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Giant magnetic anisotropy of rare-earth adatoms and dimers adsorbed by graphene oxide†

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Supplementary Information

For Tm adatom adsorbed by triple carbonyls, the minority states of $4f$ orbital mainly arise in the energy window ranging from -0.4 to 0.2 eV. The operator $\hat{L}_z$ couples two nearest states $f_{x(x^2-3y^2)}$ and $f_{y(3x^2-y^2)}$ together, which predominantly contributes to the out-of-plane anisotropy, with the weights $c^2_{f_{x(x^2-3y^2)}} = 0.741$ and $c^2_{f_{y(3x^2-y^2)}} = 0.416$ respectively. Also we take into account the SOC matrix elements Λ_{xx} and Λ_{yy}, which mainly contribute to the in-plane anisotropy with the leading matrix elements $\langle f_{z(5z^2-r^2)}|\hat{L}_x|f_{x(5z^2-r^2))}\rangle$ and $\langle f_{z(5z^2-r^2)}|\hat{L}_y|f_{y(5z^2-r^2)}\rangle$. By considering the energy-level separation $\Delta = E_{f_{y(3x^2-y^2)}} - E_{f_{x(x^2-3y^2)}} = 0.12$ and the weights $c^2_{f_{z(5z^2-r^2)}} = 0.885$ (occupied) and $c^2_{f_{x(5z^2-r^2))}} = 0.304$ (unoccupied), we get the anisotropy energy $E_{MA} = DS_z^2 = (0.741 \times 0.416 \times 9\xi^2/0.12 - 0.885 \times 0.304 \times 6\xi^2/0.26) \times 1.0^2$, which gives the constant $\xi = 63.6$ meV for Tm.

For Er adatom adsorbed by triple carbonyls, the out-of-plane anisotropy is mainly contributed by the states of $f_{x(x^2-3y^2)}$ and $f_{y(3x^2-y^2)}$ with the energy splitting of 0.40 eV as well as the weights $c^2_{f_{x(x^2-3y^2)}} = 0.745$ (unoccupied) and $c^2_{f_{y(3x^2-y^2)}} = 0.955$ (occupied). Also electron hopping from the state of $f_{z(5z^2-3r^2)}$ (the weight of 0.955) to the degenerate states of $\{f_{x(5z^2-3r^2)}, f_{y(5z^2-3r^2)}\}$ (0.520) leads to the orbital moment reversal from out-of-plane to in-plane direction. The energy splitting between two states is 0.42 eV. Therefore, the magnetic anisotropy of Er is $\Delta E_{MA} = DS_z^2 = (0.745 \times 0.955 \times 9\xi^2/0.40 - 0.520 \times 0.955 \times 6\xi^2/0.42) \times (1.0)^2$, which gives the spin-orbital coupling parameter $\xi = 73.7$ meV.

For Sm adatom upon quadruple carbonyls, spin-orbital coupling between orbitals of $f_{x(x^2-3y^2)}$ and $f_{y(3x^2-y^2)}$ contributes heavily to the out-of-plane anisotropy, with the weights of 0.417 (unoccupied) and 0.830 (occupied) respectively. The energy splitting between two states is 0.18 eV. Moreover, the operators of angular momentum $\hat{L}_x$ and $\hat{L}_y$ couple the state of $f_{z(5z^2-3r^2)}$ (0.925) with the double degenerate states of $\{f_{x(5z^2-3r^2)}, f_{y(5z^2-3r^2)}\}$ (0.251) together. The energy splitting between the states of $f_{z(5z^2-3r^2)}$ and $\{f_{x(5z^2-3r^2)}, f_{y(5z^2-3r^2)}\}$ is 0.20 eV. Considering the spin quantum number $S_z = 3$, the magnetic anisotropy of Sm is calculated as $\Delta E_{MA} = DS_z^2 = (0.830 \times 0.417 \times 9\xi^2/0.18 - 0.925 \times 0.251 \times$

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Table S1 Single RE atom adsorbed by triple carbonyls of defective graphene oxide.

