

## Supporting information

### **Two-dimensional metal-organic nanosheets composed of single-molecule magnets: structural modulation and enhanced magnetism utilizing steric hindrance effect.**

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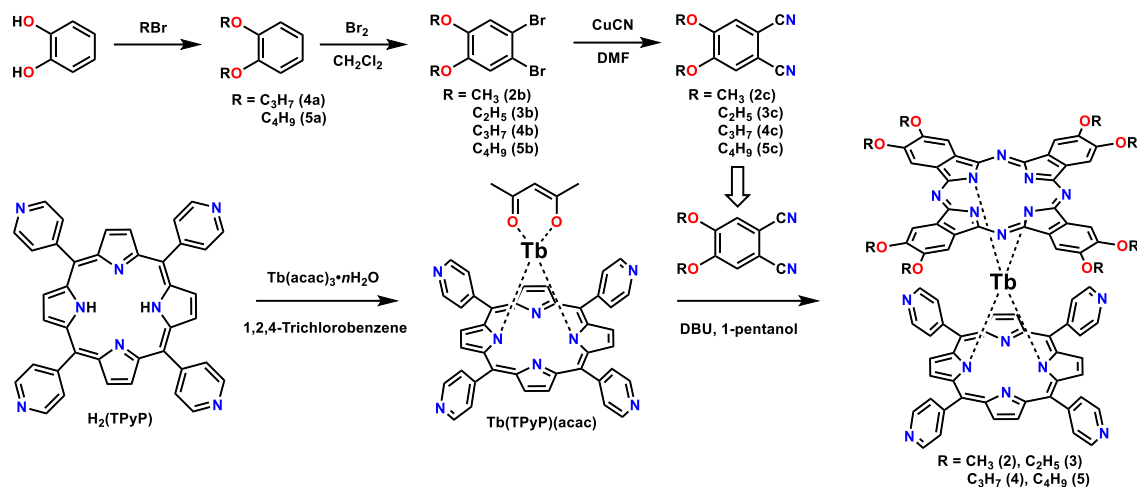
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**Scheme S1.** Synthesis of SMMs.

### Synthesis of 1,2-dimethoxy-4,5-dibromobenzene (**2b**)

The mixture of 1,2-dimethoxybenzene (Tokyo Chemical Industry Co., Ltd., 7.65 mL, 0.060 mol), I<sub>2</sub> (one bead, ca. 50 mg) and dried CH<sub>2</sub>Cl<sub>2</sub> (150 mL) was cooled to 0 °C using ice bath. The mixture of Br<sub>2</sub> (7.1 mL) and dried CH<sub>2</sub>Cl<sub>2</sub> (50 mL) was added dropwise over 1 hour. The reaction mixture was stirred for 22 hours at room temperature. The residual Br<sub>2</sub> was quenched using Na<sub>2</sub>SO<sub>3</sub> aq., and the solution was neutralized using NaHCO<sub>3</sub> aq. The CH<sub>2</sub>Cl<sub>2</sub> layer was washed for several times with the water using the separately funnel. After drying the CH<sub>2</sub>Cl<sub>2</sub> layer over MgSO<sub>4</sub>, the CH<sub>2</sub>Cl<sub>2</sub> was removed using rotary evaporator. The white solid was completely dissolved in the hot isopropanol (150 mL) and kept at -20 °C to afford the white crystalline solid of **2b** (70%).

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, TMS): δ 7.051 (s, 2H, H<sub>Ar</sub>), 3.844 (s, 6H, CH<sub>3</sub>-O).

### Synthesis of 1,2-dimethoxy-4,5-dicyanobenzene (**2c**)

The mixture of 1,2-dimethoxy-4,5-dibromobenzene (8.6 g, 0.030 mol), CuCN (7.9 g, 0.090 mol) and dried DMF (120 mL) was refluxed for 5 hours under N<sub>2</sub> atmosphere. After cooling to room temperature, NH<sub>3</sub> aq. (28%, 300 mL) was added and stirred for 3 days. The precipitate was collected by vacuum filtration, washed with water, and dried under the vacuum. The soxhlet extraction was carried out using Et<sub>2</sub>O for 3 days, and the white solid was collected by vacuum filtration. Recrystallization using CH<sub>2</sub>Cl<sub>2</sub> and Et<sub>2</sub>O afforded the white crystalline solid of **2c** (38%).

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 7.152 (s, 2H, H<sub>Ar</sub>), 3.974 (s, 6H, CH<sub>3</sub>-O).

### Synthesis of 1,2-diethoxy-4,5-dibromobenzene (**3b**)

The mixture of 1,2-diethoxybenzene (Tokyo Chemical Industry Co., Ltd., 9.86 g, 0.060 mol), I<sub>2</sub> (one bead, ca. 50 mg) and dried CH<sub>2</sub>Cl<sub>2</sub> (150 mL) was cooled to 0 °C using ice bath. The mixture of Br<sub>2</sub>

(7.1 mL) and dried CH<sub>2</sub>Cl<sub>2</sub> (50 mL) was added dropwise over 1 hour. The reaction mixture was stirred for 22 hours at room temperature. The residual Br<sub>2</sub> was quenched using Na<sub>2</sub>SO<sub>3</sub> aq., and the solution was neutralized using NaHCO<sub>3</sub> aq. The CH<sub>2</sub>Cl<sub>2</sub> layer was washed for several times with the water using the separately funnel. After drying the CH<sub>2</sub>Cl<sub>2</sub> layer over MgSO<sub>4</sub>, the CH<sub>2</sub>Cl<sub>2</sub> was removed using rotary evaporator. The product was obtained as the colourless oil of **3b** (77%).

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 7.062 (s, 2H, H<sub>Ar</sub>), 4.0 (q, 4H, CH<sub>3</sub>-CH<sub>2</sub>-O), 1.4 (t, 6H, CH<sub>3</sub>-CH<sub>2</sub>).

#### Synthesis of 1,2-diethoxy-4,5-dicyanobenzene (**3c**)

The mixture of 1,2-diethoxy-4,5-dibromobenzene (9.9 g, 0.030 mol), CuCN (8.0 g, 0.090 mol) and dried DMF (120 mL) was refluxed for 5 hours under N<sub>2</sub> atmosphere. After cooling to room temperature, NH<sub>3</sub> aq. (28%, 300 mL) was added and stirred for 3 days. The precipitate was collected by vacuum filtration, washed with water, and dried under the vacuum. The soxhlet extraction was carried out using Et<sub>2</sub>O for 4 days, and the white solid was collected by vacuum filtration. Purification with the silica gel column chromatography using CH<sub>2</sub>Cl<sub>2</sub> as the eluent and recrystallization using CH<sub>2</sub>Cl<sub>2</sub> and Et<sub>2</sub>O afforded the white crystalline solid of **3c** (41%).

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 7.119 (s, 2H, H<sub>Ar</sub>), 4.15 (q, 4H, CH<sub>3</sub>-CH<sub>2</sub>-O), 1.51 (t, 6H, CH<sub>3</sub>-CH<sub>2</sub>).

#### Synthesis of 1,2-dipropyloxybenzene (**4a**)

The mixture of catechol (8.25 g, 0.075 mol), K<sub>2</sub>CO<sub>3</sub> (41.6 g, 0.3 mol), dried acetone (83 mL), and 1-bromopropane (15 mL, 0.166 mol) was refluxed for 48 hours under N<sub>2</sub> atmosphere. After cooling to room temperature, the K<sub>2</sub>CO<sub>3</sub> was removed by vacuum filtration and washed with CH<sub>2</sub>Cl<sub>2</sub> to extract the product. The reaction product was purified with the silica gel column chromatography using CH<sub>2</sub>Cl<sub>2</sub> as the eluent, and the colourless oil of **4a** was obtained (84%).

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 6.889 (s, 2H, H<sub>Ar</sub>), 4.0 (t, 4H, CH<sub>2</sub>-CH<sub>2</sub>-O), 1.8 (sext., 4H, CH<sub>3</sub>-CH<sub>2</sub>-CH<sub>2</sub>), 1.0 (t, 6H, CH<sub>3</sub>-CH<sub>2</sub>).

#### Synthesis of 1,2-dipropyloxy-4,5-dibromobenzene (**4b**)

The mixture of 1,2-dipropyloxybenzene (12.26 g, 0.063 mol), I<sub>2</sub> (one bead, ca. 50 mg) and dried CH<sub>2</sub>Cl<sub>2</sub> (150 mL) was cooled to 0 °C using ice bath. The mixture of Br<sub>2</sub> (7.1 mL) and dried CH<sub>2</sub>Cl<sub>2</sub> (50 mL) was added dropwise over 1 hour. The reaction mixture was stirred for 22 hours at room temperature. The residual Br<sub>2</sub> was quenched using Na<sub>2</sub>SO<sub>3</sub> aq., and the solution was neutralized using NaHCO<sub>3</sub> aq. The CH<sub>2</sub>Cl<sub>2</sub> layer was washed for several times with the water using the separately funnel. After drying the CH<sub>2</sub>Cl<sub>2</sub> layer over MgSO<sub>4</sub>, the CH<sub>2</sub>Cl<sub>2</sub> was removed using rotary evaporator. Purification with the silica gel column chromatography using hexane/ethyl acetate (9:1) as the eluent afforded the white solid of **4b** (79%).

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 7.064 (s, 2H, H<sub>Ar</sub>), 3.9 (t, 4H, CH<sub>2</sub>-CH<sub>2</sub>-O), 1.8 (sext., 4H, CH<sub>3</sub>-CH<sub>2</sub>-

CH<sub>2</sub>), 1.0 (t, 6H, CH<sub>3</sub>-CH<sub>2</sub>).

#### Synthesis of 1,2-dipropoxy-4,5-dicyanobenzene (4c)

The mixture of 1,2-dipropoxy-4,5-dibromobenzene (10.53 g, 0.030 mol), CuCN (8.0 g, 0.090 mol) and dried DMF (120 mL) was refluxed for 5 hours under N<sub>2</sub> atmosphere. After cooling to room temperature, NH<sub>3</sub> aq. (28%, 300 mL) was added and stirred for 3 days. The precipitate was collected by vacuum filtration, washed with water, and dried under the vacuum. The soxhlet extraction was carried out using Et<sub>2</sub>O for 3 days, and the white solid was collected by vacuum filtration. Purification with the silica gel column chromatography using CH<sub>2</sub>Cl<sub>2</sub> as the eluent and the recrystallization using CH<sub>2</sub>Cl<sub>2</sub> and Et<sub>2</sub>O afforded the crystalline solid of **4c** (78%).

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 7.115 (s, 2H, H<sub>Ar</sub>), 4.0 (t, 4H, CH<sub>2</sub>-CH<sub>2</sub>-O), 1.9 (sext., 4H, CH<sub>3</sub>-CH<sub>2</sub>-CH<sub>2</sub>), 1.1 (t, 6H, CH<sub>3</sub>-CH<sub>2</sub>).

#### Synthesis of 1,2-dibutoxybenzene (5a)

The mixture of catechol (15 g, 0.136 mol), KOH (18.1 g, 0.27 mol), Aliquot 336 (1 mL) and 1-bromobutane (29 mL, 0.27 mol) was refluxed for 5 hours. After cooling to room temperature, the residue was extracted with CH<sub>2</sub>Cl<sub>2</sub>, washed with H<sub>2</sub>O using separatory funnel, and dried over MgSO<sub>4</sub>. After the removal of CH<sub>2</sub>Cl<sub>2</sub> using rotary evaporator, the oil was purified using vacuum distillation (91%).

#### Synthesis of 1,2-dibutoxy-4,5-dibromobenzene (5b)

The mixture of 1,2-dibutoxybenzene (12 g, 0.054 mol) and dried CH<sub>2</sub>Cl<sub>2</sub> (150 mL) was cooled to 0 °C using ice bath. The mixture of Br<sub>2</sub> (6.5 mL) and dried CH<sub>2</sub>Cl<sub>2</sub> (15 mL) was added dropwise over 0.5 hour. The reaction mixture was stirred for 30 hours at room temperature. The residual Br<sub>2</sub> was quenched using Na<sub>2</sub>SO<sub>3</sub> aq., and the solution was neutralized using NaHCO<sub>3</sub> aq. The CH<sub>2</sub>Cl<sub>2</sub> layer was washed for several times with the water using the separately funnel. After drying the CH<sub>2</sub>Cl<sub>2</sub> layer over MgSO<sub>4</sub>, the CH<sub>2</sub>Cl<sub>2</sub> was removed using rotary evaporator. Purification with the silica gel column chromatography using hexane/ethyl acetate (4:1) as the eluent afforded the colourless oil of **5b** (95%).

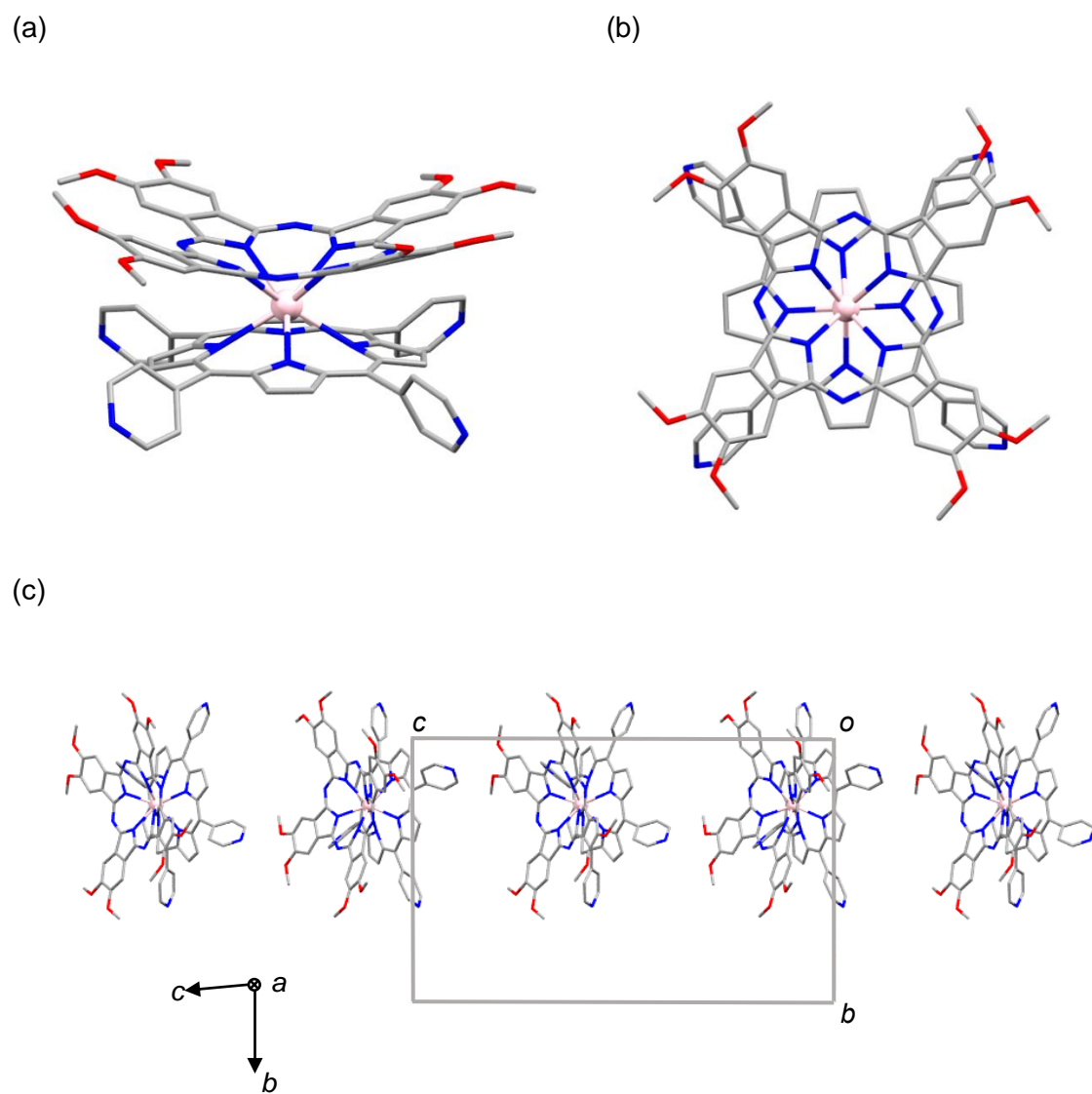
#### Synthesis of 1,2-dibutoxy-4,5-dicyanobenzene (5c)

The mixture of 1,2-dibutoxy-4,5-dibromobenzene (11.7 g, 0.034 mol), CuCN (7.5 g, 0.084 mol) and dried DMF (100 mL) was refluxed for 5 hours under N<sub>2</sub> atmosphere. After cooling to room temperature, NH<sub>3</sub> aq. (28%, 300 mL) was added and stirred for 60 hours. The precipitate was collected by vacuum filtration, washed with water, and dried under the vacuum. Purification with the silica gel column chromatography using CHCl<sub>3</sub> as the eluent and the recrystallization using CHCl<sub>3</sub> and Et<sub>2</sub>O afforded the crystalline solid of **5c** (42%).

