Electronic Supplementary Information

Coordination Structure Conversion of Protonated Bisporphyrinato Terbium(III) Double-Decker Complexes and Creation of a Kondo Assembly by Electron Injection on Au(111) Surface

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Contents

1. Hopping of H atom in [Tb(Hoep)(oep)] molecule by tunneling electron injection

When we inject tunneling electrons in to an isolated molecule of [Tb(Hoep)(oep)], a hopping of the H atom attached to the N atom is induced (see Fig. S1(a)). We observe a telegraphic noise in the tunneling current when the tip position is fixed at a ligand position of the isolated Tb(oepH)(oep) molecule and the tunneling current is measured with the feed-back loop open. The telegraphic noise shown in Fig. S1(b) is composed of three staircases. Whenever the current changes among the three groups, we observe the rotation of the lower area of the molecule as marked as arrows in Fig. S1(a). This can be best explained by a model in which there occurs a change of the H bonding site among four equivalent positions by the injection of the tunneling electrons.

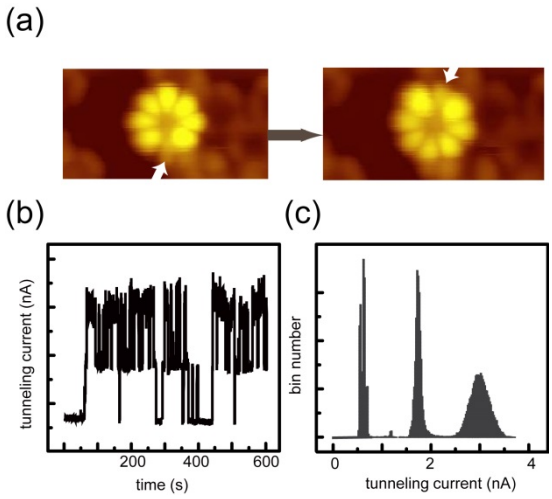

Figure S1 (a) Topographic image change with the rotation of the H atom position when the tunneling current is injected into an isolated molecule of [Tb(Hoep)(oep)]. (b) Tunneling current variation accompanied by the rotation of the H position shown in (a). (c) Histogram of the residing time at the specified tunneling current.

2. Simulation of the STM image change with a shift of the H atom from the most stable site

We simulate the appearance of the [Tb(Hoep)(oep)] molecule in the STM image when the H atom position is shifted from the most energetically stable site. We executed the structural optimization using the VASP code and found that the H atom attached to the N atom is located at the symmetric position for the most energetically stable condition. At the same time, we found that the potential curve with respect to the H position is rather flat, which makes it possible that the H atom is trapped at a pseudo stable site, in which the H atom is located at an asymmetric position. We believe that such a situation could appear after the hopping process induced by the injection of the tunneling current. We compare the simulated images corresponding to the cases where the H atom is located at the symmetric position, and shifted from the most stable site in Figure S2 (a) and (b), respectively. We note that, while the image of (a) appears as a six-lobe molecule, the one shown in (b) looks like a seven-lobe molecule. This is considerably the reason of the appearance of the seven-lobe like feature.

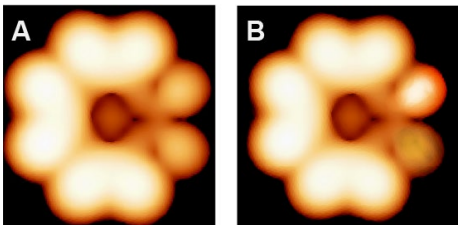

Figure S2

A comparison of the simulated STM image for [Tb(Hoep)(oep)] molecule where the H atom is placed at the symmetric position (a), and it is shifted vertically (b).

3. Change of the STM image of [Tb(Hoep)(oep)] molecule from missing-lobe appearance to the symmetric shape with the presence of the neighboring molecules

We show a change of the asymmetric shape of the [Tb(Hoep)(oep)] molecule (six-lobe shape) observed for an isolated one into the symmetric (eight-lobe shape) one for an assembly of the molecules in the STM image obtained for the occupied state. The image of the Figure S3 indicates an assembly of eight molecules of [Tb(Hoep)(oep)] on Au(111). The molecules in the perimeter of the assembly show missing lobes at the positions marked by the white arrows. On the other hand, the molecules inside of the assembly indicated by a gray arrow show no missing lobes and enhanced in z height. The variation of the appearance of the molecule is due to the overlap of the molecular orbital of the molecules in the assembly.