adatom	d_{mo} (Å)	Δh (Å)	$m_L^{\parallel}$ (μ_B)	$m_S^{\parallel}$ (μ_B)	$m_L^{\perp}$ (μ_B)	$m_S^{\perp}$ (μ_B)	M_{tot} (μ_B)	ΔE_{MA} (meV)	E_b (eV)
Co	1.84	2.28	0.15	2.03	0.34	2.03	2.78	2.9	4.3
Rh	2.04	2.58	0.19	1.27	0.29	1.28	1.44	7.3	3.4
Ir	2.03	2.56	0.30	1.04	0.70	1.07	1.22	50.4	2.7
Nd	2.12	2.76	2.49	3.33	2.47	3.35	4.22	1.5	7.4
Pm	2.12	2.76	2.72	4.48	3.03	4.46	5.22	13.1	6.8
Sm	2.13	2.76	3.12	6.03	3.56	5.99	6.22	40.3	6.1
Gd	2.06	2.74	0.15	6.82	0.09	6.83	7.55	-3.2	7.1
Dy	2.05	2.66	3.79	4.58	3.45	4.57	5.55	-34.0	6.9
Er	2.05	2.64	3.86	2.52	4.28	2.58	3.52	48.6	6.1
Tm	2.05	2.64	4.79	2.44	5.26	2.52	1.47	68.4	5.6

Table S2 Single RE atom adsorbed by quadruple carbonyls of defective graphene oxide.

adatom	d_{mo} (Å)	Δh (Å)	$m_L^{\parallel}$ (μ_B)	$m_s^{\parallel}$ (μ_B)	$m_L^{\perp}$ (μ_B)	$m_S^{\perp}$ (μ_B)	M_{tot} (μ_B)	ΔE_{MA} (meV)	E_b (eV)
Co	1.83	1.56	0.27	1.22	0.05	1.20	0.81	-3.7	5.8
Rh	1.95	1.56	0.20	0.65	0.01	0.63	0.78	-2.6	5.1
Ir	1.94	1.58	0.49	0.72	0.01	0.63	0.93	-14.4	5.4
Nd	2.21	2.41	2.23	3.17	2.51	3.24	3.47	14.5	8.4
Pm	2.19	2.37	3.11	4.17	2.94	4.39	3.50	20.6	7.8
Sm	2.21	2.34	3.57	5.45	3.70	5.43	4.84	21.5	9.7
Gd	2.13	2.26	0.09	6.80	0.09	6.81	7.56	-0.7	8.7
Dy	2.12	2.24	4.20	4.45	4.39	4.29	4.93	11.5	8.1
Er	2.13	2.25	4.29	2.80	4.32	2.78	3.55	16.7	7.2
Tm	2.13	2.24	4.96	2.37	4.89	2.32	2.40	-12.8	6.8

$6\xi^2/0.20) \times 3^2$, which gives the spin-orbital constant $\xi = 20.8$ meV.

Table S3 A-B dimers adsorbed by triple carbonyls of defective graphene oxide.

A-B	d_{mo} (Å)	Δh_{AB} (Å)	Δh (Å)	$m_{L_A}^{\parallel}$ (μ_B)	$m_{L_B}^{\parallel}$ (μ_B)	$m_{S_A}^{\parallel}$ (μ_B)	$m_{S_B}^{\parallel}$ (μ_B)	$m_{L_A}^{\perp}$ (μ_B)	$m_{L_B}^{\perp}$ (μ_B)	$m_{S_A}^{\perp}$ (μ_B)	$m_{S_B}^{\perp}$ (μ_B)	M_{tot} (μ_B)	ΔE_{MA} (meV)	E_b (eV)
Co-Ir	1.98	2.13	2.53	0.32	0.54	2.11	2.06	-0.66	0.89	2.15	2.02	4.25	9.1	7.9
Ir-Co	2.15	2.11	2.75	0.28	0.29	1.69	2.01	0.81	0.29	1.49	1.67	4.12	69.6	6.5
Sm-Ir	2.24	2.46	2.86	1.26	0.78	6.13	-1.75	3.10	1.59	5.58	-1.54	3.46	232.7	9.3
Ir-Sm	2.22	2.22	2.83	0.02	2.40	-0.46	6.25	0.77	3.60	-0.53	6.04	5.85	105.4	6.4
Er-Ir	2.16	2.49	2.74	3.60	0.92	2.60	1.64	4.02	1.74	2.75	1.47	4.56	134.9	9.4
Ir-Er	2.14	2.39	2.71	0.31	3.83	1.09	2.67	1.05	4.16	1.03	2.67	4.57	58.5	6.3
Tm-Ir	2.15	2.53	2.73	3.84	0.82	2.11	1.26	4.71	1.84	2.20	1.34	3.61	256.0	8.9
Ir-Tm	2.12	2.43	2.69	0.30	4.13	0.99	1.99	1.06	4.72	0.99	2.21	3.51	114.0	5.9

Table S4 A-B dimers adsorbed by quadruple carbonyls of defective graphene oxide.