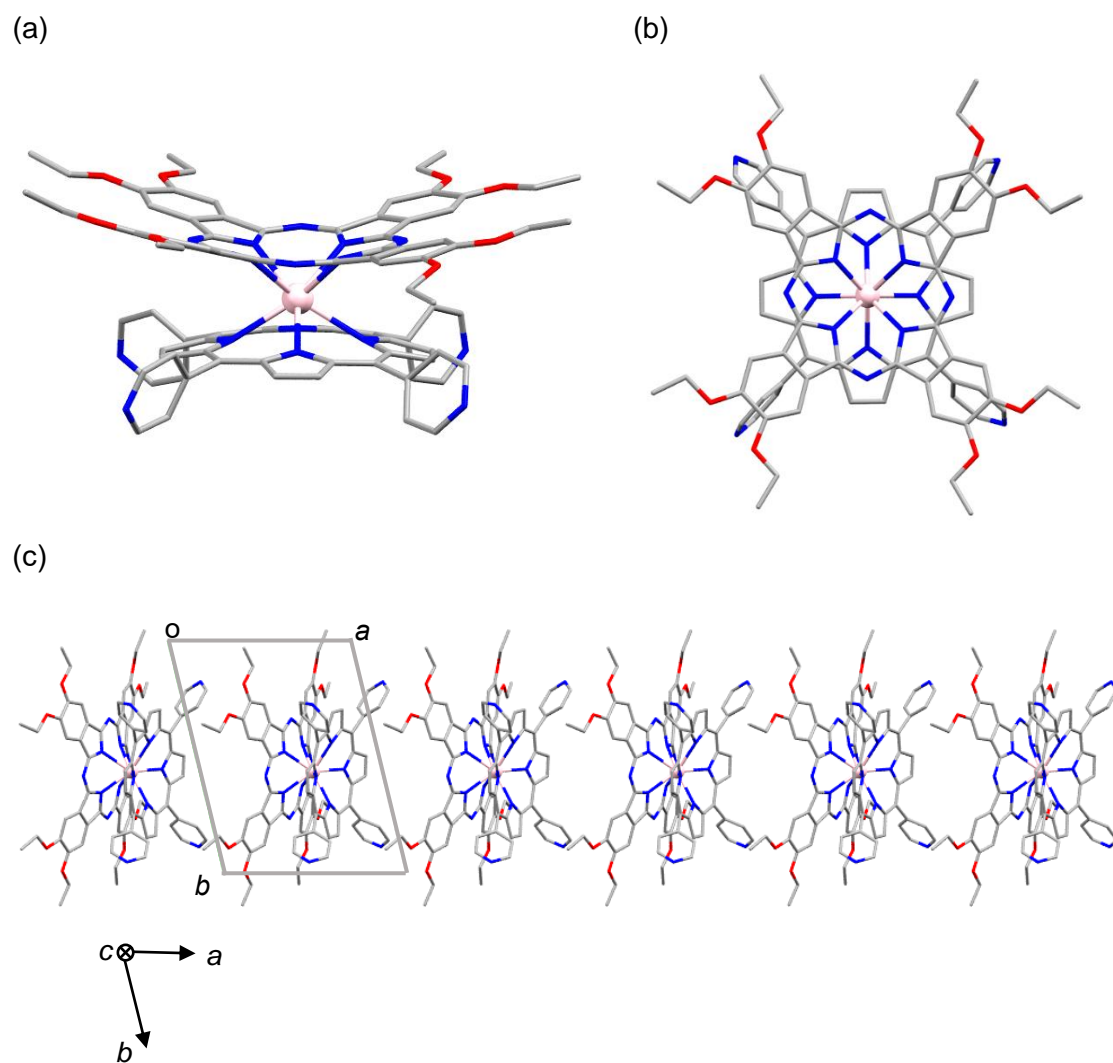
$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.115 (s, 2H,  $\text{H}_{\text{Ar}}$ ), 4.06 (t, 4H,  $\text{CH}_2\text{-CH}_2\text{-O}$ ), 1.84 (quin., 4H,  $\text{CH}_2\text{-CH}_2\text{-CH}_2$ ), 1.51 (sext., 4H,  $\text{CH}_3\text{-CH}_2\text{-CH}_2$ ), 1.0 (t, 6H,  $\text{CH}_3\text{-CH}_2$ ).

**Table S1.** Crystalline cell parameters for **1-5**. The parameters for **1** were taken from the literature.<sup>1</sup>

	<b>1</b>	<b>2</b>	<b>3</b>	<b>4</b>	<b>5</b>
<i>T</i> / K	153	153	153	153	153
Formula	C <sub>74</sub> H <sub>44</sub> Cl <sub>4</sub> N <sub>16</sub> Tb	C <sub>82</sub> H <sub>60</sub> Cl <sub>4</sub> N <sub>16</sub> O <sub>8</sub> Tb	C <sub>94</sub> H <sub>85</sub> Cl <sub>6</sub> N <sub>16</sub> O <sub>8</sub> Tb	C <sub>100.79</sub> H <sub>98.79</sub> Cl <sub>3.58</sub> N <sub>16</sub> O <sub>8</sub> Tb	C <sub>105.47</sub> H <sub>106.94</sub> Cl <sub>2.94</sub> N <sub>16</sub> O <sub>8</sub> Tb
Crystal system	Triclinic	Monoclinic	Triclinic	Triclinic	Triclinic
Space group	<i>P</i> -1	<i>P</i> 2 <sub>1</sub> / <i>n</i>	<i>P</i> -1	<i>P</i> -1	<i>P</i> -1
<i>Z</i>	2	4	2	2	2
<i>a</i> / Å	12.7976(5)	13.9287(4)	12.4898(2)	12.68090(10)	13.14280(10)
<i>b</i> / Å	14.0071(6)	18.9066(4)	16.8197(3)	17.4595(2)	17.69370(10)
<i>c</i> / Å	18.1335(7)	30.4607(9)	23.7164(5)	24.1597(2)	21.7886(2)
<i>α</i> / °	93.068(3)	90	71.843(2)	69.7820(10)	106.1290(10)
<i>β</i> / °	105.135(4)	92.075(3)	77.170(2)	75.3100(10)	103.3890(10)
<i>γ</i> / °	100.887(3)	90	73.3800(10)	70.6080(10)	94.4290(10)
<i>V</i> / Å <sup>3</sup>	3063.1(2)	8016.4(4)	4487.75(16)	4676.06(9)	4680.46(7)
<i>ρ</i> / g cm <sup>-3</sup>	1.581	1.407	1.434	1.383	1.412
GOF	1.035	1.012	1.059	1.049	1.041
<i>R</i> <sub>1</sub> (gt)	0.0638	0.0558	0.0417	0.0460	0.0335
<i>wR</i> <sub>2</sub> (gt)	0.1359	0.1146	0.0432	0.1231	0.0902
<i>R</i> <sub>1</sub> (all)	0.0995	0.1082	0.0432	0.0501	0.0345
<i>wR</i> <sub>2</sub> (ref)	0.1516	0.1330	0.1174	0.1259	0.0909
CCDC number	2205797	2293113	2293116	2293114	2293115

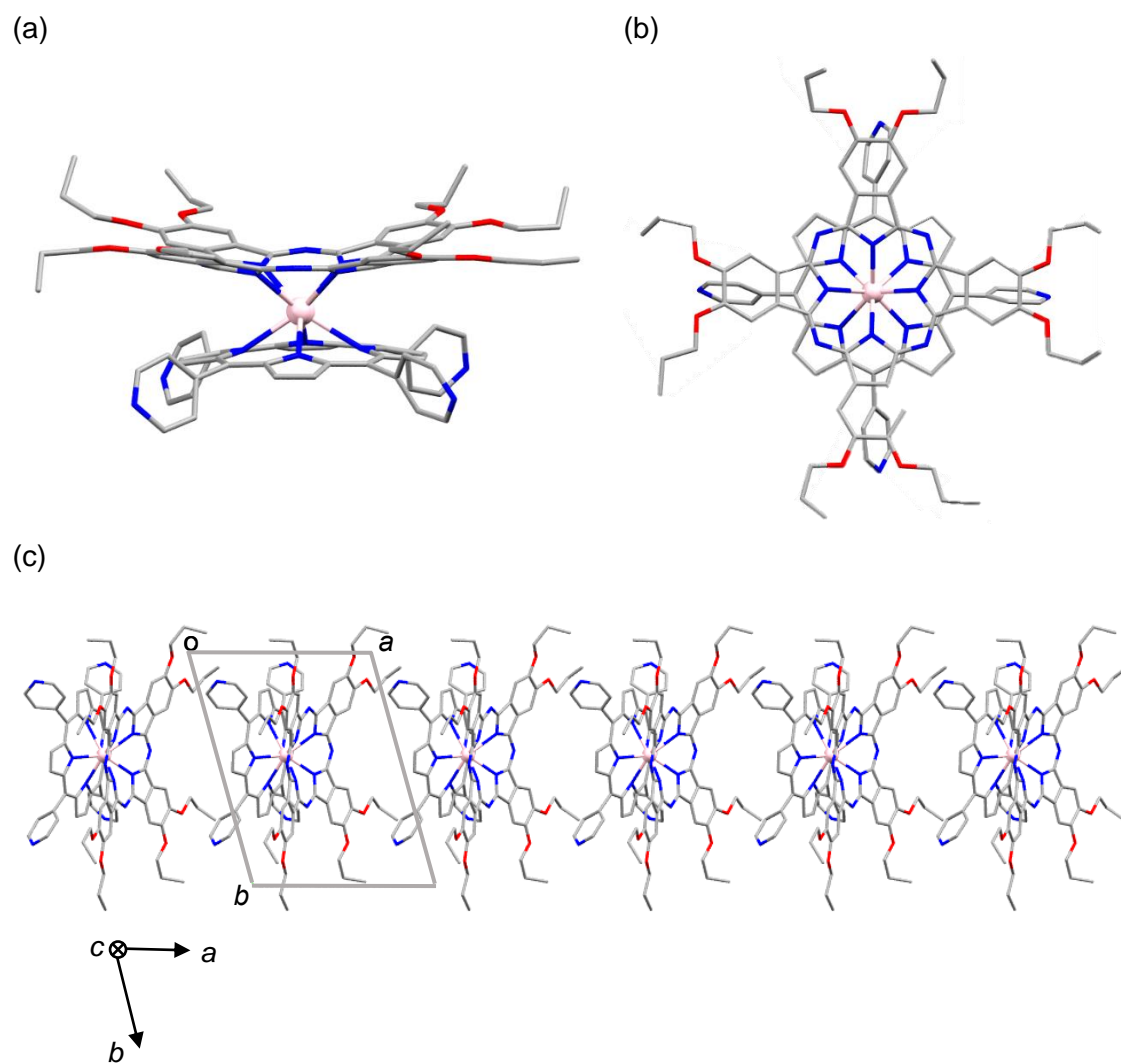


**Fig. S1** Crystal structure of **2** at 153 K. (a) Side view, (b) top view and (c) crystal packing. Solvent molecules and hydrogen atoms are omitted for clarity. Tb pink; C grey; N blue; O red.

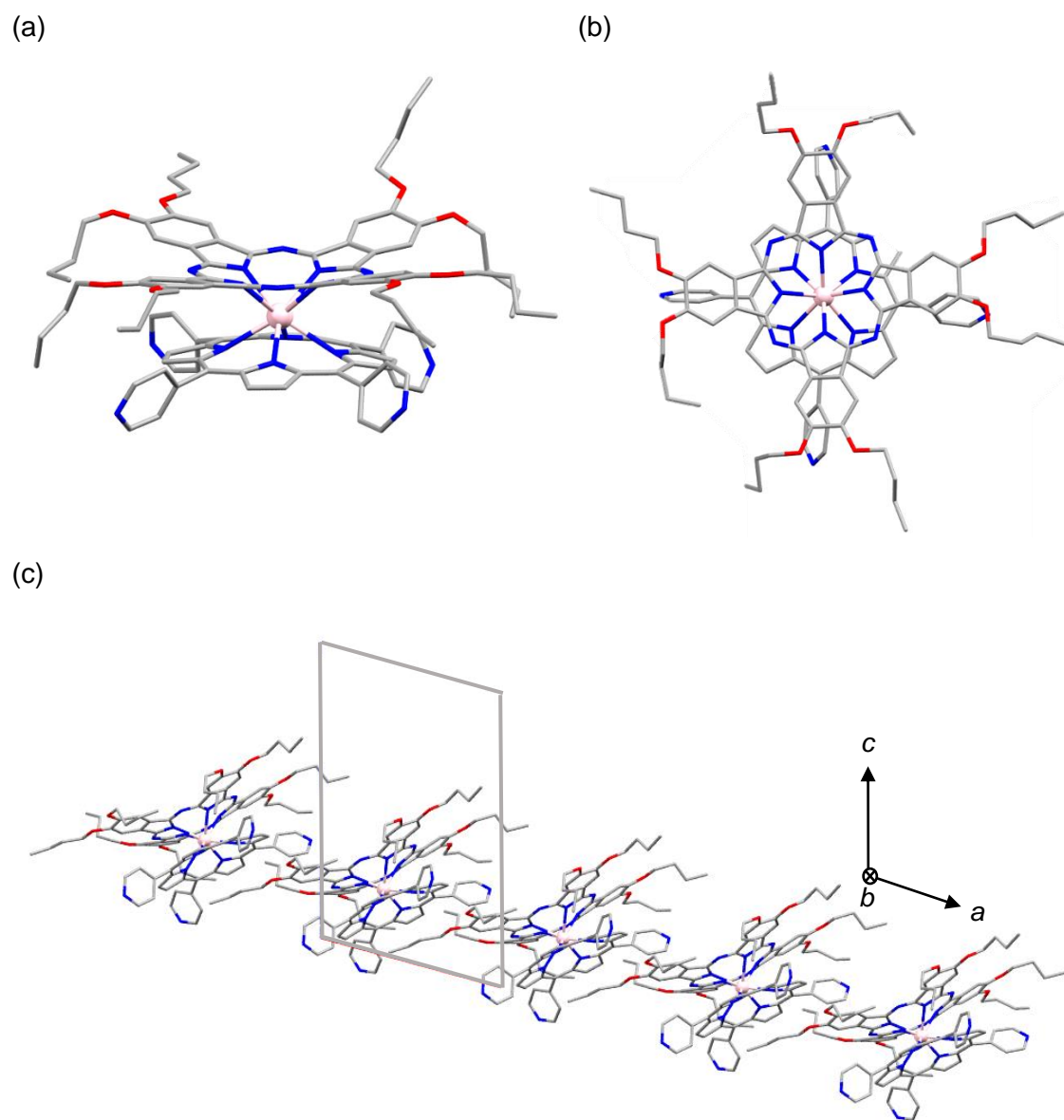


**Fig. S2** Crystal structure of **3** at 153 K. (a) Side view, (b) top view and (c) crystal packing. Solvent molecules and hydrogen atoms are omitted for clarity. Tb pink; C grey; N blue; O red.

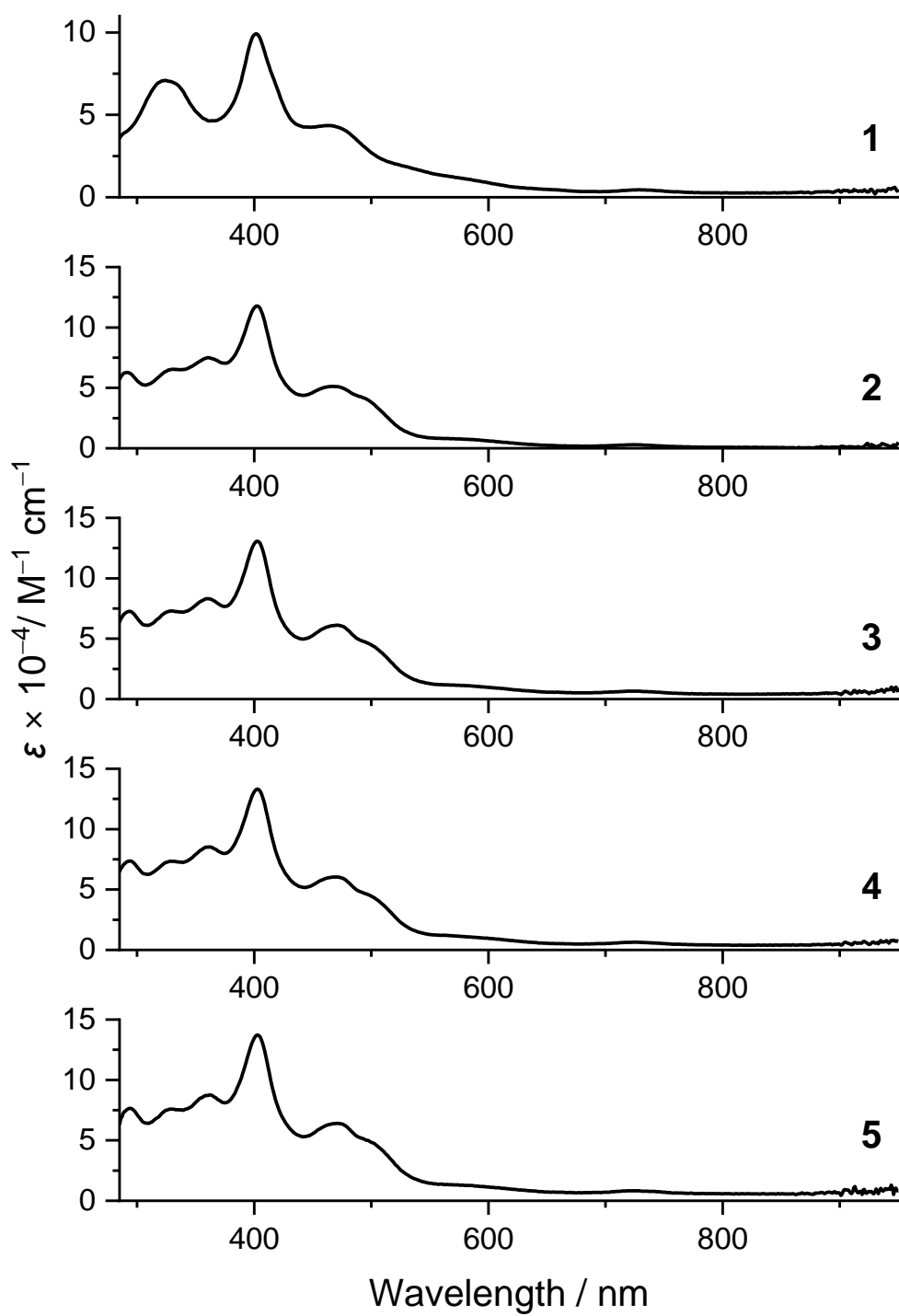




**Fig. S3** Crystal structure of **4** at 153 K. (a) Side view, (b) top view and (c) crystal packing. Solvent molecules and hydrogen atoms are omitted for clarity. Tb pink; C grey; N blue; O red.



**Fig. S4** Crystal structure of **5** at 153 K. (a) Side view, (b) top view and (c) crystal packing. Solvent molecules and hydrogen atoms are omitted for clarity. Tb pink; C grey; N blue; O red.