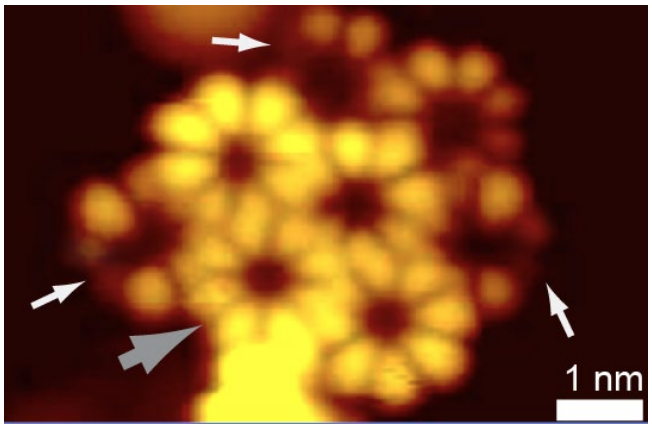

Figure S3

STM topographic image of an assembly of eight molecules of [Tb(Hoep)(oep)] on Au(111) surface obtained at an occupied state ($V_s = -0.8$ V, $I_t = 0.2$ nA, 5×7.5 nm^2).

4. Temperature dependence of zero-bias peaks of deprotonated [Tb(oep)$_2$] molecules as proof of Kondo resonance

In order to prove that zero-bias peaks (ZBPs) originate from Kondo resonance, we examined the change in the peak widths with the sample temperature. The peaks were fitted using Fano functions; the fitted curves are plotted in Figure S1 for the dipobserved for the deprotonated molecule.

Nagaoka et al. have suggested a function to describe the dependence of the Kondo peak width (W) on the sample temperature (T) using Fermi liquid theory: [1] (Note that W corresponds to 2Γ, where Γ is the fitted parameter of the Fano function mentioned in the main text)

$$W(\mathrm{T}) = 2\sqrt{(\pi k_B T)^2 + 2(k_B T_K)^2} \quad \text{--------- (1)}$$

where k_B is the Boltzmann constant and T_K is the Kondo temperature.

First, the zero-bias features measured for four sample temperatures were analyzed using Fano functions (these are shown in the left-hand panel), which gave W(T) for each temperature. Next, the W(T) values were plotted as a function of the temperature (see the right-hand panel) and then fitted using Formula (1). The result is shown by the red solid curve in the plot. The curves are for the deprotonated molecules in Figure S1. The fitting curves for the W vs. temperature relationship reproduce the measured points well within the accuracy of the error bars. This rationalizes the assignment of both the dip and the peak features to the Kondo resonance. T_K was determined to be 37 K for the deprotonated molecule.

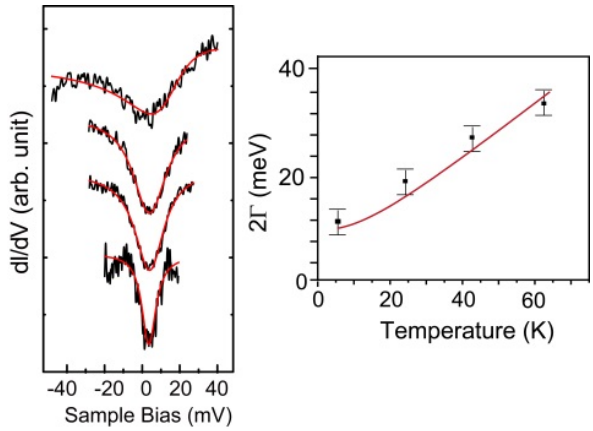

Figure S4 Temperature dependence of the zero-bias features measured in the region 4.7–64 K for the deprotonated molecule. The peak width (2Γ) vs. temperature curve is also plotted in the right-hand panel along with error bars. The solid curve indicates the curve fitted using Formula (1) stated in the text, in which T_K is the fitting parameter.