A-B	d_{mo} (Å)	Δh_{AB} (Å)	Δh (Å)	$m_{L_A}^{\parallel}$ (μ_B)	$m_{L_B}^{\parallel}$ (μ_B)	$m_{S_A}^{\parallel}$ (μ_B)	$m_{S_B}^{\parallel}$ (μ_B)	$m_{L_A}^{\perp}$ (μ_B)	$m_{L_B}^{\perp}$ (μ_B)	$m_{S_A}^{\perp}$ (μ_B)	$m_{S_B}^{\perp}$ (μ_B)	M_{tot} (μ_B)	ΔE_{MA} (meV)	E_b (eV)
Co-Ir	2.00	2.23	1.99	0.27	0.84	2.11	2.37	0.04	1.35	2.11	2.30	4.28	21.3	8.1
Ir-Co	2.00	2.22	1.64	0.12	0.25	0.58	2.18	0.03	0.35	0.59	2.24	3.26	13.0	7.8
Sm-Ir	2.32	2.57	2.54	1.75	0.92	5.72	-1.88	3.29	1.34	5.48	-1.69	3.64	120.0	9.8
Ir-Sm	2.00	2.46	1.57	0.02	3.88	-0.19	5.64	0.01	3.56	-0.19	5.64	6.00	18.1	8.3
Er-Ir	2.21	2.57	2.37	3.72	0.99	2.77	1.69	4.19	1.36	2.83	1.68	4.71	63.4	10.2
Ir-Er	2.00	2.51	1.63	0.01	4.45	0.08	2.90	0.02	5.48	0.07	2.96	2.77	-37.4	8.0
Tm-Ir	2.21	2.64	2.38	4.17	1.00	2.37	1.68	4.75	1.39	2.44	1.66	3.40	76.3	9.4
Ir-Tm	2.01	2.53	1.63	0.01	4.83	0.11	2.76	0.02	5.45	0.11	2.83	1.78	50.9	7.6
Pm-Ir	2.31	2.44	2.53	1.86	0.06	4.07	0.18	-3.22	0.97	3.95	0.41	4.67	143.6	10.4
Ir-Pm	2.01	2.46	1.60	0.02	2.75	-0.17	4.64	0.01	3.06	-0.18	4.50	5.99	19.8	8.8

Table S5 Results of GGA+U calculations for single adatom adsorbed by triple carbonyls.

adatom	$m_L^{\parallel}$ (μ_B)	$m_S^{\parallel}$ (μ_B)	$m_L^{\perp}$ (μ_B)	$m_S^{\perp}$ (μ_B)	M_{tot} (μ_B)	ΔE_{MA} (meV)
Co	0.08	2.24	0.12	2.24	2.78	0.7
Rh	0.13	1.56	0.18	1.56	1.44	2.7
Ir	0.26	1.34	0.43	1.34	1.22	46.7
Nd	0.49	3.39	0.49	3.40	4.12	1.3
Pm	0.49	4.49	0.54	4.49	5.21	0.1
Sm	0.18	6.30	0.68	6.34	6.22	12.4
Gd	0.02	7.06	0.02	7.06	7.56	-0.3
Dy	0.72	4.65	0.80	4.76	5.15	17.8
Er	0.76	2.91	1.20	2.93	3.51	17.6
Tm	0.73	1.63	0.98	1.65	2.56	25.3

Table S6 Results of GGA+U calculations for single adatom adsorbed by quadruple carbonyls.

adatom	$m_L^{\parallel}$ (μ_B)	$m_S^{\parallel}$ (μ_B)	$m_L^{\perp}$ (μ_B)	$m_S^{\perp}$ (μ_B)	M_{tot} (μ_B)	ΔE_{MA} (meV)
Co	0.09	1.76	0.03	1.76	1.04	-1.0
Rh	0.11	0.86	0.0	0.85	1.00	-0.9
Ir	0.30	0.83	0.01	0.81	1.00	-4.9
Nd	0.45	3.21	0.45	3.20	3.61	-0.4
Pm	0.50	4.36	0.49	4.36	3.28	-0.8
Sm	0.40	5.99	0.74	5.82	4.97	13.6
Gd	0.02	7.03	0.02	7.03	7.56	0.0
Dy	0.68	4.76	0.59	4.83	4.50	-2.0
Er	0.83	2.76	0.82	2.76	3.60	-1.6
Tm	0.52	1.89	1.23	1.94	2.26	18.4

Table S7 Results of GGA+U calculations of metal dimer absorbed by triple carbonyls.