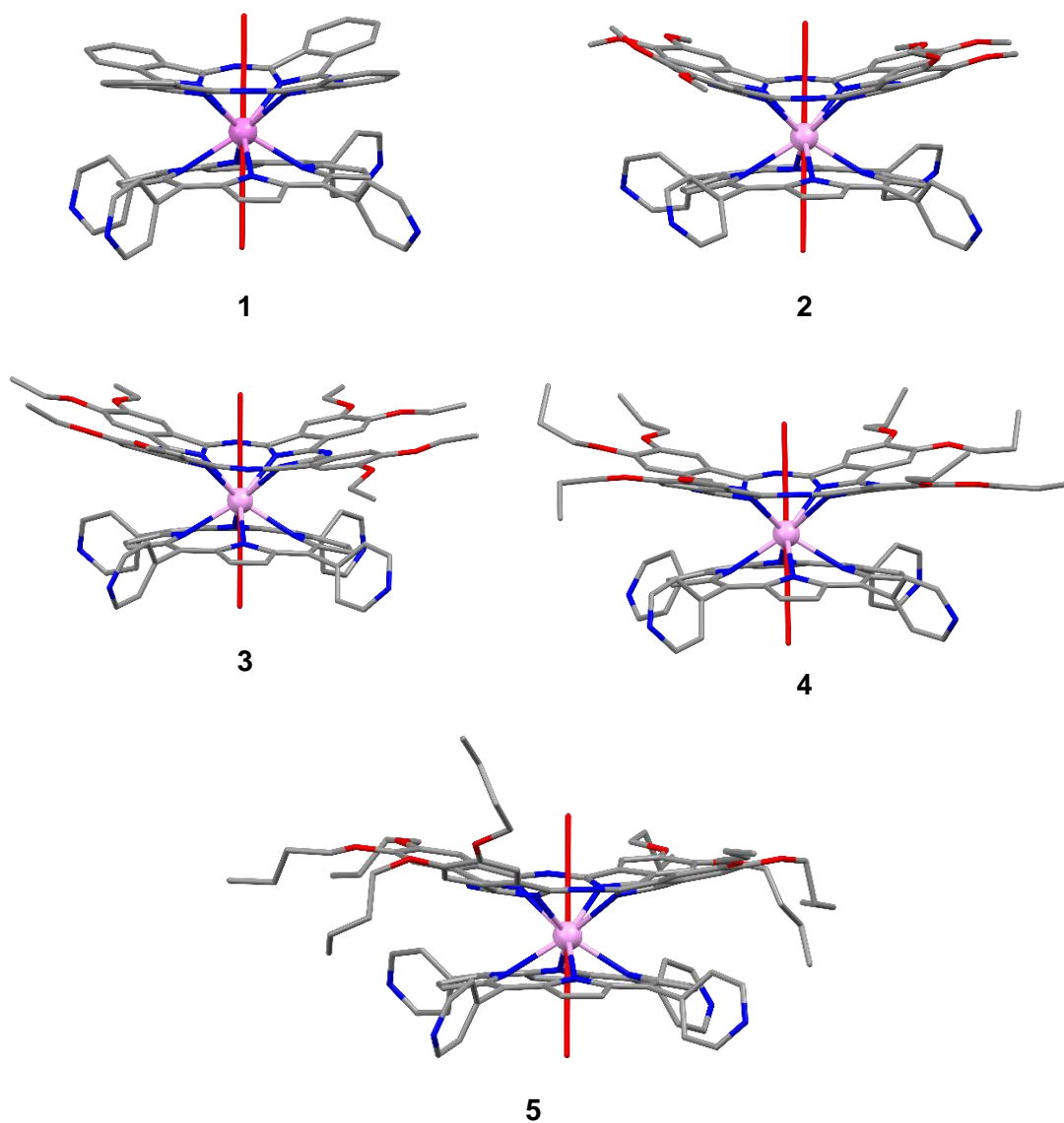
**Fig. S5** UV-Vis-NIR spectra for 1-5 in toluene.

**Table S2.** Basis sets used for CASSCF-SOC calculations.

Atom	Basis set
Tb	SARC2-DKH-QZVP <sup>2</sup>
Coordinating N	DKH-Def2-TZVP <sup>3</sup>
Remaining atoms	DKH-Def2-SVP <sup>3</sup>

**Table S3.** Mulliken charges on the coordinating N atoms.

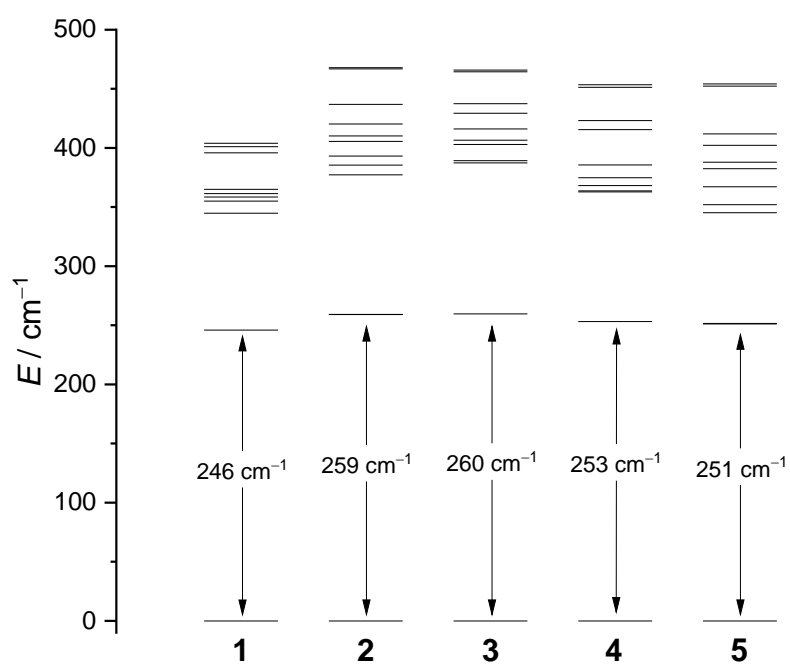
	1	2	3	4	5
Pc	-0.7479	-0.7525	-0.7472	-0.7720	-0.7719
	-0.7506	-0.7770	-0.7493	-0.7642	-0.8377
	-0.7410	-0.7559	-0.7643	-0.7857	-0.7694
	-0.7337	-0.7550	-0.7669	-0.7676	-0.8138
Average	-0.7433	-0.7601	-0.7570	-0.7724	-0.7982
TPyP	-0.8556	-0.8436	-0.8520	-0.8585	-0.8493
	-0.8726	-0.8452	-0.8554	-0.7988	-0.9242
	-0.8498	-0.8472	-0.8518	-0.8593	-0.8610
	-0.8524	-0.8511	-0.8526	-0.7925	-0.9164
Average	-0.8576	-0.8468	-0.8530	-0.8273	-0.8877



**Fig. S6** Magnetic easy axis of the ground quasi-doublet states of **1-5** derived from CASSCF-SO calculations.

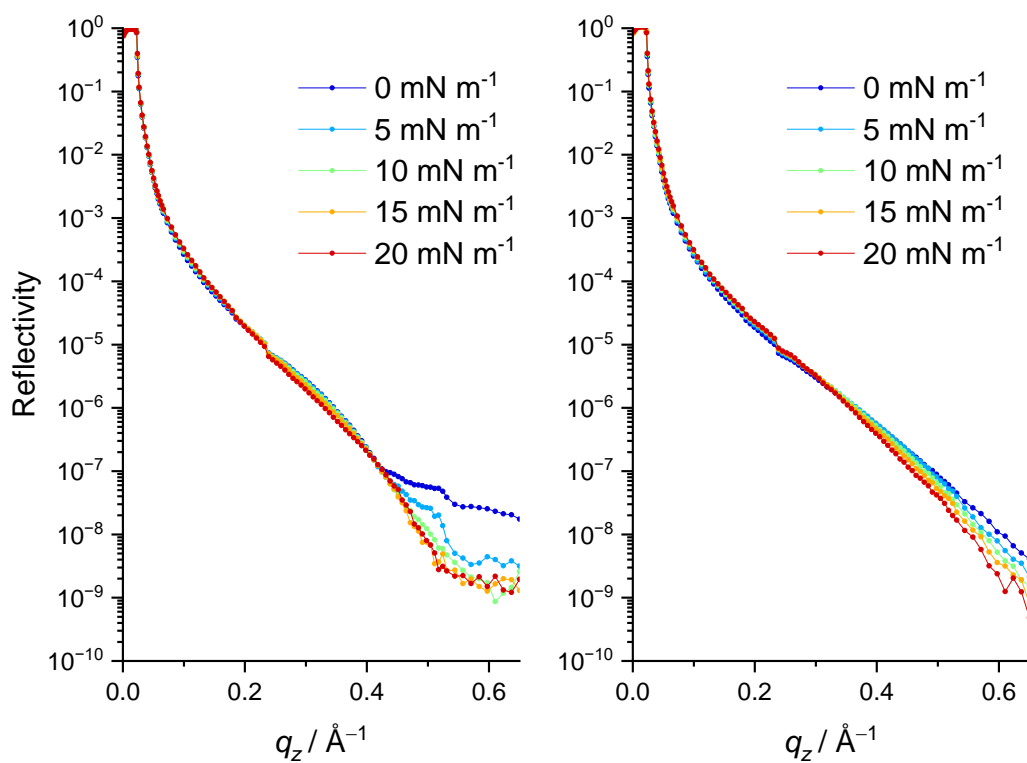




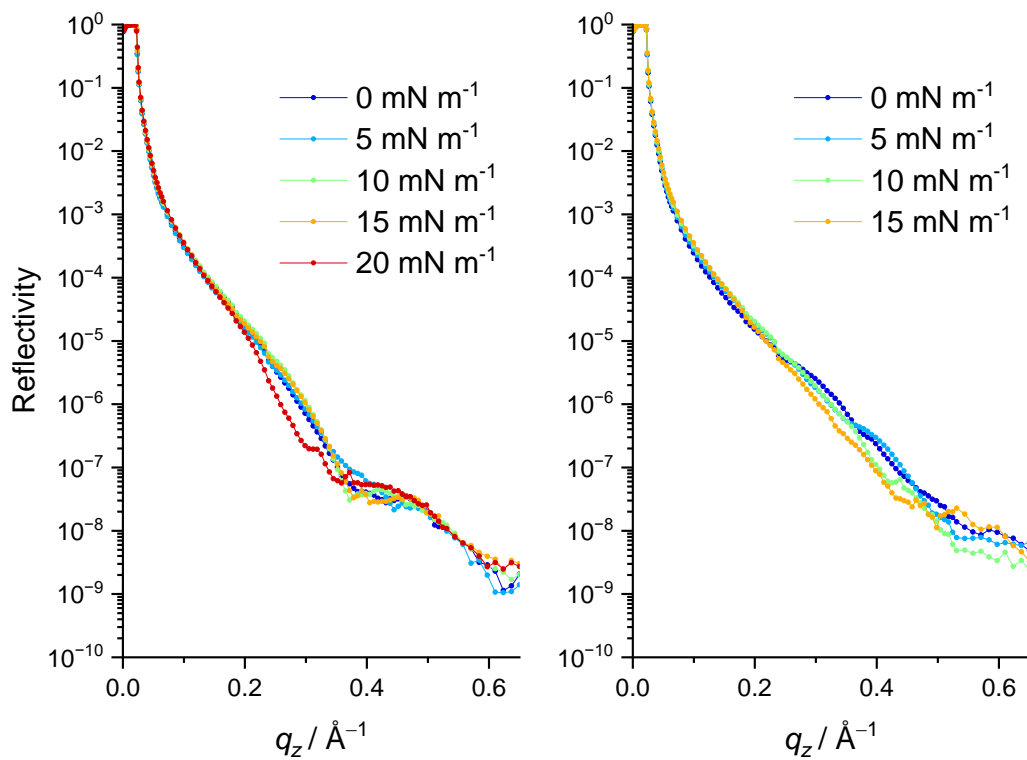


**Fig. S7** Ligand-field energy diagram of **1-5** based on CASSCF-SO calculations.

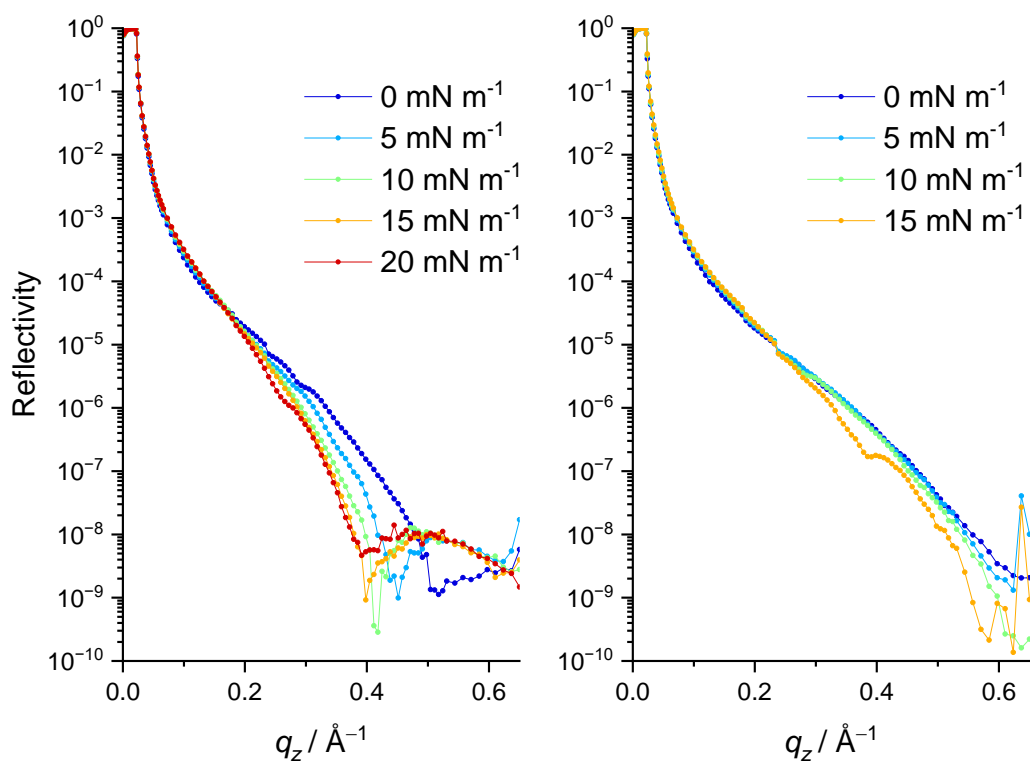




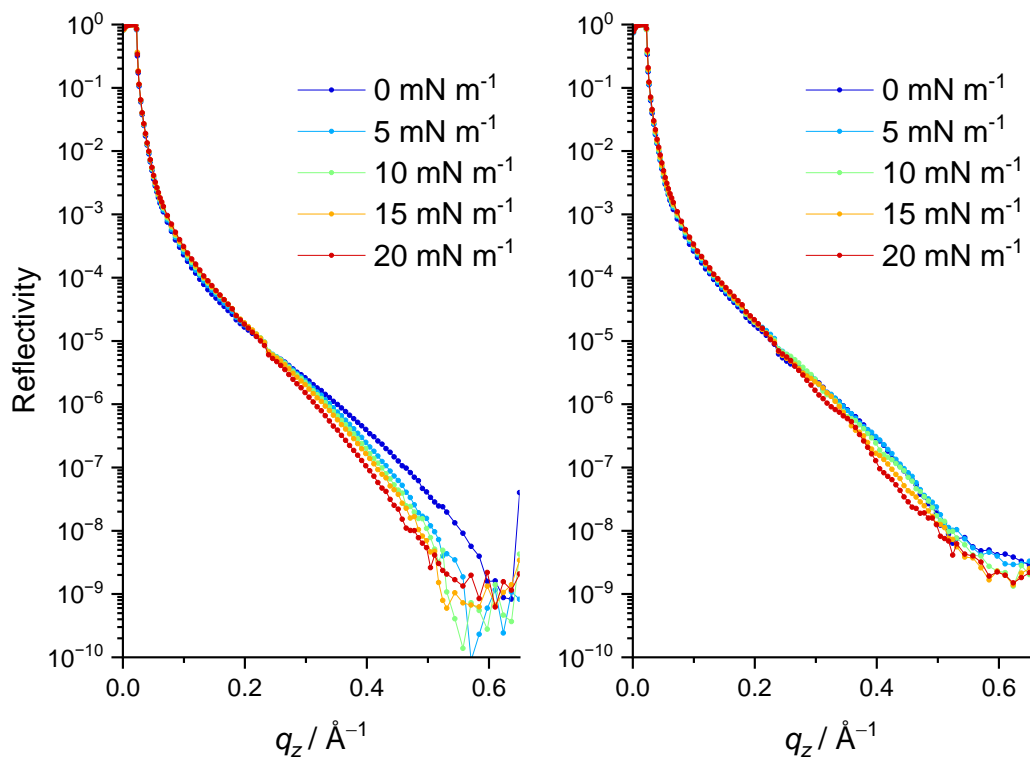
**Fig. S8** X-ray reflectivity of **1** on ultra-pure water (left) and  $\text{Na}_2[\text{PdCl}_4]$  aq. (right)



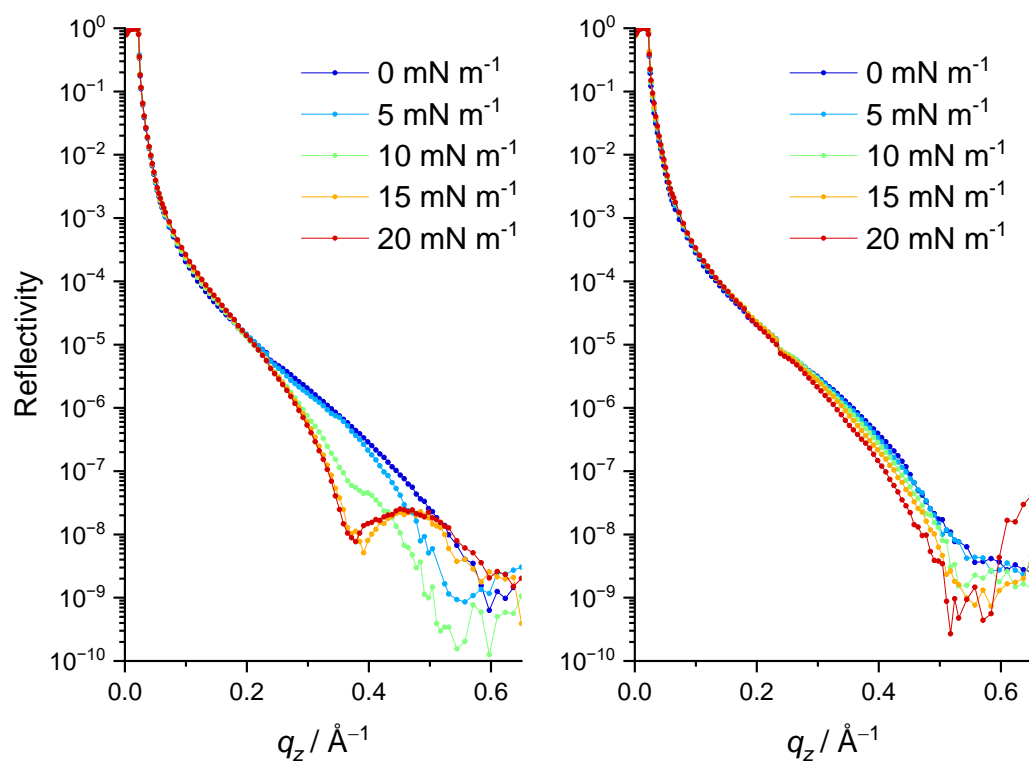
**Fig. S9** X-ray reflectivity of **2** on ultra-pure water (left) and  $\text{Na}_2[\text{PdCl}_4]$  aq. (right)