1. Nagaoka, K.; Jamneala, T.; Grobis, M.; Crommie, M. F., Temperature dependence of a single Kondo impurity. *Phys. Rev. Lett.* **2002,** *88,* 077205.

5. Coordinates of the optimized structures of [Tb(oep)$_2$] and [Tb(Hoep)(oep)]

In the following two tables (Table S1 ~ Table S2), the results for the VASP-optimized structures of [Tb(oep)$_2$] and [Tb(Hoep)(oep)] are listed. All the coordinates are shown using the standard coordinate system used for VASP calculations, which is called POSCAR. Lines 3 to 5 correspond to the three vectors of the unit cell. Lines 5 and 6 correspond to the elements and their number in the molecule, respectively. Line 7 indicates that the coordinates shown below are expressed using the three unit vectors. The length unit is expressed in Å.

Supplementary Table S1. Coordination after optimization for [Tb(oep)$_2$].

[Tb(oep)$_2$]
1
25 0 0
0 25 0
0 0 25
C N H Tb
72 8 88 1
Direct
0.958 0.890 0.904
0.894 0.951 0.903
0.114 0.058 0.935
0.050 0.119 0.937
0.059 0.893 0.915
0.118 0.957 0.926
0.889 0.051 0.917
0.948 0.116 0.930
0.911 0.864 0.880
0.871 0.902 0.878
0.141 0.111 0.929
0.100 0.149 0.930
0.111 0.868 0.904
0.149 0.908 0.911
0.860 0.102 0.908
0.897 0.143 0.916
0.009 0.867 0.905
0.868 0.001 0.904
0.998 0.142 0.933
0.141 0.009 0.929
0.048 0.885 0.048
0.960 0.882 0.040
0.038 0.118 0.077
0.950 0.115 0.070
0.115 0.959 0.065
0.111 0.047 0.077
0.886 0.952 0.044
0.883 0.040 0.055
0.033 0.828 0.056
0.977 0.826 0.051
0.019 0.171 0.097
0.963 0.169 0.092

0.165	0.975	0.093
0.163	0.030	0.100
0.830	0.965	0.058
0.828	0.020	0.065
0.100	0.905	0.056
0.906	0.899	0.039
0.898	0.094	0.064
0.092	0.100	0.082
0.910	0.807	0.858
0.815	0.899	0.853
0.200	0.119	0.922
0.104	0.209	0.923
0.121	0.810	0.888
0.209	0.905	0.905
0.802	0.106	0.892
0.890	0.203	0.911
0.070	0.780	0.066
0.941	0.778	0.057
0.053	0.217	0.117
0.924	0.213	0.107
0.208	0.936	0.113
0.202	0.065	0.131
0.786	0.924	0.068
0.781	0.054	0.084
0.908	0.777	0.109
0.786	0.076	0.142
0.082	0.209	0.171
0.189	0.901	0.161
0.235	0.100	0.970
0.898	0.233	0.964
0.768	0.906	0.893
0.107	0.770	0.934
0.917	0.763	0.902
0.762	0.084	0.934
0.085	0.241	0.973
0.240	0.918	0.958
0.181	0.084	0.186
0.103	0.781	0.118
0.794	0.891	0.120
0.887	0.202	0.156
0.946	0.942	0.920
0.064	0.946	0.931
0.059	0.065	0.943
0.941	0.061	0.934
0.003	0.916	0.038
0.083	0.004	0.055
0.996	0.086	0.060
0.917	0.998	0.041
0.132	0.876	0.062
0.966	0.741	0.055
0.913	0.776	0.022
0.876	0.867	0.040
0.744	0.029	0.081
0.775	0.088	0.056
0.865	0.122	0.072
0.027	0.253	0.121

