *wR*2 = 0.0718 |
| Largest diff. peak/hole/e Å−3 | 0.58/−0.21 |

**Table S7.** Crystal data and structure refinement for **10**.

|  |  |
| --- | --- |
| **Identification Code** | **K(18c6)Zn10** |
| Empirical formula | C38H78KN4O7Si4Zn |
| Formula weight | 919.87 |
| Temperature/K | 100.0 |
| Crystal system | monoclinic |
| Space group | P21/*c* |
| *a*/Å | 12.1899(7) |
| *b*/Å | 18.4365(10) |
| *c*/Å | 22.8273(13) |
| *α*/° | 90 |
| *β*/° | 95.423(2) |
| *γ*/° | 90 |
| Volume/Å3 | 5107.2(5) |
| *Z* | 4 |
| *ρ*calc g/cm3 | 1.196 |
| *μ*/mm−1 | 0.700 |
| *F*(000) | 1980.0 |
| Crystal size / mm3 | 0.492 × 0.383 × 0.15 |
| Radiation | Mo Kα (*λ* = 0.71073) |
| *2Θ* range for data collection/° | 4.268 to 49.998 |
| Index ranges | −14 ≤ h ≤ 14, −21 ≤ k ≤ 21, −27 ≤ l ≤ 27 |
| Reflections collected | 96672 |
| Independent reflections | 8987 [*R*int = 0.0946, *R*sigma = 0.0427] |
| Data/restraints/parameters | 8987/1293/603 |
| Goodness-of-fit on *F*2 | 1.077 |
| Final *R* indexes [*I*>=2σ (*I*)] | *R*1 = 0.1301, *wR*2 = 0.2536 |
| Final *R* indexes [all data] | *R*1 = 0.1530, *wR*2 = 0.2636 |
| Largest diff. peak/hole/e Å−3 | 1.75/−1.94 |

**Table S 8.** Crystal data and structure refinement for **1**-**4**, **10**.

|  |  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- | --- |
| Identification code | K(18c6)Cr5 |  | K(18c6)Mn6 | K(18c6)Fe7 | K(18c6)Co8 | K(18c6)Zn10 |  |  |  |
| Empirical formula | C42H84CrKN4O8Si4 |  | C34H68KMnN4O6Si4 | C42H83FeKN4O8Si4 | C42H84CoKN4O8Si4 | C38H78KN4O7Si4Zn |  |  |  |
| Formula weight | 976.59 |  | 835.32 | 978.61 | 983.52 | 919.87 |  |  |  |
| Temperature / *K* | 100.0 |  | 100.0 | 100.0 | 100.0 | 100.0 |  |  |  |
| Crystal system | triclinic |  | monoclinic | triclinic | triclinic | monoclinic |  |  |  |
| Space group | P−1 |  | C2 | P−1 | P−1 | P21/*c* |  |  |  |
| *a*/Å | 11.6269(2) |  | 34.8403(17) | 10.8613(5) | 10.8097(5) | 12.1899(7) |  |  |  |
| *b*/Å | 21.5546(4) |  | 18.4715(11) | 13.2627(6) | 13.2648(6) | 18.4365(10) |  |  |  |
| *c*/Å | 21.8560(4) |  | 14.5302(8) | 19.8669(9) | 19.9051(10) | 22.8273(13) |  |  |  |
| *α*/° | 95.633(2) |  | 90 | 77.5970(10) | 77.712(2) | 90 |  |  |  |
| *β*/° | 89.8920(10) |  | 96.555(4) | 80.062(2) | 80.199(2) | 95.423(2) |  |  |  |
| *γ*/° | 90.377(2) |  | 90 | 83.452(2) | 83.606(2) | 90 |  |  |  |
| Volume/Å3 | 5450.83(17) |  | 9289.8(9) | 2744.3(2) | 2739.7(2) | 5107.2(5) |  |  |  |
| *Z* | 4 |  | 8 | 2 | 2 | 4 |  |  |  |
| *ρ*calc g/cm3 | 1.190 |  | 1.194 | 1.184 | 1.192 | 1.196 |  |  |  |
| *μ*/mm−1 | 0.422 |  | 0.518 | 0.485 | 0.524 | 0.700 |  |  |  |
| *F*(000) | 2108.0 |  | 3584.0 | 1055.0 | 1060.0 | 1980.0 |  |  |  |
| Crystal size/mm3 | 0.3494 × 0.2903 × 0.2027 |  | 0.27 × 0.18 × 0.07 | 0.21 × 0.2 × 0.11 | 0.23 × 0.14 × 0.07 | 0.492 × 0.383 × 0.15 |  |  |  |
| Radiation | Mo Kα (λ = 0.71073) |  | Mo Kα (*λ* = 0.71073) | Mo Kα (*λ* = 0.71073) | Mo Kα (*λ* = 0.71073) | Mo Kα (*λ* = 0.71073) |  |  |  |
| *2Θ* range for data collection/° | 3.504 to 50 |  | 3.668 to 54.998 | 4.646 to 55.124 | 4.238 to 55.058 | 4.268 to 49.998 |  |  |  |
| Index ranges | −13 ≤ h ≤ 13, −25 ≤ k ≤ 25, −25 ≤ l ≤ 25 |  | −45 ≤ h ≤ 43, −24 ≤ k ≤ 24, −18 ≤ l ≤ 18 | −14 ≤ h ≤ 14, −17 ≤ k ≤ 17, −25 ≤ l ≤ 25 | −14 ≤ h ≤ 14, −16 ≤ k ≤ 17, −25 ≤ l ≤ 25 | −14 ≤ h ≤ 14, −21 ≤ k ≤ 21, −27 ≤ l ≤ 27 |  |  |  |
| Reflections collected | 88325 |  | 52126 | 103782 | 89930 | 96672 |  |  |  |
| Independent reflections | 19148 [*R*int = 0.0630, *R*sigma = 0.0368] |  | 21354 [*R*int = 0.0285, *R*sigma = 0.0488] | 12642 [*R*int = 0.0332, *R*sigma = 0.0201] | 12549 [*R*int = 0.0853, *R*sigma = 0.0565] | 8987 [*R*int = 0.0946, *R*sigma = 0.0427] |  |  |  |
| Data/restraints/parameters | 19148/0/1112 |  | 21354/1546/1264 | 12642/276/683 | 12549/57/584 | 8987/1293/603 |  |  |  |
| Goodness-of-fit on *F*2 | 1.073 |  | 0.917 | 1.054 | 1.017 | 1.077 |  |  |  |
| Final *R* indexes [*I*>=2σ (*I*)] | *R*1 = 0.0512, *wR*2 = 0.1293 |  | *R*1 = 0.0376, *wR*2 = 0.0780 | *R*1 = 0.0279, *wR*2 = 0.0618 | *R*1 = 0.0420, *wR*2 = 0.0739 | *R*1 = 0.1301, *wR*2 = 0.2536 |  |  |  |
| Final *R* indexes [all data] | *R*1 = 0.0571, *wR*2 = 0.1323 |  | *R*1 = 0.0521, *wR*2 = 0.0815 | *R*1 = 0.0383, *wR*2 = 0.0658 | *R*1 = 0.0780, *wR*2 = 0.0831 | *R*1 = 0.1530, *wR*2 = 0.2636 |  |  |  |
| Largest diff. peak/hole/e Å−3 | 0.79/−0.47 |  | 0.81/−0.39 | 0.34/−0.24 | 0.29/−0.49 | 1.75/−1.94 |  |  |  |
|  |  |  |  |  |  |  |  |  |  |