A-B	$m_{L_A}^{\parallel}$ (μ_B)	$m_{L_B}^{\parallel}$ (μ_B)	$m_{S_A}^{\parallel}$ (μ_B)	$m_{S_B}^{\parallel}$ (μ_B)	$m_{L_A}^{\perp}$ (μ_B)	$m_{L_B}^{\perp}$ (μ_B)	$m_{S_A}^{\perp}$ (μ_B)	$m_{S_B}^{\perp}$ (μ_B)	M_{tot} (μ_B)	ΔE_{MA} (meV)
Co-Ir	0.19	0.41	2.46	2.17	0.04	0.66	2.45	2.17	4.39	17.5
Ir-Co	0.32	0.18	1.98	2.40	0.55	0.15	1.97	2.41	4.22	7.0
Sm-Ir	0.61	0.26	6.04	-2.00	0.85	0.44	5.98	-1.74	3.44	64.7
Ir-Sm	0.11	0.10	-0.61	6.65	0.48	0.70	-0.65	6.65	6.52	45.8
Er-Ir	0.83	0.41	2.80	1.76	0.79	1.44	2.79	1.32	4.72	142.7
Ir-Er	0.24	0.83	1.31	2.73	0.97	0.82	1.29	2.75	4.77	69.2
Tm-Ir	0.74	0.44	1.71	1.80	0.53	1.49	1.72	1.28	3.78	70.4
Ir-Tm	0.27	0.87	1.49	1.72	0.73	0.92	1.48	1.63	3.46	126.8

Table S8 Results of GGA+U calculations of metal dimer absorbed by quadruple carbonyls.

A-B	$m_{L_A}^{\parallel}$ (μ_B)	$m_{L_B}^{\parallel}$ (μ_B)	$m_{S_A}^{\parallel}$ (μ_B)	$m_{S_B}^{\parallel}$ (μ_B)	$m_{L_A}^{\perp}$ (μ_B)	$m_{L_B}^{\perp}$ (μ_B)	$m_{S_A}^{\perp}$ (μ_B)	$m_{S_B}^{\perp}$ (μ_B)	M_{tot} (μ_B)	ΔE_{MA} (meV)
Co-Ir	0.18	0.52	2.29	2.34	0.03	0.72	2.31	2.42	4.27	5.8
Ir-Co	0.14	0.06	0.62	2.57	0.02	0.07	0.61	2.55	3.77	9.7
Sm-Ir	0.42	0.53	5.83	-1.88	0.50	0.65	5.80	-1.89	3.54	15.9
Ir-Sm	0.04	0.26	-0.15	6.48	0.01	0.15	-0.15	6.48	6.81	-3.2
Er-Ir	0.77	0.53	2.84	1.83	0.82	0.63	2.79	1.83	5.11	15.0
Ir-Er	0.01	1.06	0.07	2.82	0.0	0.72	0.07	2.74	3.00	-18.6
Tm-Ir	0.78	0.54	1.89	1.85	0.92	0.64	1.89	1.86	3.75	9.7
Ir-Tm	0.02	1.29	0.08	1.88	0.01	0.83	0.09	1.82	2.00	-15.0
Pm-Ir	0.37	0.24	4.07	1.21	0.44	0.62	4.07	1.22	5.62	10.5
Ir-Pm	0.03	0.21	-0.14	5.01	0.01	0.26	0.14	5.03	6.09	8.2

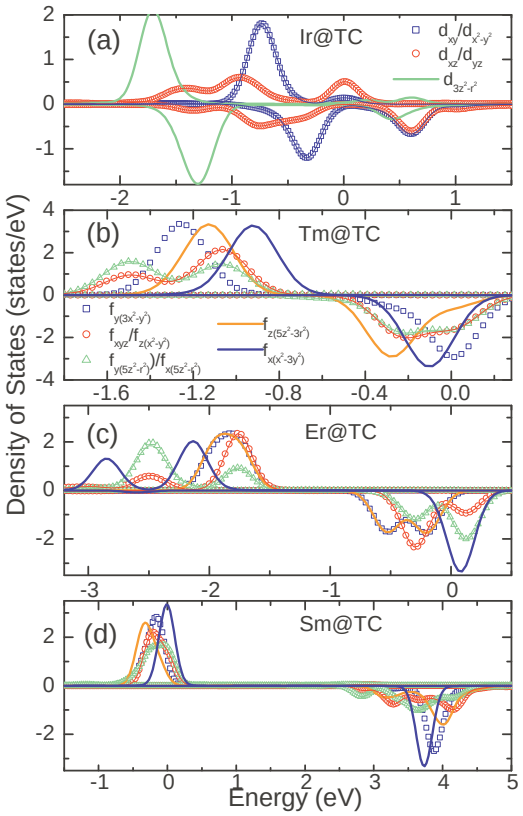

Fig. S1 (Color online) Projected density of states for Ir(a), Tm(b), Er(c) and Sm (d) adatoms adsorbed by triple carbonyls. The Fermi level is set to be zero.