**Fig. S10** X-ray reflectivity of **3** on ultra-pure water (left) and  $\text{Na}_2[\text{PdCl}_4]$  aq. (right)

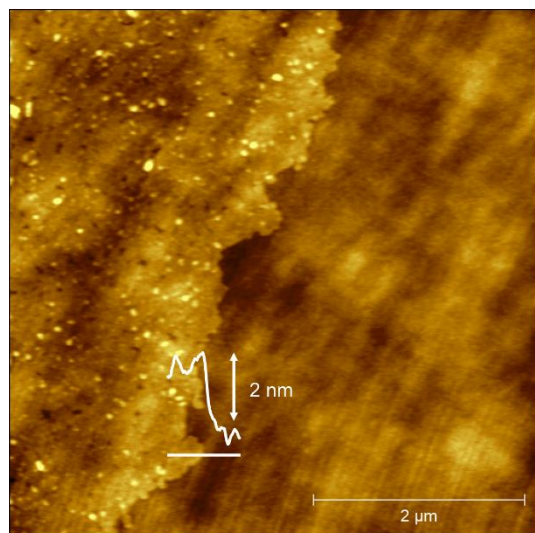


**Fig. S11** X-ray reflectivity of **4** on ultra-pure water (left) and  $\text{Na}_2[\text{PdCl}_4]$  aq. (right)

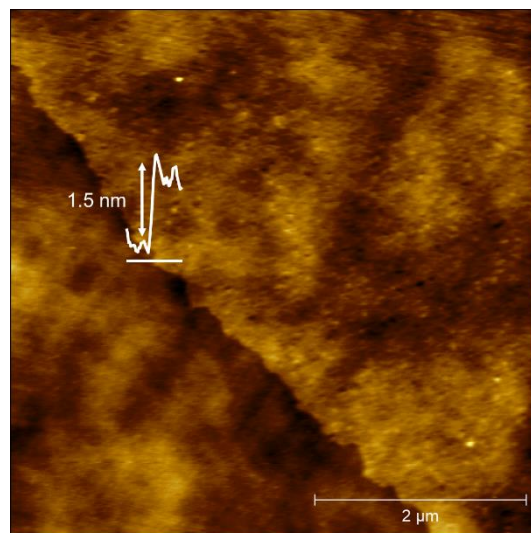


**Fig. S12** X-ray reflectivity of **5** on ultra-pure water (left) and  $\text{Na}_2[\text{PdCl}_4]$  aq. (right)

(a)

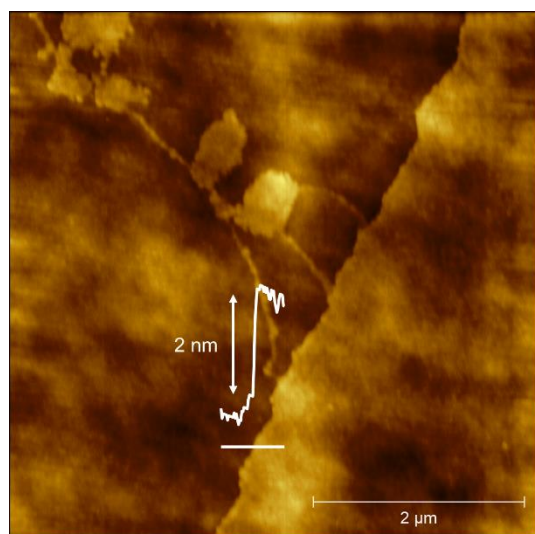


(b)

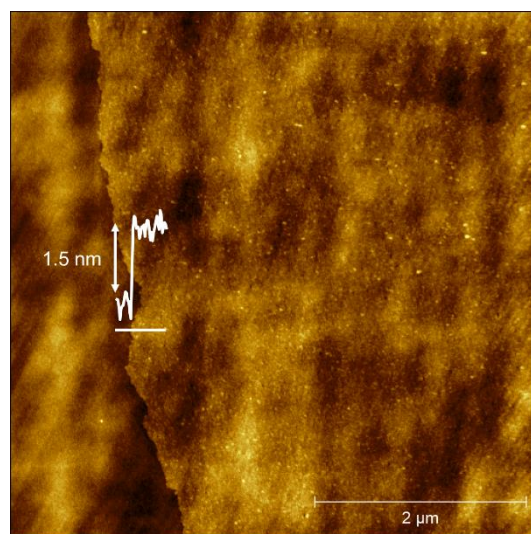


**Fig. S13** AFM image of (a)  $1^{aq}$  and (b)  $1^{Pd}$  on the Si wafer.

(a)

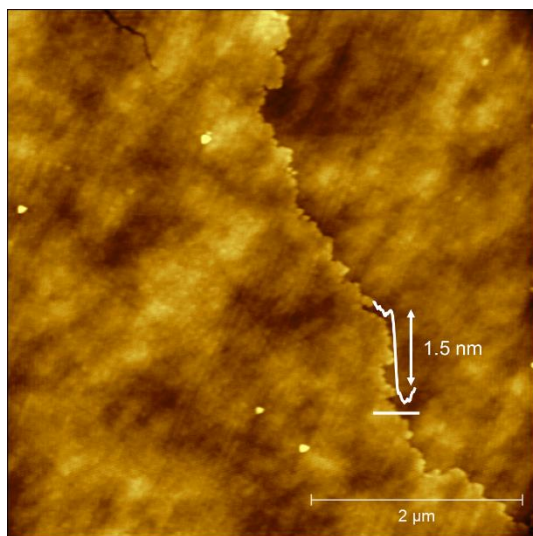


(b)

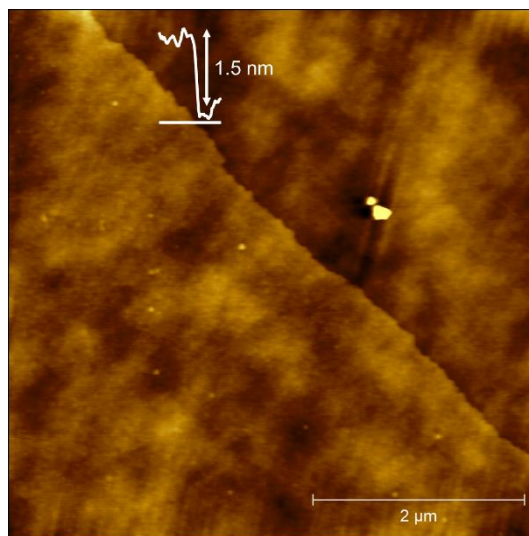


**Fig. S14** AFM image of (a)  $2^{aq}$  and (b)  $2^{Pd}$  on the Si wafer.

(a)

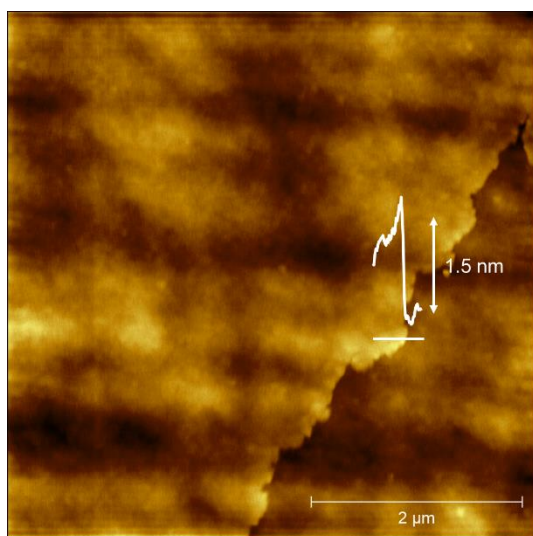


(b)

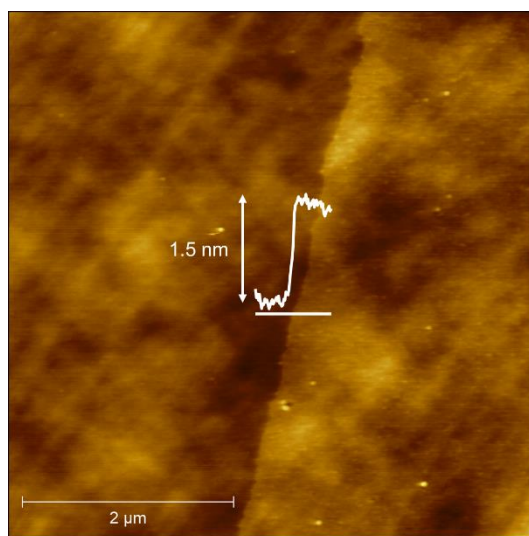


**Fig. S15** AFM image of (a)  $3^{aq}$  and (b)  $3^{Pd}$  on the Si wafer.

(a)



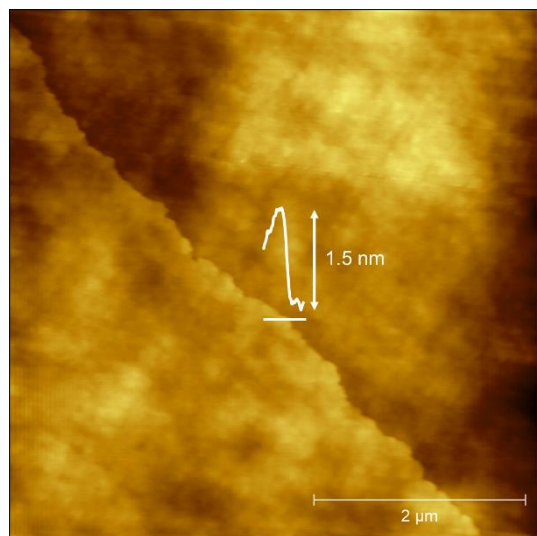
(b)



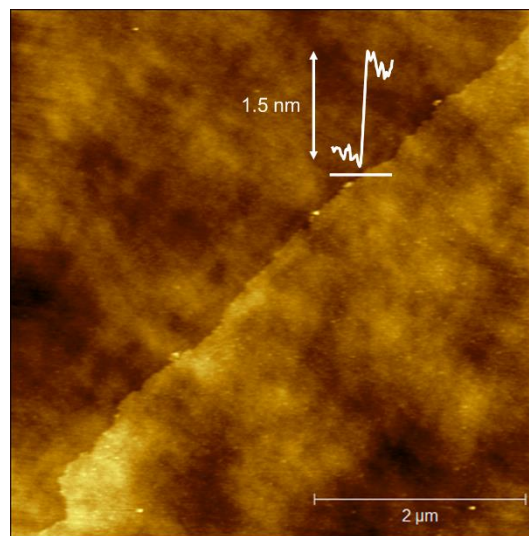
**Fig. S16** AFM image of (a)  $4^{aq}$  and (b)  $4^{Pd}$  on the Si wafer.



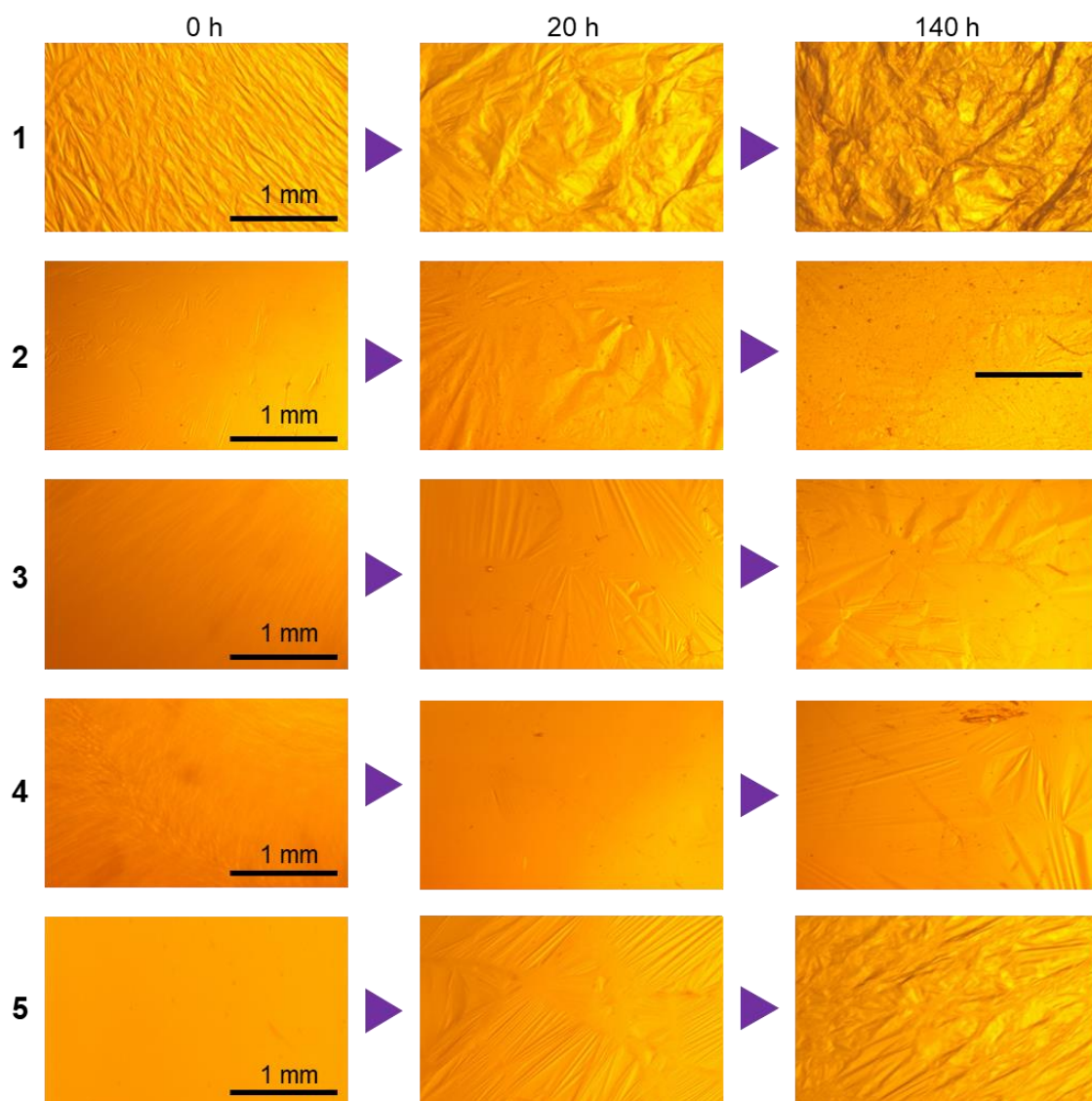
(a)



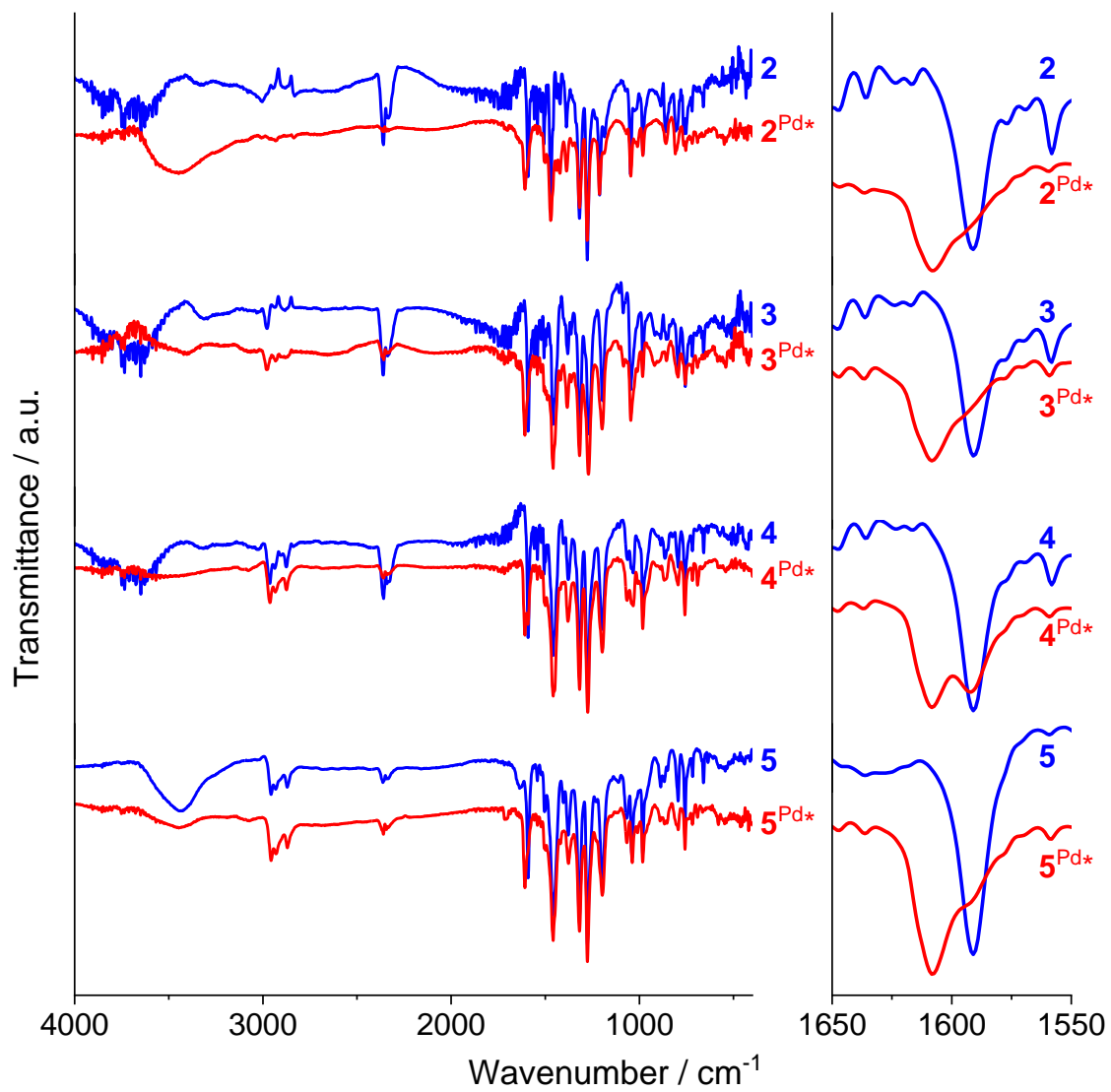
(b)



**Fig. S17** AFM image of (a)  $5^{aq}$  and (b)  $5^{Pd}$  on the Si wafer.

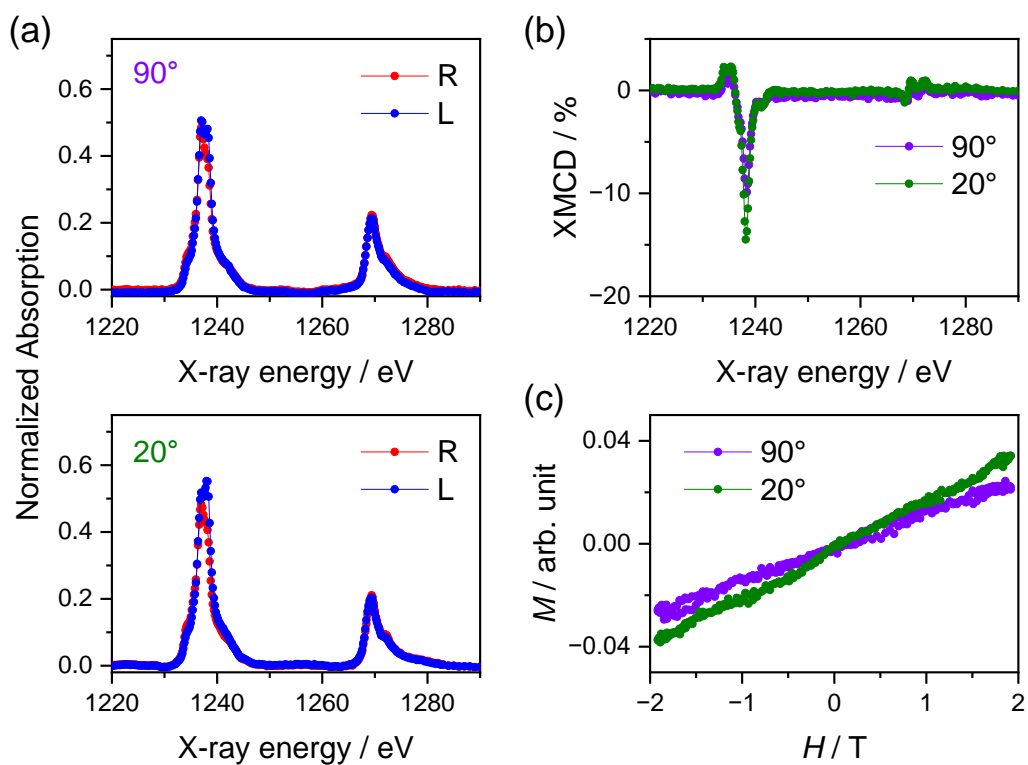


**Fig. S18** Optical microscope images of the liquid-liquid interface of the SMM solution and  $\text{Na}_2[\text{PdCl}_4]$  aq. The thickness of the film seemed to be increased over time. The images for **1** were taken from ref. 1.