0.083	0.228	0.086
0.121	0.129	0.096
0.244	0.959	0.126
0.222	0.910	0.080
0.997	0.186	0.927
0.208	0.162	0.914
0.214	0.097	0.885
0.849	0.211	0.895
0.918	0.219	0.880
0.827	0.001	0.887
0.163	0.804	0.876
0.096	0.800	0.852
0.012	0.825	0.890
0.184	0.011	0.921
0.871	0.800	0.837
0.942	0.802	0.828
0.915	0.722	0.884
0.955	0.767	0.923
0.884	0.766	0.932
0.729	0.902	0.872
0.770	0.875	0.925
0.769	0.945	0.912
0.812	0.929	0.821
0.811	0.859	0.833
0.792	0.149	0.884
0.795	0.085	0.853
0.720	0.088	0.921
0.769	0.041	0.943
0.766	0.106	0.973
0.892	0.277	0.959
0.869	0.218	0.995
0.938	0.226	0.981
0.146	0.220	0.914
0.080	0.221	0.888
0.088	0.285	0.966
0.043	0.232	0.983
0.109	0.231	0.008
0.278	0.107	0.963
0.223	0.122	0.007
0.229	0.057	0.979
0.220	0.865	0.891
0.223	0.933	0.873
0.284	0.914	0.952
0.232	0.958	0.973
0.228	0.889	0.990
0.112	0.728	0.921
0.134	0.778	0.968
0.065	0.775	0.948
0.239	0.042	0.138
0.213	0.100	0.106
0.210	0.111	0.206
0.143	0.107	0.182
0.172	0.051	0.213
0.220	0.871	0.172
0.179	0.926	0.196
0.152	0.879	0.150

0.045	0.744	0.066
0.098	0.777	0.033
0.127	0.743	0.121
0.132	0.814	0.119
0.078	0.784	0.155
0.883	0.741	0.112
0.934	0.779	0.145
0.881	0.812	0.111
0.747	0.945	0.071
0.783	0.897	0.033
0.750	0.101	0.152
0.789	0.043	0.171
0.821	0.101	0.146
0.762	0.861	0.125
0.833	0.869	0.119
0.796	0.917	0.156
0.947	0.250	0.115
0.898	0.222	0.072
0.859	0.236	0.163
0.862	0.166	0.148
0.910	0.194	0.193
0.105	0.245	0.182
0.054	0.199	0.204
0.111	0.176	0.168
1.001	1.002	0.989

Supplementary Table S2. Coordination after optimization for [Tb(Hoep)(oep)]

[Tb(Hoep)(oep)]
1
25 0 0
0 25 0
0 0 25
C N H Tb
72 8 89 1
Direct
-0.091 0.086 -0.073
-0.126 -0.009 -0.073
-0.011 0.124 -0.075
-0.088 -0.089 -0.073
-0.132 0.047 -0.075
-0.1 0.144 -0.085
-0.169 -0.048 -0.082
-0.049 0.167 -0.087
-0.145 -0.098 -0.082
0.046 0.13 -0.078
-0.048 -0.13 -0.076
0.085 0.09 -0.074
0.008 -0.123 -0.074
0.122 0.009 -0.073
0.088 -0.086 -0.074
0.129 -0.047 -0.076
0.142 0.098 -0.086
0.046 -0.166 -0.088
0.165 0.048 -0.086
0.097 -0.143 -0.087
-0.154 0.171 -0.087
-0.228 -0.033 -0.084
-0.035 0.225 -0.095
-0.172 -0.152 -0.083
0.17 0.152 -0.09
0.032 -0.225 -0.096
0.224 0.033 -0.093
0.151 -0.169 -0.093
-0.171 -0.177 -0.026
-0.248 -0.019 -0.027
-0.178 0.174 -0.03
-0.021 0.252 -0.04
0.172 0.178 -0.034
0.249 0.02 -0.038
0.179 -0.173 -0.037
0.022 -0.252 -0.041
-0.022 0.121 0.067
-0.107 0.064 0.068
0.065 0.107 0.068
-0.122 -0.023 0.07
-0.079 0.113 0.07
0.003 0.173 0.079
-0.163 0.058 0.086
0.058 0.164 0.079
-0.172 0.003 0.088
0.114 0.08 0.073