**Table S9.** Crystal data and structure refinement for **4** and **9**.

|  |  |  |  |
| --- | --- | --- | --- |
| **Identification Code** | **Co4** | **Zn9** |  |
| Empirical formula | C44H88Co2N8Si8 | C44H88N8Si8Zn2 |  |
| Formula weight | 1071.80 | 1084.68 |  |
| Temperature / *K* | 100 | 100 |  |
| Crystal system | orthorhombic | orthorhombic |  |
| Space group | P*ca*21 | P*ca*21 |  |
| *a*/Å | 18.7674(9) | 18.8806(12) |  |
| *b*/Å | 18.1030(8) | 18.0560(13) |  |
| *c*/Å | 17.5930(7) | 17.6133(17) |  |
| *α*/° | 90 | 90 |  |
| *β*/° | 90 | 90 |  |
| *γ*/° | 90 | 90 |  |
| Volume / Å3 | 5977.2(5) | 6004.5(8) |  |
| *Z* | 4 | 4 |  |
| *ρ*calc g/cm3 | 1.191 | 1.200 |  |
| *μ*/mm−1 | 0.751 | 0.994 |  |
| *F*(000) | 2296.0 | 2320.0 |  |
| Crystal size / mm3 | 0.31 × 0.2 × 0.2 | 0.254 × 0.189 × 0.085 |  |
| Radiation | Mo Kα (*λ* = 0.71073) | Mo Kα (*λ* = 0.71073) |  |
| *2Θ* range for data collection/° | 3.89 to 51.998 | 4.314 to 51.996 |  |
| Index ranges | −23 ≤ h ≤ 21, −19 ≤ k ≤ 22, −19 ≤ l ≤ 21 | −23 ≤ h ≤ 23, −21 ≤ k ≤ 22, −21 ≤ l ≤ 21 |  |
| Reflections collected | 20518 | 52603 |  |
| Independent reflections | 10939 [*R*int = 0.0219, *R*sigma = 0.0228] | 11789 [*R*int = 0.0737, *R*sigma = 0.0589] |  |
| Data/restraints/parameters | 10939/1/588 | 11789/1/584 |  |
| Goodness-of-fit on *F*2 | 1.014 | 0.969 |  |
| Final *R* indexes [*I*>=2σ (*I*)] | *R*1 = 0.0280, *wR*2 = 0.0670 | *R*1 = 0.0340, *wR*2 = 0.0700 |  |
| Final *R* indexes [all data] | *R*1 = 0.0307, *wR*2 = 0.0679 | *R*1 = 0.0445, *wR*2 = 0.0718 |  |
| Largest diff. peak/hole/e Å-3 | 0.45/−0.25 | 0.58/−0.21 |  |

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