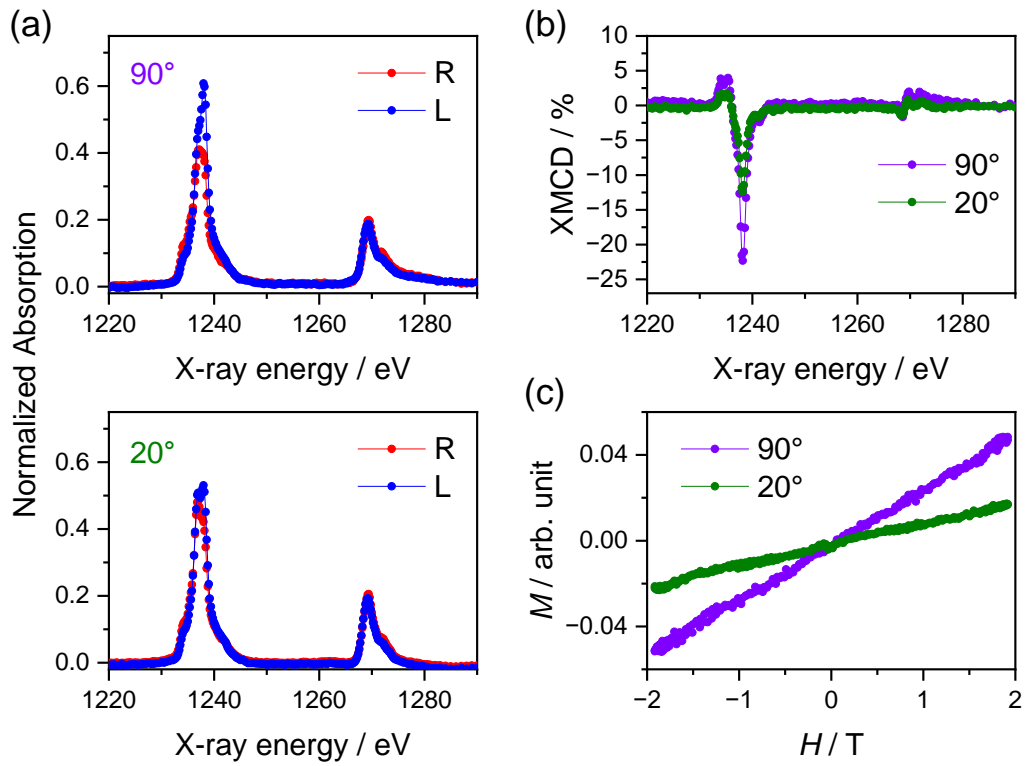


**Fig. S19** IR spectra for 2-5 and 2<sup>Pd\*</sup>-5<sup>Pd\*</sup> acquired using KBr pellet method. Enlarged spectra corresponding to the C=C stretching modes of Py units are shown for comparison.

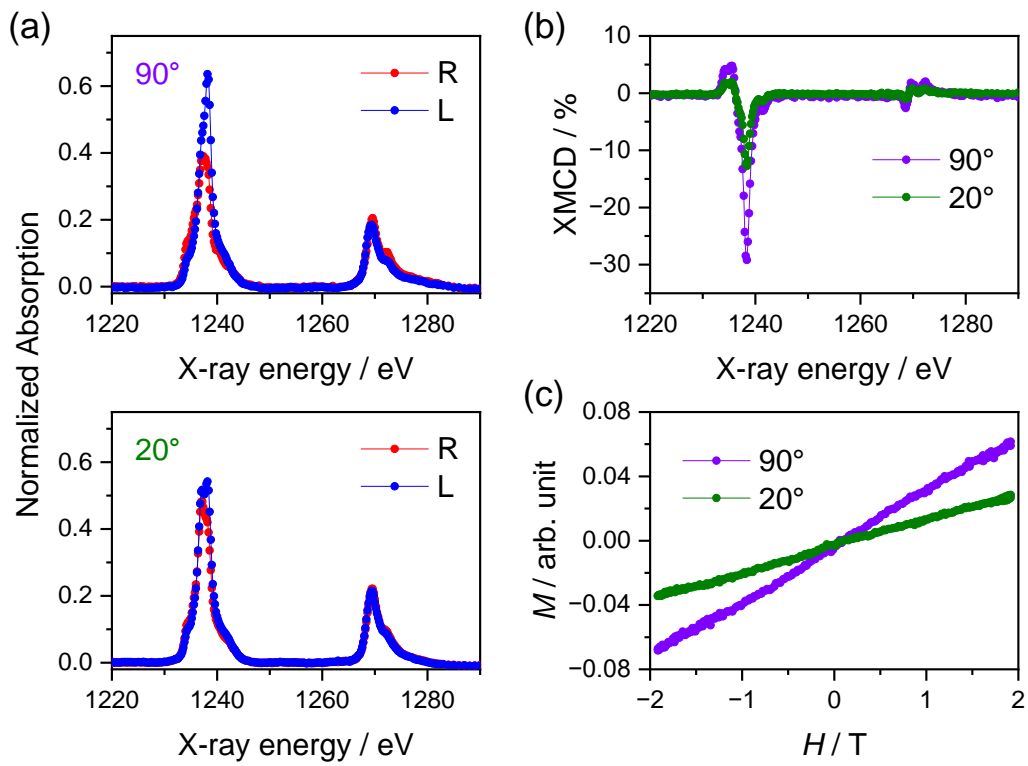




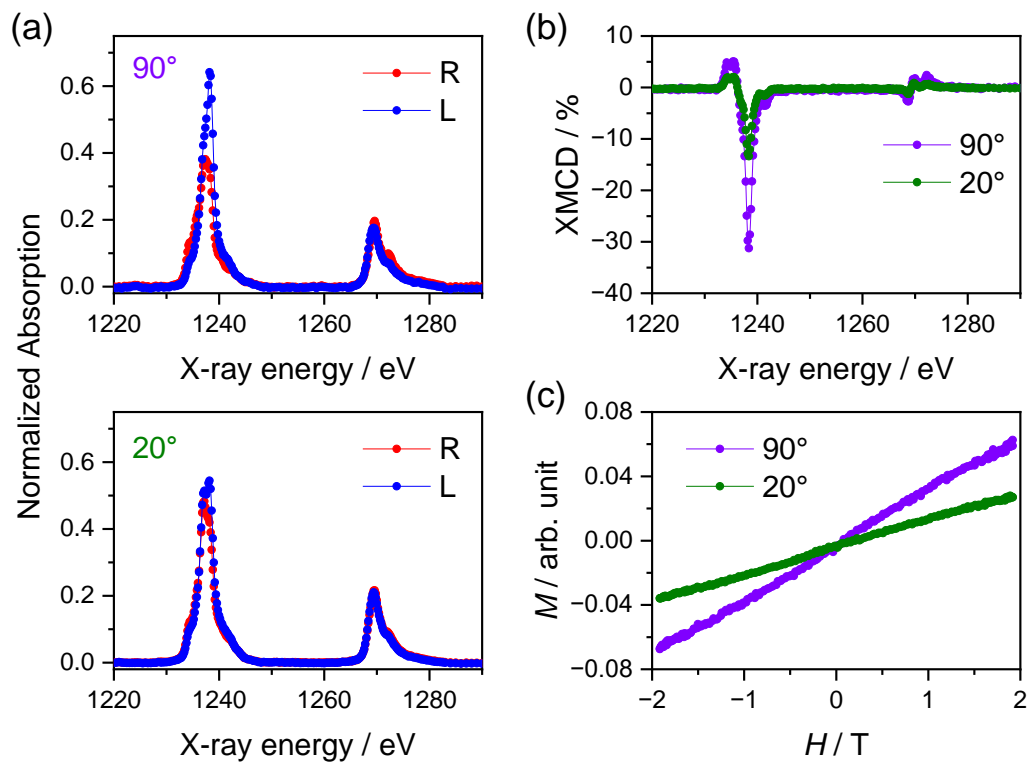
**Fig. S20** (a) Normalized X-ray absorption, (b) XMCD spectra of  $2^{aq}$  deposited on the Si wafer measured at 11 K in the Tb  $M_{4,5}$  region in an applied field of 1.9 T. Magnetic field was applied perpendicular ( $90^\circ$ ) and in-plane ( $20^\circ$ ) direction. (c)  $M$  vs.  $H$  curves derived from H-dependence of the XMCD intensity.



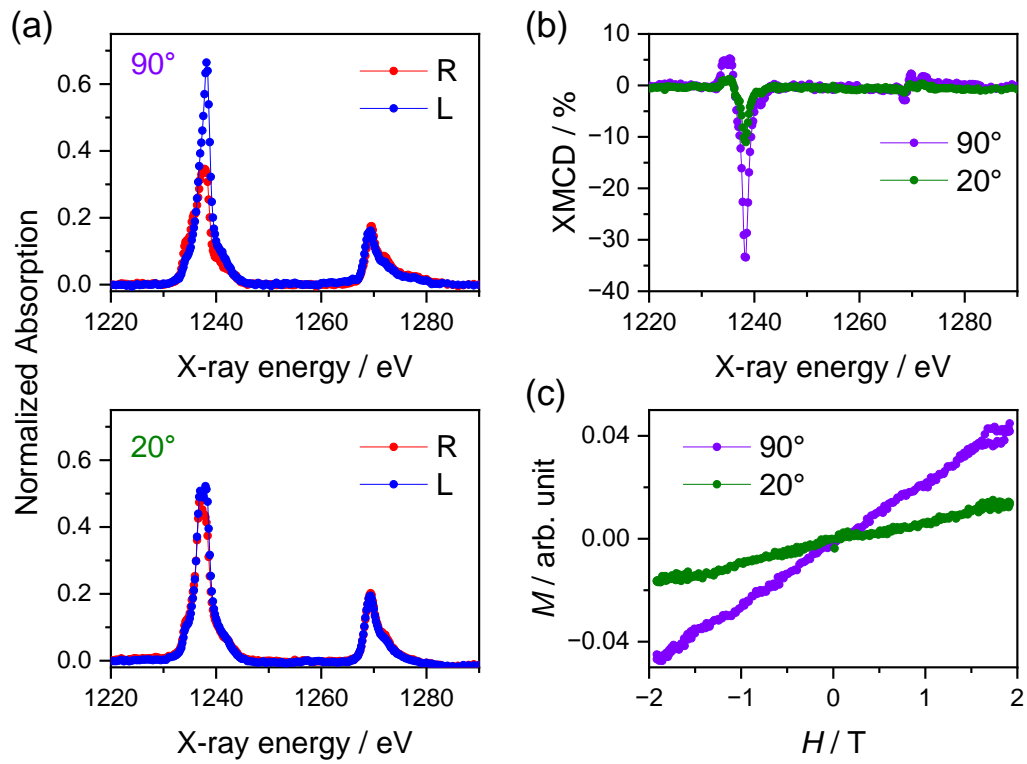
**Fig. S21** (a) Normalized X-ray absorption, (b) XMCD spectra of  $3^{aq}$  deposited on the Si wafer measured at 11 K in the Tb  $M_{4,5}$  region in an applied field of 1.9 T. Magnetic field was applied perpendicular ( $90^\circ$ ) and in-plane ( $20^\circ$ ) direction. (c)  $M$  vs.  $H$  curves derived from H-dependence of the XMCD intensity.



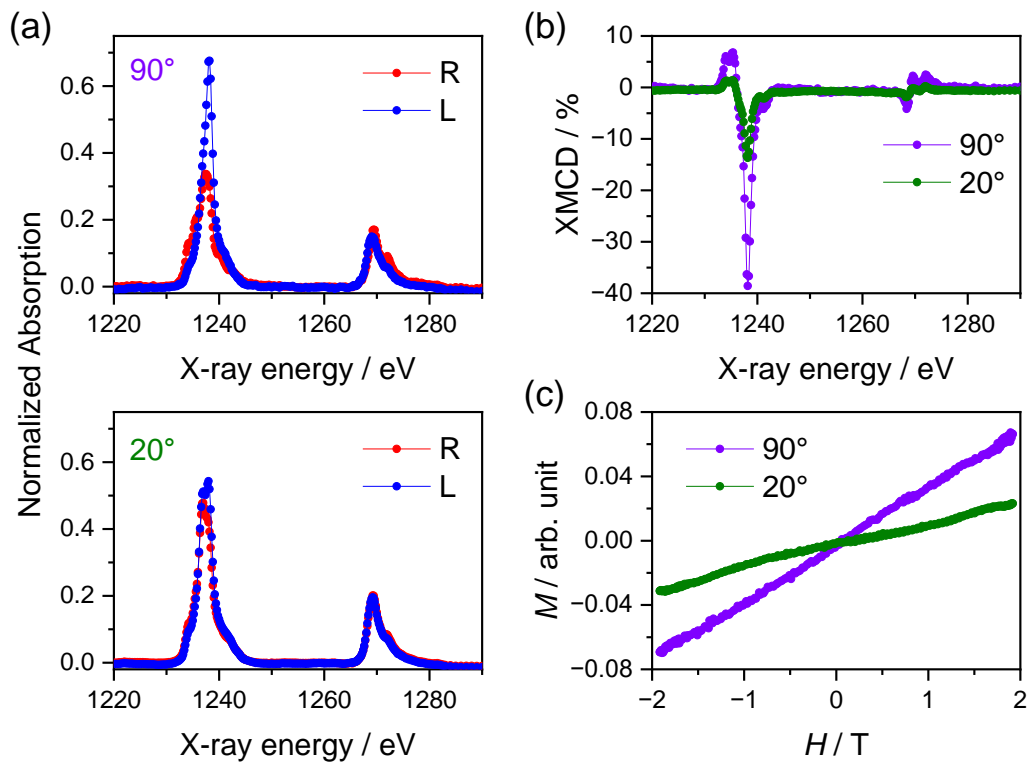
**Fig. S22** (a) Normalized X-ray absorption, (b) XMCD spectra of  $4^{\text{aq}}$  deposited on the Si wafer measured at 11 K in the Tb  $M_{4,5}$  region in an applied field of 1.9 T. Magnetic field was applied perpendicular ( $90^\circ$ ) and in-plane ( $20^\circ$ ) direction. (c)  $M$  vs.  $H$  curves derived from H-dependence of the XMCD intensity.



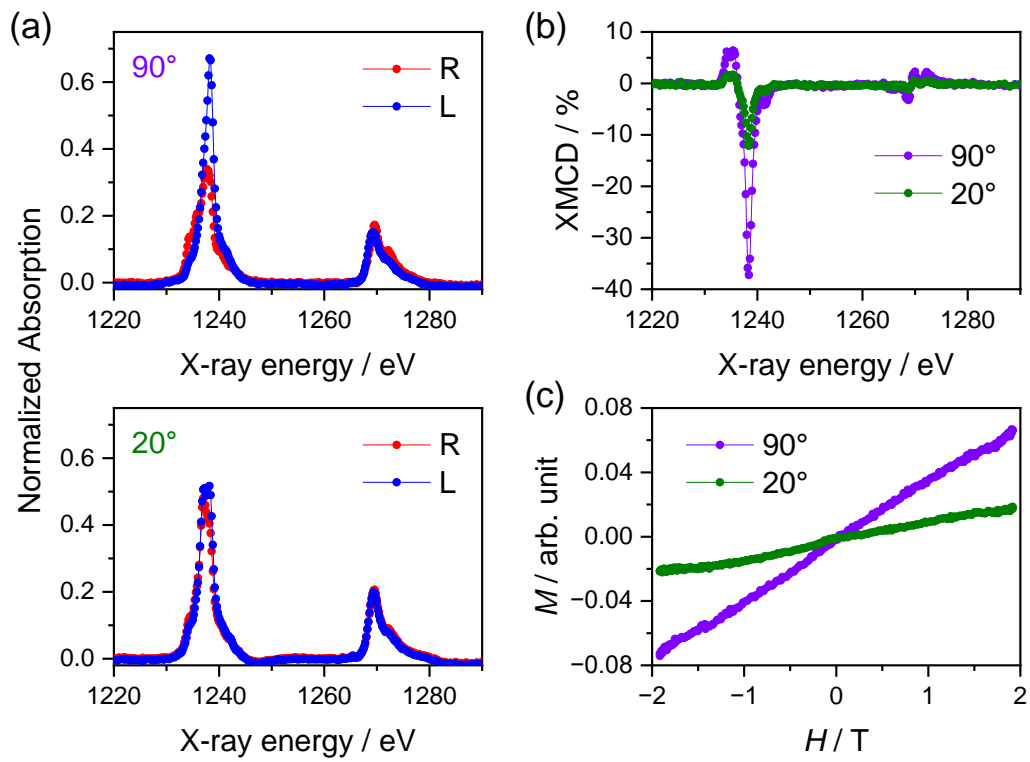
**Fig. S23** (a) Normalized X-ray absorption, (b) XMCD spectra of  $5^{\text{aq}}$  deposited on the Si wafer measured at 11 K in the Tb  $M_{4,5}$  region in an applied field of 1.9 T. Magnetic field was applied perpendicular ( $90^\circ$ ) and in-plane ( $20^\circ$ ) direction. (c)  $M$  vs.  $H$  curves derived from H-dependence of the XMCD intensity.