-0.113	-0.079	0.072
0.123	0.024	0.075
-0.063	-0.106	0.069
0.108	-0.066	0.074
0.024	-0.122	0.069
0.08	-0.115	0.072
0.174	-0.003	0.083
-0.057	-0.164	0.081
0.165	-0.058	0.081
-0.002	-0.174	0.08
-0.027	0.226	0.088
-0.202	0.103	0.096
0.102	0.205	0.085
-0.224	-0.026	0.101
0.227	0.026	0.09
-0.102	-0.204	0.089
0.205	-0.103	0.086
0.026	-0.227	0.087
-0.234	-0.042	0.161
-0.206	0.124	0.155
-0.041	0.24	0.147
0.125	0.213	0.143
0.24	0.042	0.149
0.211	-0.126	0.144
0.043	-0.242	0.145
-0.121	-0.213	0.148
-0.037	0.076	-0.066
-0.077	-0.035	-0.066
0.074	0.036	-0.063
0.034	-0.075	-0.064
0.016	0.081	0.059
-0.084	0.015	0.056
0.084	-0.015	0.07
-0.013	-0.082	0.06
-0.173	0.062	-0.082
0.06	0.17	-0.088
-0.063	-0.17	-0.085
0.169	-0.061	-0.087
-0.152	-0.18	-0.111
-0.214	-0.148	-0.096
-0.128	-0.182	-0.013
-0.19	-0.15	0.003
-0.19	-0.217	-0.024
-0.235	0.001	-0.111
-0.251	-0.068	-0.1
-0.242	-0.054	0
-0.224	0.014	-0.009
-0.291	-0.009	-0.026
-0.182	0.148	-0.113
-0.15	0.211	-0.105
-0.182	0.134	-0.013
-0.151	0.197	-0.003
-0.218	0.194	-0.029
-0.069	0.247	-0.114
0	0.229	-0.123
-0.056	0.25	-0.014

0.012	0.23	-0.02
-0.009	0.294	-0.045
0.148	0.179	-0.119
0.211	0.147	-0.107
0.13	0.183	-0.019
0.193	0.152	-0.006
0.192	0.218	-0.034
0.246	0.067	-0.112
0.229	-0.001	-0.121
0.246	0.055	-0.012
0.227	-0.013	-0.019
0.292	0.008	-0.041
0.146	-0.21	-0.11
0.177	-0.147	-0.121
0.185	-0.133	-0.021
0.154	-0.195	-0.009
0.219	-0.194	-0.04
-0.003	-0.229	-0.121
0.066	-0.246	-0.116
0.059	-0.25	-0.016
-0.009	-0.23	-0.018
0.01	-0.294	-0.044
0.045	-0.008	0.082
-0.102	0.149	0.079
0.15	0.105	0.079
-0.147	-0.103	0.083
0.104	-0.151	0.077
-0.226	-0.063	0.077
-0.258	-0.001	0.088
-0.203	-0.07	0.175
-0.235	-0.007	0.188
-0.273	-0.063	0.164
-0.193	0.137	0.07
-0.243	0.089	0.084
-0.218	0.092	0.183
-0.166	0.139	0.168
-0.235	0.157	0.157
-0.064	0.225	0.065
-0.002	0.258	0.071
-0.068	0.21	0.165
-0.004	0.243	0.172
-0.061	0.279	0.148
0.088	0.244	0.07
0.136	0.193	0.059
0.094	0.228	0.171
0.141	0.175	0.159
0.158	0.242	0.142
0.227	0.063	0.065
0.26	0.001	0.074
0.209	0.07	0.165
0.242	0.007	0.175
0.279	0.063	0.151
0.245	-0.089	0.071
0.193	-0.136	0.059
0.224	-0.094	0.172
0.172	-0.141	0.158

0.24	-0.159	0.144
0	-0.259	0.071
0.063	-0.227	0.062
0.071	-0.212	0.162
0.008	-0.245	0.172
0.064	-0.281	0.145
-0.138	-0.191	0.066
-0.09	-0.243	0.071
-0.089	-0.229	0.173
-0.136	-0.175	0.166
-0.155	-0.242	0.148
-0.005	0.001	-0.015