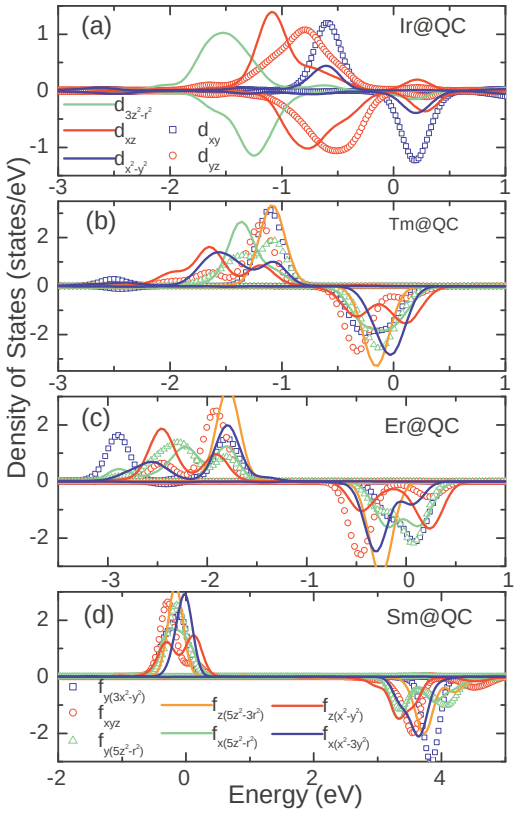

Fig. S2 (Color online) Projected density of states for Ir(a), Tm(b), Er(c) and Sm (d) adatoms adsorbed by quadruple carbonyls. The Fermi level is set to be zero.

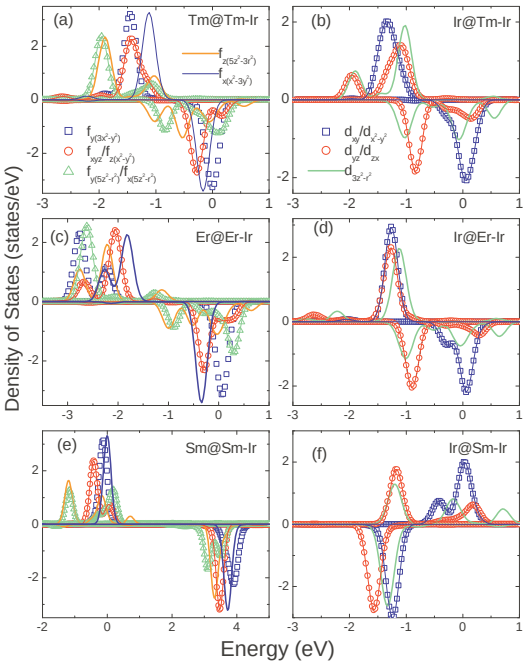

Fig. S3 (Color online) Projected density of states for Tm-Ir(a,b), Er-Ir(c,d) and Sm-Ir(e,f) dimers adsorbed by triple carbonyls. The Fermi level is set to be zero.

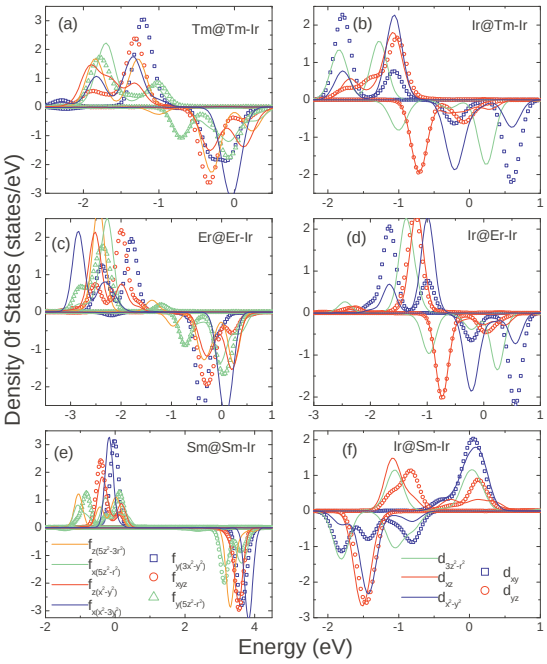

Fig. S4 (Color online) Projected density of states for Tm-Ir(a,b), Er-Ir(c,d) and Sm-Ir(e,f) dimers adsorbed by quadruple carbonyls. The Fermi level is set to be zero.