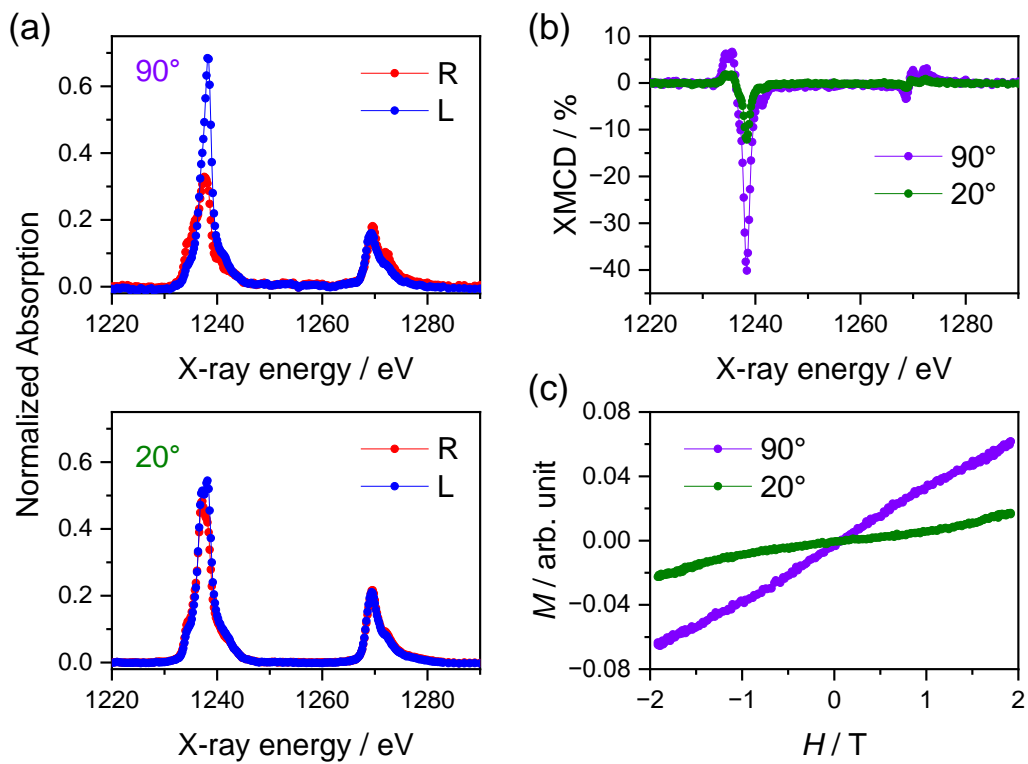
**Fig. S24** (a) Normalized X-ray absorption, (b) XMCD spectra of  $2^{\text{Pd}}$  deposited on the Si wafer measured at 11 K in the Tb  $M_{4,5}$  region in an applied field of 1.9 T. Magnetic field was applied perpendicular ( $90^\circ$ ) and in-plane ( $20^\circ$ ) direction. (c)  $M$  vs.  $H$  curves derived from H-dependence of the XMCD intensity.



**Fig. S25** (a) Normalized X-ray absorption, (b) XMCD spectra of  $3^{\text{Pd}}$  deposited on the Si wafer measured at 11 K in the Tb  $M_{4,5}$  region in an applied field of 1.9 T. Magnetic field was applied perpendicular ( $90^\circ$ ) and in-plane ( $20^\circ$ ) direction. (c)  $M$  vs.  $H$  curves derived from H-dependence of the XMCD intensity.

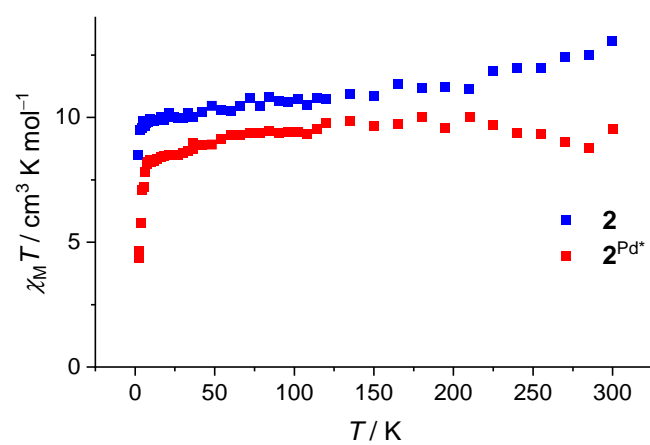


**Fig. S26** (a) Normalized X-ray absorption, (b) XMCD spectra of  $4^{\text{Pd}}$  deposited on the Si wafer measured at 11 K in the Tb  $M_{4,5}$  region in an applied field of 1.9 T. Magnetic field was applied perpendicular ( $90^\circ$ ) and in-plane ( $20^\circ$ ) direction. (c)  $M$  vs.  $H$  curves derived from H-dependence of the XMCD intensity.

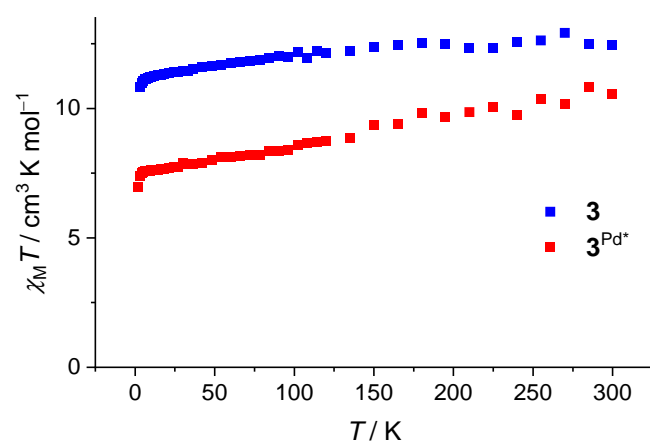


**Fig. S27** (a) Normalized X-ray absorption, (b) XMCD spectra of  $5^{\text{Pd}}$  deposited on the Si wafer measured at 11 K in the Tb  $M_{4,5}$  region in an applied field of 1.9 T. Magnetic field was applied perpendicular ( $90^\circ$ ) and in-plane ( $20^\circ$ ) direction. (c)  $M$  vs.  $H$  curves derived from H-dependence of the XMCD intensity.

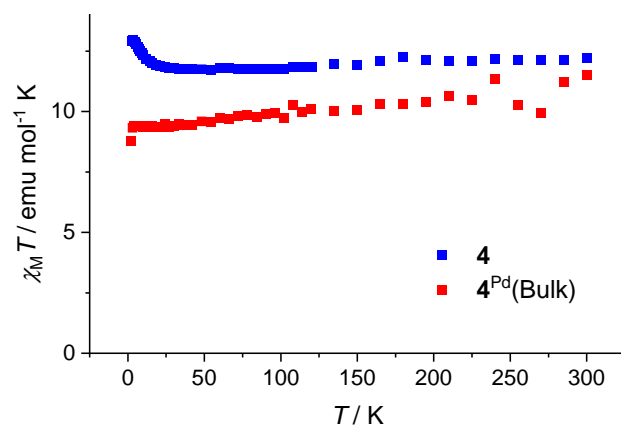




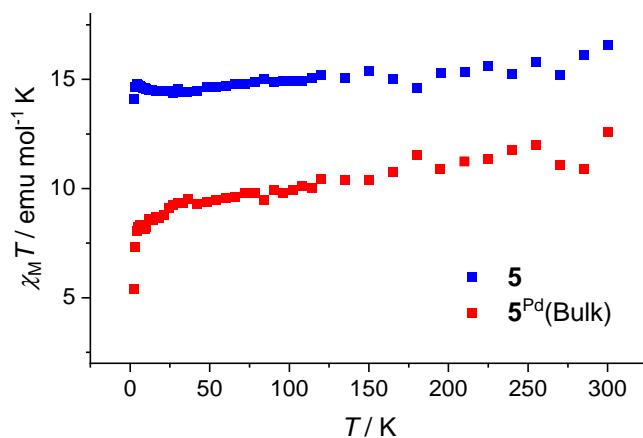
**Fig. S28**  $\chi_M T$  vs.  $T$  plots for **2** and **2<sup>Pd\*</sup>** at 1 kOe.  $\chi_M T$  values were calculated based on the composition of  $C_{80}H_{56}N_{16}O_8Tb \cdot 2(CH_2Cl_2)$  for **2** and  $[C_{80}H_{56}N_{16}O_8TbPd][PdCl_4]$  (2+ densely-packed structure with a 2- counter anion) for **2<sup>Pd\*</sup>**.



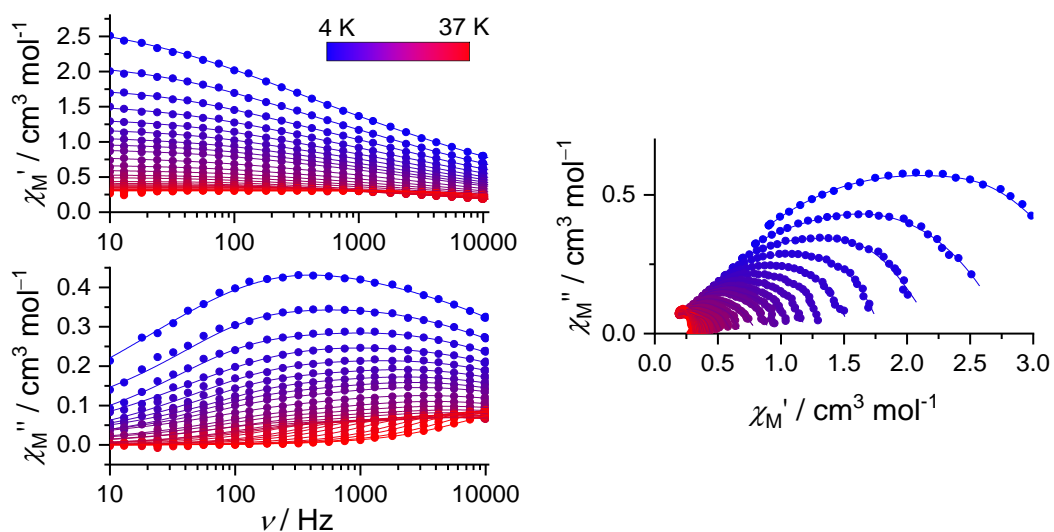
**Fig. S29**  $\chi_M T$  vs.  $T$  plots for **3** and **3<sup>Pd\*</sup>** at 1 kOe.  $\chi_M T$  values were calculated based on the composition of  $C_{88}H_{72}N_{16}O_8Tb \cdot 3(CH_2Cl_2)$  for **3** and charge neutral  $C_{88}H_{72}N_{16}O_8TbPd_2Cl_4$  for **3<sup>Pd\*</sup>**.



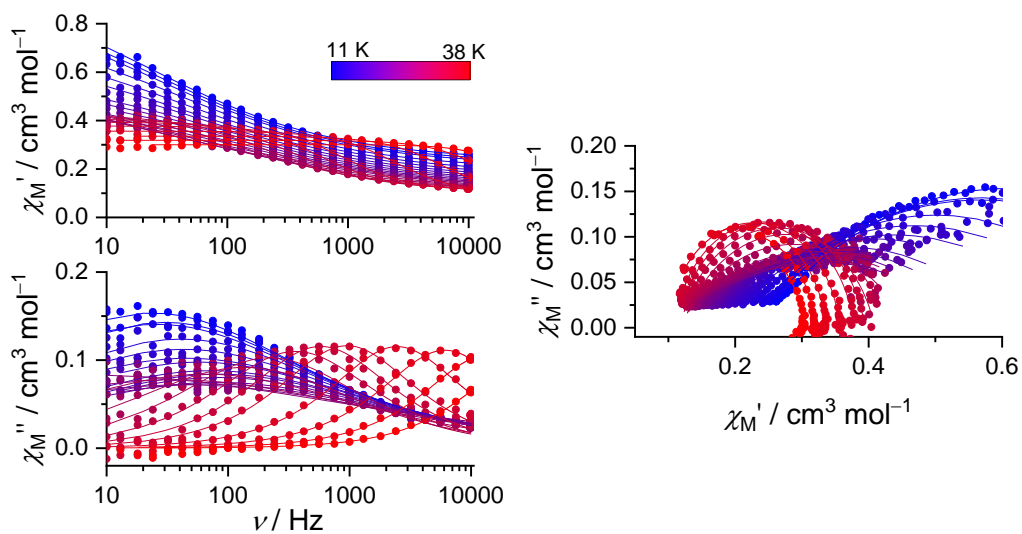
**Fig. S30**  $\chi_M T$  vs.  $T$  plots for **4** and **4<sup>Pd\*</sup>** at 1 kOe.  $\chi_M T$  values were calculated based on the composition of  $C_9H_{88}N_{16}O_8Tb \cdot 2(CH_2Cl_2) \cdot (C_6H_{14})$  for **4** and charge neutral  $C_9H_{88}N_{16}O_8TbPd_2Cl_4$  for **4<sup>Pd\*</sup>**. **4** exhibited an increase in  $\chi_M T$  values due to intermolecular ferromagnetic interactions.



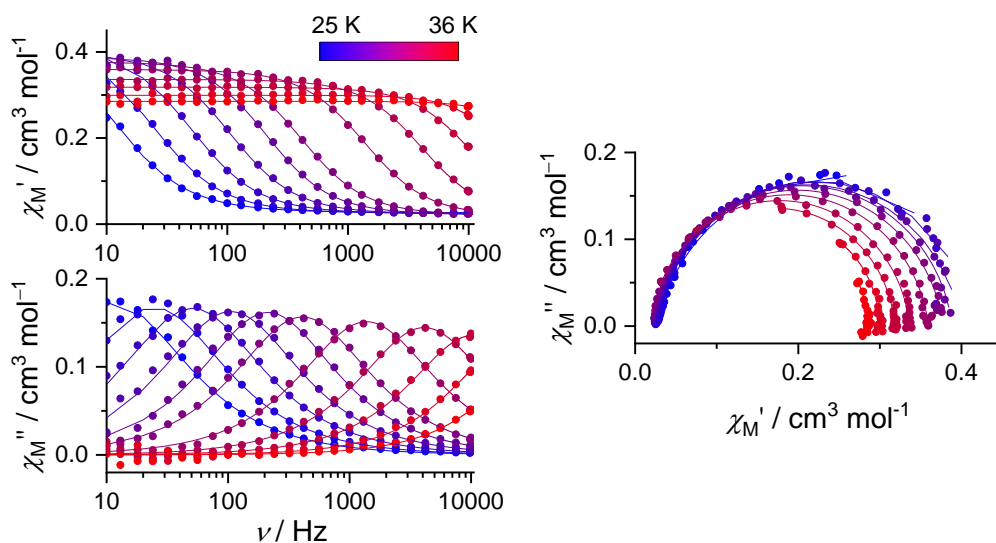
**Fig. S31**  $\chi_M T$  vs.  $T$  plots for **5** and **5<sup>Pd\*</sup>** at 1 kOe.  $\chi_M T$  values were calculated based on the composition of  $C_{104}H_{104}N_{16}O_8Tb \cdot 3(CH_2Cl_2)$  for **5** and charge neutral  $C_{104}H_{104}N_{16}O_8TbPd_2Cl_4$  for **5<sup>Pd\*</sup>**.



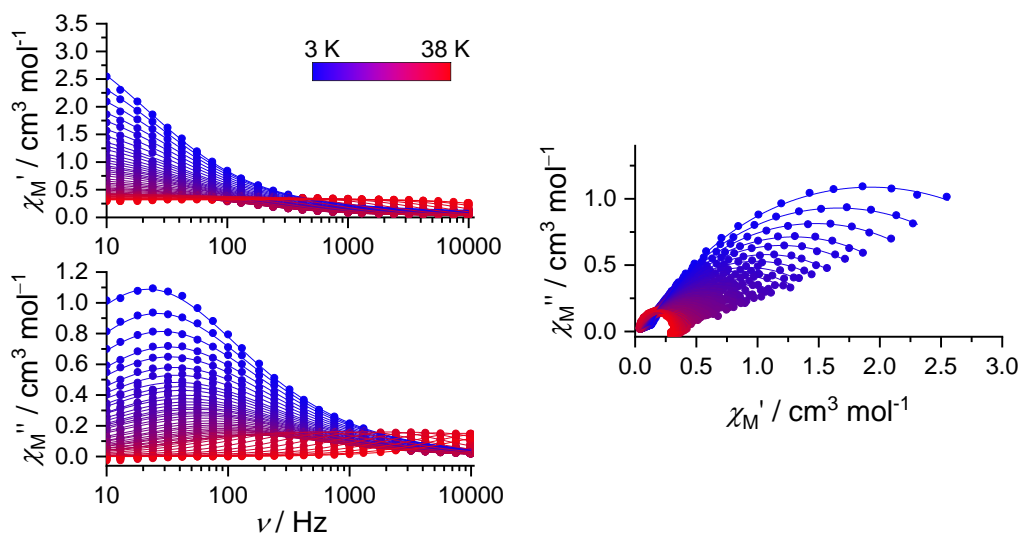
**Fig. S32** AC magnetic susceptibility (left) and Argand plots (right) for **2** in a zero dc magnetic field. Solid curves represent a fit using extended Debye model.



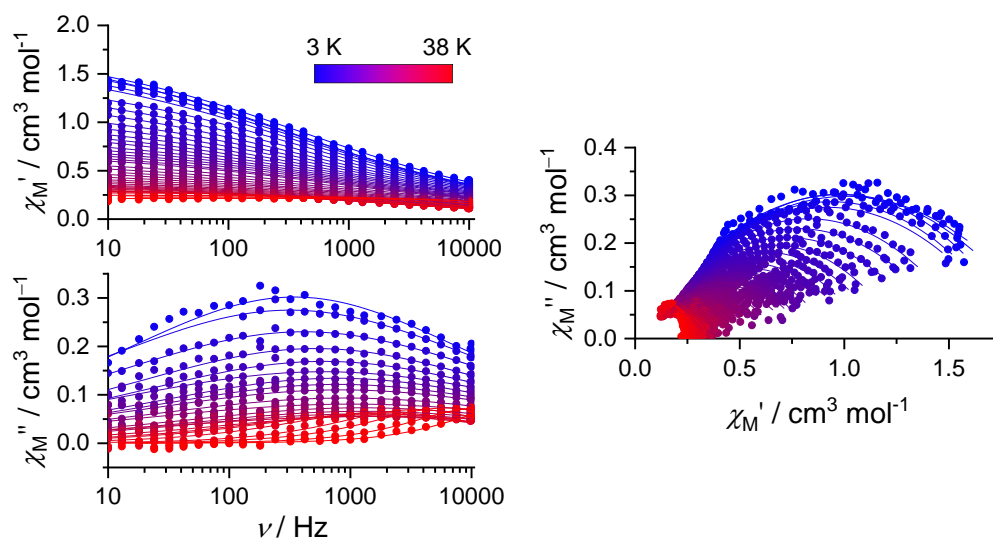
**Fig. S33** AC magnetic susceptibility (left) and Argand plots (right) for **3** in a zero dc magnetic field. Solid curves represent a fit using generalized Debye model.



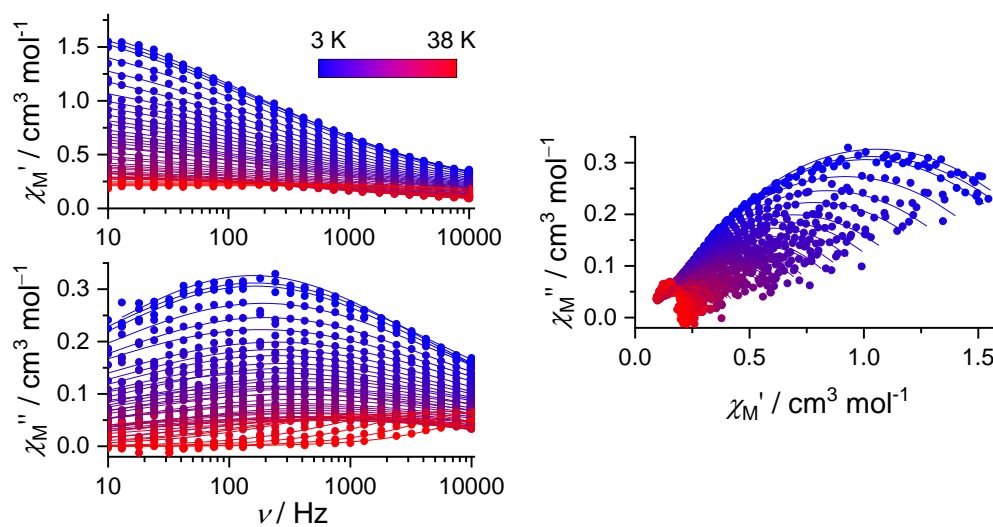
**Fig. S34** AC magnetic susceptibility (left) and Argand plots (right) for **4** in a zero dc magnetic field. Solid curves represent a fit using generalized Debye model.



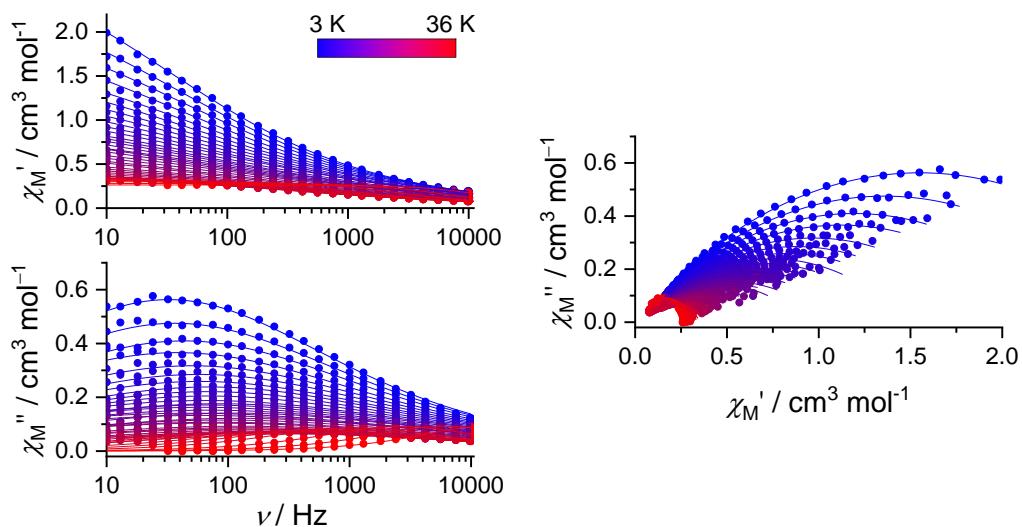
**Fig. S35** AC magnetic susceptibility (left) and Argand plots (right) for **5** in a zero dc magnetic field. Solid curves represent a fit using generalized Debye model.



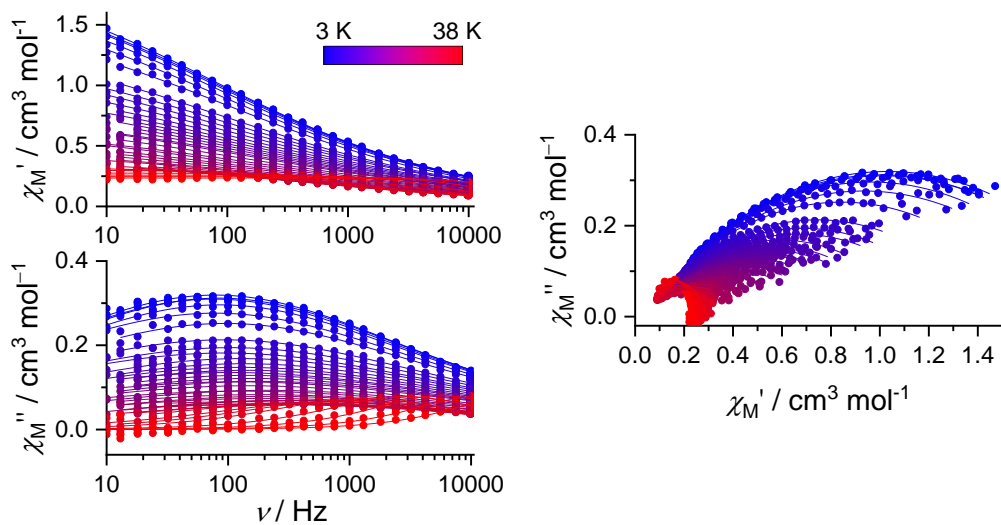
**Fig. S36** AC magnetic susceptibility (left) and Argand plots (right) for  $2^{Pd*}$  in a zero dc magnetic field. Solid curves represent a fit using generalized Debye model.



**Fig. S37** AC magnetic susceptibility (left) and Argand plots (right) for  $3^{Pd*}$  in a zero dc magnetic field. Solid curves represent a fit using generalized Debye model.



**Fig. S38** AC magnetic susceptibility (left) and Argand plots (right) for  $4^{\text{Pd}^*}$  in a zero dc magnetic field. Solid curves represent a fit using generalized Debye model.



**Fig. S39** AC magnetic susceptibility (left) and Argand plots (right) for  $5^{\text{Pd}^*}$  in a zero dc magnetic field. Solid curves represent a fit using generalized Debye model.

**Table S8.** Parameters obtained by fitting the  $\chi_M'$  and  $\chi_M''$  vs.  $\nu$  plots of **2** at zero dc field using extended Debye model.

$T / \text{K}$	$\chi_T / \text{cm}^3 \text{mol}^{-1}$	$\chi_s / \text{cm}^3 \text{mol}^{-1}$	$\tau_1 / \text{s}$	$\alpha_1$	$\tau_2 / \text{s}$	$\alpha_2$	$g$
4.0	2.79(3)	0.21(2)	$8(4) \times 10^{-4}$	0.51(3)	$2(1) \times 10^{-5}$	0.5(2)	0.7(3)
5.0	2.23(4)	0.13(4)	$1.4(2) \times 10^{-4}$	0.1(2)	$1.2(4) \times 10^{-4}$	0.60(1)	0.07(6)
6.0	1.80(3)	0.17(5)	$1.5(2) \times 10^{-3}$	0.2(2)	$7(4) \times 10^{-5}$	0.54(5)	0.2(2)
7.0	1.56(2)	0.1(2)	$8(7) \times 10^{-4}$	0.4(2)	$3(5) \times 10^{-5}$	0.5(2)	0.4(7)
8.0	1.35(3)	0.1(1)	$9(5) \times 10^{-4}$	0.3(2)	$3(4) \times 10^{-5}$	0.5(2)	0.3(5)
9.0	1.22(1)	0.10(2)	$1.1(1) \times 10^{-3}$	0.1(2)	$5(1) \times 10^{-5}$	0.56(2)	0.08(5)
10.0	1.11(1)	0.08(2)	$9(1) \times 10^{-4}$	0.05(17)	$5(1) \times 10^{-5}$	0.58(1)	0.05(3)
11.0	0.99(2)	0.11(3)	$1.1(2) \times 10^{-3}$	0.1(3)	$5(2) \times 10^{-5}$	0.53(5)	0.1(1)
12.0	0.93(1)	0.08(2)	$1.0(2) \times 10^{-3}$	0	$4.9(9) \times 10^{-5}$	0.57(2)	0.04(3)
14.0	0.820(7)	0.046(9)	$10(1) \times 10^{-4}$	0	$4.6(5) \times 10^{-5}$	0.60(1)	0.02(2)
16.0	0.68(1)	0.08(3)	$10(2) \times 10^{-4}$	0.05(39)	$4(1) \times 10^{-5}$	0.54(5)	0.06(8)
18.0	0.62(1)	0.06(2)	$9(2) \times 10^{-4}$	0	$3.2(8) \times 10^{-5}$	0.55(3)	0.05(5)
20.0	0.54(1)	0.06(4)	$6(2) \times 10^{-4}$	0.2(4)	$2(1) \times 10^{-5}$	0.5(1)	0.1(2)
22.0	0.501(9)	0.08(3)	$1.1(2) \times 10^{-3}$	0.04(27)	$3.0(5) \times 10^{-5}$	0.50(8)	0.08(9)
24.0	0.440(4)	0.10(3)	$6(1) \times 10^{-4}$	0.07(20)	$2.3(5) \times 10^{-5}$	0.4(1)	0.2(2)
26.0	0.414(7)	0.08(6)	$5(2) \times 10^{-4}$	0.1(3)	$1.8(9) \times 10^{-5}$	0.4(3)	0.2(4)
28.0	0.393(4)	0.09(4)	$4(1) \times 10^{-4}$	0.1(2)	$2.1(8) \times 10^{-5}$	0.4(2)	0.2(3)
29.0	0.377(4)	0.10(4)	$4(1) \times 10^{-4}$	0	$2.4(7) \times 10^{-5}$	0.3(2)	0.2(3)
30.0	0.362(3)	0.11(5)	$2.3(5) \times 10^{-4}$	0	$1.8(7) \times 10^{-5}$	0.2(3)	0.3(4)
31.0	0.356(2)	0.11(4)	$1.7(9) \times 10^{-4}$	0.02(25)	$1.9(9) \times 10^{-5}$	0.2(3)	0.3(5)
32.0	0.348(1)	0.10(3)	$1.1(4) \times 10^{-4}$	0.03(19)	$1.6(7) \times 10^{-5}$	0.2(2)	0.3(4)
33.0	0.334(2)	0.12(6)	$8(5) \times 10^{-5}$	0	$1.3(5) \times 10^{-5}$	0.004(564)	0.4(7)
34.0	0.321(2)	0.1(4)	$0.4(10) \times 10^{-5}$	0	$9(9) \times 10^{-6}$	0	0.43
35.0	0.315(2)	0.1(6)	$3(9) \times 10^{-5}$	0	$0.6(10) \times 10^{-5}$	0	0.37
36.0	0.309(1)	0.12(1)	$1.3(1) \times 10^{-5}$	0.06(3)	0	0	1
37.0	0.3029(6)	0.10(1)	$8.1(9) \times 10^{-6}$	0.09(2)	0	0	1

\* fixed at  $0 \text{ cm}^3 \text{ mol}^{-1}$

**Table S9.** Parameters obtained by fitting the  $\chi_M'$  and  $\chi_M''$  vs.  $\nu$  plots of **3** at zero dc field using generalized Debye model.

$T / \text{K}$	$\chi_T / \text{cm}^3 \text{mol}^{-1}$	$\chi_S / \text{cm}^3 \text{mol}^{-1}$	$\tau / \text{s}$	$\alpha$
11.0	0.99(3)	0.231(5)	$6.7(9) \times 10^{-3}$	0.51(2)
11.5	0.92(2)	0.221(4)	$5.3(5) \times 10^{-3}$	0.51(1)
12.0	0.93(3)	0.209(5)	$6.1(8) \times 10^{-3}$	0.53(2)
13.0	0.81(2)	0.196(5)	$3.9(4) \times 10^{-3}$	0.51(2)
14.0	0.76(2)	0.176(5)	$3.7(4) \times 10^{-3}$	0.53(2)
15.0	0.72(2)	0.161(6)	$3.5(5) \times 10^{-3}$	0.55(2)
16.0	0.66(1)	0.154(4)	$2.8(2) \times 10^{-3}$	0.53(1)
17.0	0.61(2)	0.144(5)	$2.2(3) \times 10^{-3}$	0.54(2)
18.0	0.57(1)	0.138(4)	$2.0(2) \times 10^{-3}$	0.53(1)
19.0	0.55(1)	0.130(4)	$1.9(2) \times 10^{-3}$	0.54(1)
20.0	0.54(2)	0.119(7)	$2.0(3) \times 10^{-3}$	0.56(2)
21.0	0.54(2)	0.110(6)	$2.3(3) \times 10^{-3}$	0.58(2)
26.0	0.458(9)	0.117(5)	$1.17(9) \times 10^{-3}$	0.37(2)
27.0	0.432(5)	0.120(3)	$7.3(3) \times 10^{-4}$	0.26(2)
28.0	0.409(4)	0.117(4)	$4.4(2) \times 10^{-4}$	0.18(2)
29.0	0.395(2)	0.114(3)	$2.75(7) \times 10^{-4}$	0.12(1)
30.0	0.378(2)	0.109(3)	$1.67(4) \times 10^{-4}$	0.09(1)
32.0	0.357(2)	0.098(4)	$6.5(2) \times 10^{-5}$	0.07(1)
34.0	0.3356(7)	0.091(4)	$2.62(5) \times 10^{-5}$	0.06(1)
36.0	0.3187(5)	0.095(7)	$1.20(5) \times 10^{-5}$	0.04(1)
38.0	0.300(1)	0.12(4)	$7(2) \times 10^{-6}$	0

\* fixed at  $0 \text{ cm}^3 \text{mol}^{-1}$



**Table S10.** Parameters obtained by fitting the  $\chi_M'$  and  $\chi_M''$  vs.  $\nu$  plots of **4** at zero dc field using generalized Debye model.

$T / \text{K}$	$\chi_T / \text{cm}^3 \text{mol}^{-1}$	$\chi_S / \text{cm}^3 \text{mol}^{-1}$	$\tau / \text{s}$	$\alpha$
25.0	0.460(8)	0.0263(7)	$1.44(5) \times 10^{-2}$	0.51(2)
26.0	0.425(5)	0.0250(9)	$6.5(1) \times 10^{-3}$	0.51(1)
27.0	0.415(3)	0.0239(9)	$3.14(4) \times 10^{-3}$	0.53(2)
28.0	0.399(3)	0.023(1)	$1.51(2) \times 10^{-3}$	0.51(2)
29.0	0.389(2)	0.022(1)	$7.48(9) \times 10^{-4}$	0.53(2)
30.0	0.378(1)	0.020(1)	$3.89(3) \times 10^{-4}$	0.55(2)
32.0	0.3595(8)	0.018(1)	$1.16(1) \times 10^{-4}$	0.53(1)
34.0	0.336(1)	0.018(3)	$3.88(6) \times 10^{-5}$	0.54(2)
36.0	0.318(1)	0.02(1)	$1.53(8) \times 10^{-5}$	0.53(1)
38.0	0.299(1)	0.06(3)	$8(1) \times 10^{-6}$	0.54(1)

\* fixed at  $0 \text{ cm}^3 \text{mol}^{-1}$

**Table S11.** Parameters obtained by fitting the  $\chi_M'$  and  $\chi_M''$  vs.  $\nu$  plots of **5** at zero dc field using generalized Debye model.

$T / \text{K}$	$\chi_T / \text{cm}^3 \text{mol}^{-1}$	$\chi_S / \text{cm}^3 \text{mol}^{-1}$	$\tau / \text{s}$	$\alpha$
3.0	3.30(2)	0.090(4)	$7.2(1) \times 10^{-3}$	0.315(4)
3.5	2.84(2)	0.083(3)	$6.06(8) \times 10^{-3}$	0.317(3)
4.0	2.52(1)	0.075(2)	$5.51(7) \times 10^{-3}$	0.326(3)
4.5	2.21(1)	0.070(2)	$4.91(6) \times 10^{-3}$	0.326(3)
5.0	2.04(1)	0.065(2)	$4.77(6) \times 10^{-3}$	0.332(3)
5.5	1.83(1)	0.061(2)	$4.40(7) \times 10^{-3}$	0.335(4)
6.0	1.68(1)	0.059(2)	$4.23(7) \times 10^{-3}$	0.337(4)
6.5	1.56(2)	0.053(5)	$4.2(2) \times 10^{-3}$	0.35(1)
7.0	1.444(9)	0.055(2)	$3.86(7) \times 10^{-3}$	0.334(5)
7.5	1.373(9)	0.052(2)	$3.83(7) \times 10^{-3}$	0.337(5)
8.0	1.251(8)	0.053(2)	$3.48(5) \times 10^{-3}$	0.326(4)
8.5	1.215(8)	0.048(2)	$3.66(6) \times 10^{-3}$	0.343(4)
9.0	1.125(8)	0.049(2)	$3.35(6) \times 10^{-3}$	0.331(5)
9.5	0.359(4)	0.047(2)	$3.19(6) \times 10^{-3}$	0.26(2)
10.0	0.998(7)	0.046(2)	$3.02(6) \times 10^{-3}$	0.324(6)
10.5	0.960(4)	0.046(1)	$2.97(4) \times 10^{-3}$	0.320(4)
11.0	0.918(8)	0.042(2)	$2.91(7) \times 10^{-3}$	0.331(7)
11.5	0.878(7)	0.042(2)	$2.85(6) \times 10^{-3}$	0.326(6)
12.0	0.821(7)	0.0043(2)	$2.60(5) \times 10^{-3}$	0.313(7)
13.0	0.776(5)	0.040(2)	$2.54(5) \times 10^{-3}$	0.315(6)
14.0	0.703(6)	0.039(2)	$2.25(5) \times 10^{-3}$	0.300(7)
15.0	0.662(5)	0.037(2)	$2.15(4) \times 10^{-3}$	0.303(6)
16.0	0.614(5)	0.037(2)	$1.93(4) \times 10^{-3}$	0.288(8)
17.0	0.589(6)	0.034(2)	$1.89(5) \times 10^{-3}$	0.30(1)
18.0	0.544(6)	0.034(3)	$1.74(5) \times 10^{-3}$	0.29(1)
19.0	0.514(6)	0.032(3)	$1.57(5) \times 10^{-3}$	0.28(1)
20.0	0.491(3)	0.032(2)	$1.45(3) \times 10^{-3}$	0.272(7)
21.0	0.472(4)	0.030(2)	$1.41(3) \times 10^{-3}$	0.280(8)
22.0	0.439(2)	0.031(1)	$1.23(2) \times 10^{-3}$	0.258(6)
23.0	0.419(3)	0.028(2)	$1.17(3) \times 10^{-3}$	0.27(1)
24.0	0.388(6)	0.029(3)	$9.9(4) \times 10^{-4}$	0.24(2)
25.0	0.392(3)	0.028(2)	$1.00(2) \times 10^{-3}$	0.249(9)
26.0	0.394(3)	0.027(2)	$9.5(2) \times 10^{-4}$	0.24(1)

27.0	0.385(4)	0.028(3)	$8.1(2) \times 10^{-4}$	0.22(1)
28.0	0.377(3)	0.030(2)	$6.4(1) \times 10^{-4}$	0.17(1)
29.0	0.368(3)	0.031(3)	$4.6(1) \times 10^{-4}$	0.12(1)
30.0	0.354(2)	0.031(3)	$3.06(7) \times 10^{-4}$	0.08(1)
31.0	0.341(2)	0.031(3)	$1.95(5) \times 10^{-4}$	0.05(1)
32.0	0.333(2)	0.027(3)	$1.22(2) \times 10^{-4}$	0.05(1)
33.0	0.321(2)	0.028(4)	$7.5(2) \times 10^{-5}$	0.03(1)
34.0	0.310(2)	0.026(6)	$4.6(1) \times 10^{-5}$	0.01(2)
35.0	0.304(1)	0.028(6)	$2.99(9) \times 10^{-5}$	0.01(2)
36.0	0.295(2)	0.03(1)	$1.9(1) \times 10^{-5}$	0.001(28)
37.0	0.287(2)	0.02(2)	$1.2(1) \times 10^{-5}$	0
38.0	0.280(2)	0.03(4)	$8.7(2) \times 10^{-6}$	0

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\* fixed at  $0 \text{ cm}^3 \text{ mol}^{-1}$

**Table S12.** Parameters obtained by fitting the  $\chi_M'$  and  $\chi_M''$  vs.  $\nu$  plots of  $\mathbf{2}^{\text{Pd*}}$  at zero dc field using generalized Debye model.

$T / \text{K}$	$\chi_T / \text{cm}^3 \text{mol}^{-1}$	$\chi_S / \text{cm}^3 \text{mol}^{-1}$	$\tau / \text{s}$	$\alpha$
4.0	1.88(3)	0.06(3)	$4.6(3) \times 10^{-4}$	0.5904(2)
5.0	1.83(6)	0.02(2)	$5.0(6) \times 10^{-4}$	0.6246(4)
6.0	1.54(1)	0.01(1)	$3.9(1) \times 10^{-4}$	0.62784(3)
7.0	1.29(2)	0.04(2)	$3.1(2) \times 10^{-4}$	0.6151
8.0	1.13(1)	0.03(2)	$2.6(1) \times 10^{-4}$	0.61817(4)
9.0	1.06(2)	0*	$2.7(2) \times 10^{-4}$	0.65469(4)
10.0	0.90(1)	0.03(2)	$2.1(2) \times 10^{-4}$	0.61622(6)
11.0	0.83(1)	0.03(2)	$2.0(2) \times 10^{-4}$	0.62283(4)
12.0	0.78(1)	0.02(2)	$1.9(2) \times 10^{-4}$	0.63991(3)
14.0	0.66(1)	0.02(2)	$1.7(2) \times 10^{-4}$	0.6398
16.0	0.60(2)	0*	$1.5(3) \times 10^{-4}$	0.66695(4)
18.0	0.492(9)	0.04(2)	$1.3(2) \times 10^{-4}$	0.60994(3)
20.0	0.446(8)	0.04(2)	$1.2(2) \times 10^{-4}$	0.59834(3)
22.0	0.411(9)	0.04(2)	$1.2(2) \times 10^{-4}$	0.59633(3)
24.0	0.41(1)	0*	$1.0(3) \times 10^{-4}$	0.66344(4)
26.0	0.346(6)	0.05(1)	$1.2(2) \times 10^{-4}$	0.53854(3)
28.0	0.325(6)	0.07(1)	$1.2(2) \times 10^{-4}$	0.45977(8)
29.0	0.319(4)	0.067(9)	$1.0(1) \times 10^{-4}$	0.42708(4)
30.0	0.300(3)	0.080(8)	$8.6(8) \times 10^{-5}$	0.32773(4)
32.0	0.271(3)	0.08(1)	$4.5(5) \times 10^{-5}$	0.20523(9)
34.0	0.264(2)	0.08(1)	$2.6(2) \times 10^{-5}$	0.1633
36.0	0.248(1)	0.08(1)	$1.5(1) \times 10^{-5}$	0.08479(1)
38.0	0.235(1)	0.09(3)	$8(2) \times 10^{-6}$	0.03088(2)

\* fixed at  $0 \text{ cm}^3 \text{mol}^{-1}$

**Table S13.** Parameters obtained by fitting the  $\chi_M'$  and  $\chi_M''$  vs.  $\nu$  plots of  $\mathbf{3}^{\text{Pd*}}$  at zero dc field using generalized Debye model.

$T / \text{K}$	$\chi_T / \text{cm}^3 \text{mol}^{-1}$	$\chi_S / \text{cm}^3 \text{mol}^{-1}$	$\tau / \text{s}$	$\alpha$
3.0	1.94(2)	0.08(1)	$9.7(3) \times 10^{-4}$	0.59704(5)
3.5	2.02(2)	0.09(1)	$1.02(5) \times 10^{-3}$	0.58574(9)
4.0	2.02(3)	0.05(2)	$9.7(6) \times 10^{-4}$	0.60858(1)
4.5	1.80(3)	0.04(2)	$8.4(6) \times 10^{-4}$	0.6179(1)
5.0	1.64(4)	0.04(3)	$8.1(8) \times 10^{-4}$	0.6204(2)
5.5	1.54(2)	0.02(1)	$8.6(4) \times 10^{-4}$	0.63788(4)
6.0	1.36(3)	0.02(2)	$6.6(5) \times 10^{-4}$	0.63092(9)
6.5	1.25(2)	0.04(2)	$6.5(5) \times 10^{-4}$	0.62406(8)
7.0	1.16(3)	0.05(2)	$6.6(5) \times 10^{-4}$	0.61757(9)
7.5	1.08(2)	0.04(2)	$5.8(4) \times 10^{-4}$	0.62565(6)
8.0	0.99(2)	0.05(2)	$5.2(5) \times 10^{-4}$	0.6085(1)
8.5	1.02(3)	0.02(2)	$7.2(7) \times 10^{-4}$	0.65079(6)
9.0	0.89(2)	0.03(2)	$4.7(5) \times 10^{-4}$	0.62874(7)
9.5	0.84(2)	0.05(2)	$4.8(4) \times 10^{-4}$	0.61598(7)
10.0	0.89(3)	0*	$6.5(9) \times 10^{-4}$	0.67815(7)
10.5	0.79(2)	0.04(2)	$5.3(5) \times 10^{-4}$	0.63161(5)
11.0	0.73(2)	0.06(2)	$5.0(6) \times 10^{-4}$	0.6038(1)
11.5	0.73(3)	0.02(3)	$5.0(9) \times 10^{-4}$	0.6527(1)
12.0	0.68(2)	0.06(2)	$5.0(6) \times 10^{-4}$	0.60695(7)
13.0	0.62(2)	0.04(2)	$3.9(5) \times 10^{-4}$	0.61434(6)
14.0	0.59(2)	0.03(2)	$4.4(7) \times 10^{-4}$	0.64078(7)
15.0	0.58(1)	0.03(1)	$4.8(5) \times 10^{-4}$	0.64574(2)
16.0	0.48(2)	0.06(2)	$3.2(5) \times 10^{-4}$	0.5687(1)
17.0	0.47(2)	0.05(2)	$3.4(7) \times 10^{-4}$	0.5979(1)
18.0	0.47(2)	0.03(2)	$4.0(7) \times 10^{-4}$	0.63375(6)
19.0	0.44(1)	0.05(1)	$4.0(4) \times 10^{-4}$	0.60281(3)
20.0	0.41(2)	0.04(2)	$3.1(7) \times 10^{-4}$	0.6196
21.0	0.38(2)	0.04(3)	$3.1(9) \times 10^{-4}$	0.5973(1)
22.0	0.37(2)	0.05(2)	$3.3(7) \times 10^{-4}$	0.58586(9)
23.0	0.44(3)	0*	$6.3(2) \times 10^{-4}$	0.70984(4)
24.0	0.31(1)	0.06(2)	$2.3(5) \times 10^{-4}$	0.4885(1)
25.0	0.36(1)	0.03(1)	$3.5(4) \times 10^{-4}$	0.61483(2)
26.0	0.33(2)	0.03(2)	$2.3(6) \times 10^{-4}$	0.59813(9)

27.0	0.302(8)	0.06(1)	$2.3(4) \times 10^{-4}$	0.47653(8)
28.0	0.284(7)	0.06(1)	$1.7(3) \times 10^{-4}$	0.4097(1)
29.0	0.279(5)	0.058(9)	$1.4(2) \times 10^{-4}$	0.39286(5)
30.0	0.275(4)	0.063(8)	$1.2(1) \times 10^{-4}$	0.33697(7)
32.0	0.247(3)	0.065(9)	$5.4(6) \times 10^{-5}$	0.22364(7)
34.0	0.235(2)	0.06(1)	$2.6(3) \times 10^{-5}$	0.18009(3)
36.0	0.221(2)	0.07(3)	$1.4(4) \times 10^{-5}$	0.09616(8)
38.0	0.211(2)	0.08(5)	$8(4) \times 10^{-6}$	0.07271(5)

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\* fixed at 0 cm<sup>3</sup> mol<sup>-1</sup>

**Table S14.** Parameters obtained by fitting the  $\chi_M'$  and  $\chi_M''$  vs.  $\nu$  plots of  $\mathbf{4}^{\text{Pd*}}$  at zero dc field using generalized Debye model.

$T / \text{K}$	$\chi_T / \text{cm}^3 \text{mol}^{-1}$	$\chi_S / \text{cm}^3 \text{mol}^{-1}$	$\tau / \text{s}$	$\alpha$
3.0	3.09(4)	0.008(8)	$4.9(2) \times 10^{-3}$	0.555(5)
3.5	2.72(4)	0*	$4.4(3) \times 10^{-3}$	0.572(7)
4.0	2.39(3)	0*	$3.7(2) \times 10^{-3}$	0.579(5)
4.5	2.24(5)	0*	$4.2(4) \times 10^{-3}$	0.60(1)
5.0	1.94(4)	0*	$3.1(3) \times 10^{-3}$	0.60(1)
5.5	1.76(4)	0*	$2.8(2) \times 10^{-3}$	0.60(1)
6.0	1.65(3)	0*	$2.7(2) \times 10^{-3}$	0.61(1)
6.5	1.49(3)	0*	$2.3(2) \times 10^{-3}$	0.607(9)
7.0	1.42(3)	0*	$2.3(2) \times 10^{-3}$	0.61(1)
7.5	1.34(3)	0*	$2.3(2) \times 10^{-3}$	0.62(1)
8.0	1.29(5)	0*	$2.5(4) \times 10^{-3}$	0.64(2)
8.5	1.16(3)	0*	$1.9(2) \times 10^{-3}$	0.62(1)
9.0	1.16(3)	0*	$2.4(3) \times 10^{-3}$	0.63(1)
9.5	1.14(3)	0*	$2.7(3) \times 10^{-3}$	0.65(1)
10.0	1.06(4)	0*	$2.3(4) \times 10^{-3}$	0.64(2)
10.5	0.93(3)	0.003(12)	$1.5(2) \times 10^{-3}$	0.62(1)
11.0	1.04(6)	0*	$3.3(8) \times 10^{-3}$	0.66(2)
11.5	0.97(4)	0*	$2.7(5) \times 10^{-3}$	0.66(2)
12.0	0.81(3)	0.004(15)	$1.3(2) \times 10^{-3}$	0.63(2)
13.0	0.81(3)	0*	$1.7(3) \times 10^{-3}$	0.65(2)
14.0	0.77(4)	0*	$1.9(4) \times 10^{-3}$	0.66(2)
15.0	0.75(2)	0*	$2.1(2) \times 10^{-3}$	0.66(1)
16.0	0.64(2)	0.003(13)	$1.3(2) \times 10^{-3}$	0.64(2)
17.0	0.60(2)	0.006(10)	$1.2(1) \times 10^{-3}$	0.64(2)
18.0	0.58(2)	0*	$1.2(2) \times 10^{-3}$	0.65(2)
19.0	0.51(2)	0.02(1)	$9(1) \times 10^{-4}$	0.61(2)
20.0	0.48(2)	0.02(1)	$7.5(9) \times 10^{-4}$	0.60(2)
21.0	0.44(1)	0.027(9)	$6.6(7) \times 10^{-4}$	0.58(2)
22.0	0.47(2)	0.01(1)	$9.4(1) \times 10^{-4}$	0.63(2)
23.0	0.42(1)	0.02(9)	$6.8(8) \times 10^{-4}$	0.60(2)
24.0	0.37(1)	0.029(9)	$4.4(5) \times 10^{-4}$	0.54(3)
25.0	0.43(1)	0.020(7)	$8.2(8) \times 10^{-4}$	0.59(2)
26.0	0.39(1)	0.031(6)	$5.6(5) \times 10^{-4}$	0.52(2)

27.0	0.377(6)	0.038(4)	$4.4(2) \times 10^{-4}$	0.47(2)
28.0	0.353(4)	0.044(4)	$3.1(1) \times 10^{-4}$	0.40(1)
29.0	0.338(3)	0.045(3)	$2.09(7) \times 10^{-4}$	0.35(1)
30.0	0.322(2)	0.048(3)	$1.39(4) \times 10^{-4}$	0.29(1)
32.0	0.301(1)	0.044(3)	$6.0(2) \times 10^{-5}$	0.22(1)
34.0	0.281(1)	0.041(4)	$2.61(8) \times 10^{-5}$	0.16(1)
36.0	0.2632(5)	0.053(6)	$1.30(6) \times 10^{-5}$	0.10(1)

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\* fixed at  $0 \text{ cm}^3 \text{ mol}^{-1}$



**Table S15.** Parameters obtained by fitting the  $\chi_M'$  and  $\chi_M''$  vs.  $\nu$  plots of  $5^{\text{Pd*}}$  at zero dc field using generalized Debye model.

$T / \text{K}$	$\chi_T / \text{cm}^3 \text{mol}^{-1}$	$\chi_S / \text{cm}^3 \text{mol}^{-1}$	$\tau / \text{s}$	$\alpha$
3.0	2.34(3)	0.005(12)	$2.0(1) \times 10^{-3}$	0.616(6)
3.5	2.29(3)	0*	$1.9(1) \times 10^{-3}$	0.617(7)
4.0	2.30(3)	0*	$2.1(1) \times 10^{-3}$	0.622(6)
4.5	2.19(3)	$1.4 \times 10^{-4}$	$1.9(1) \times 10^{-3}$	0.620(8)
5.0	2.12(3)	0*	$2.0(1) \times 10^{-3}$	0.634(8)
5.5	1.92(3)	0*	$1.7(1) \times 10^{-3}$	0.631(7)
6.0	1.63(4)	0.024(9)	$1.1(1) \times 10^{-3}$	0.607(9)
6.5	1.69(2)	0*	$1.7(1) \times 10^{-3}$	0.645(7)
7.0	1.56(3)	0*	$1.5(1) \times 10^{-3}$	0.649(9)
7.5	1.51(4)	0*	$1.7(2) \times 10^{-3}$	0.66(1)
8.0	1.35(2)	0.002(10)	$1.24(6) \times 10^{-3}$	0.647(7)
8.5	1.27(3)	0*	$1.2(1) \times 10^{-3}$	0.65(1)
9.0	1.22(3)	0*	$1.2(1) \times 10^{-3}$	0.66(1)
9.5	1.14(2)	0.009(9)	$1.13(7) \times 10^{-3}$	0.650(8)
10.0	1.17(4)	0*	$1.5(2) \times 10^{-3}$	0.67(2)
10.5	1.06(2)	0.009(9)	$1.14(8) \times 10^{-3}$	0.655(9)
11.0	0.99(3)	0.02(1)	$1.0(1) \times 10^{-3}$	0.65(1)
11.5	0.93(3)	0.01(2)	$8.8(9) \times 10^{-4}$	0.65(2)
12.0	0.99(2)	0*	$1.4(1) \times 10^{-3}$	0.675(9)
13.0	0.87(2)	0.02(1)	$1.07(9) \times 10^{-3}$	0.66(1)
14.0	0.76(1)	0.02(1)	$7.4(5) \times 10^{-4}$	0.64(1)
15.0	0.80(2)	0.01(1)	$1.2(1) \times 10^{-3}$	0.67(1)
16.0	0.70(2)	0.02(1)	$8.5(9) \times 10^{-4}$	0.66(1)
17.0	0.63(2)	0.03(1)	$6.9(8) \times 10^{-4}$	0.63(2)
18.0	0.62(3)	0.02(2)	$8(1) \times 10^{-4}$	0.65(3)
19.0	0.53(1)	0.041(9)	$5.2(4) \times 10^{-4}$	0.61(2)
20.0	0.52(2)	0.04(1)	$5.4(7) \times 10^{-4}$	0.60(3)
21.0	0.60(3)	0.008(14)	$1.2(3) \times 10^{-3}$	0.69(2)
22.0	0.53(1)	0.016(9)	$6.8(7) \times 10^{-4}$	0.66(2)
23.0	0.46(1)	0.033(8)	$4.3(4) \times 10^{-4}$	0.61(2)
24.0	0.51(1)	0.014(7)	$7.8(8) \times 10^{-4}$	0.66(1)
25.0	0.44(1)	0.031(6)	$4.5(3) \times 10^{-4}$	0.60(2)
26.0	0.433(8)	0.039(7)	$4.3(3) \times 10^{-4}$	0.57(2)

27.0	0.407(7)	0.052(5)	$3.5(2) \times 10^{-4}$	0.51(2)
28.0	0.368(5)	0.063(6)	$2.2(1) \times 10^{-4}$	0.42(2)
29.0	0.355(6)	0.065(9)	$1.7(1) \times 10^{-4}$	0.37(3)
30.0	0.343(2)	0.069(4)	$1.21(5) \times 10^{-4}$	0.30(2)
32.0	0.314(3)	0.069(9)	$5.5(4) \times 10^{-5}$	0.20(3)
34.0	0.294(3)	0.07(1)	$2.8(3) \times 10^{-5}$	0.12(4)
36.0	0.279(2)	0.08(2)	$1.4(2) \times 10^{-5}$	0.08(5)
38.0	0.267(2)	0.07(6)	$7(3) \times 10^{-6}$	0.07(8)

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\* fixed at  $0 \text{ cm}^3 \text{ mol}^{-1}$

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