Electronic Supplementary Information

Mechanistic study of Eu single atoms occupying four vacancy centers as potential electrocatalysts for oxygen reduction reaction

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S1. Calculation method

All DFT calculations in this article are performed using the DMol^3 module in Material Studio software.[1] The effects of electron exchange and correlation are described by choosing the Generalized Gradient Approximation (GGA) in Perdew Burke Ernzerhof (PBE). This study used DFT-D with Grimme method to correct for van der Waals interactions. When simulating the water (H_2O) environment, a conductor like shielding model (COSMO) with a dielectric constant of 78.54 was used.[2] DFT semi nuclear pseudopotential was used in the calculation to handle nuclear electrons, and the basis set of the 4.4 version of the dual numerical positive polarization (DNP) function was used. In addition, in order to deal with the Eu element, the density functional semi-core pseudo potential (DSPP) approximation is also used. To ensure the accuracy of the results, convergence tolerances were set for energy, displacement, and force to 1.0 × 10^{-5} Ha, 0.05 Å, and 0.02 Ha · $Å^{-1}$, respectively. Monkhorst Pack K point grid set to 5 × 5 × 1, and the real space global orbital cutoff radius was set as high as 5.8 Å.

The adsorption free energy can be used to describe the thermodynamic stability of the adsorption process, that is, whether the adsorption process will occur spontaneously. Calculate using the following formula:

$$\Delta G_{*OOH} = G_{*OOH} - G_{*} - \left(2G_{H_2O} - \frac{3}{2}G_{H_2}\right) \quad (1)$$

$$\Delta G_{*O} = G_{*O} - G_{*} - \left(G_{H_2O} - G_{H_2}\right) \quad (2)$$

$$\Delta G_{*OH} = G_{*OH} - G_{*} - \left(G_{H_2O} - \frac{1}{2}G_{H_2}\right) \quad (3)$$

$$\Delta G_{*2OH} = G_{*2OH} - G_{*} - \left(2G_{H_2O} - G_{H_2}\right) \quad (4)$$

Where G_{*OOH}, G_{*O} and G_{*OH} are the free energy of reaction intermediates, and G_{*} is the energy of pristine catalyst.

The reaction of each electron transfer step can be calculated using the following formula:[3]

$$\Delta G_i = \Delta E_i + \Delta ZPE_i - T\Delta S_i + \Delta G_U + \Delta G_{pH} \quad (5)$$

here ΔE_i, ΔZPE_i, ΔS_i, ΔG_U and ΔG_{pH} represents the reaction heat of each reaction

electron, zero vibration energy, entropy change, potential, and the influence of pH in each step. $\Delta G_U = -eU$ and $\Delta G_{pH} = pH \times k_B \times T \times ln10$, where U, T, pH, and k_B is the applied potential, temperature, hydrogen ion index and Boltzmann constant respectively. T is at room temperature, 298.15K.

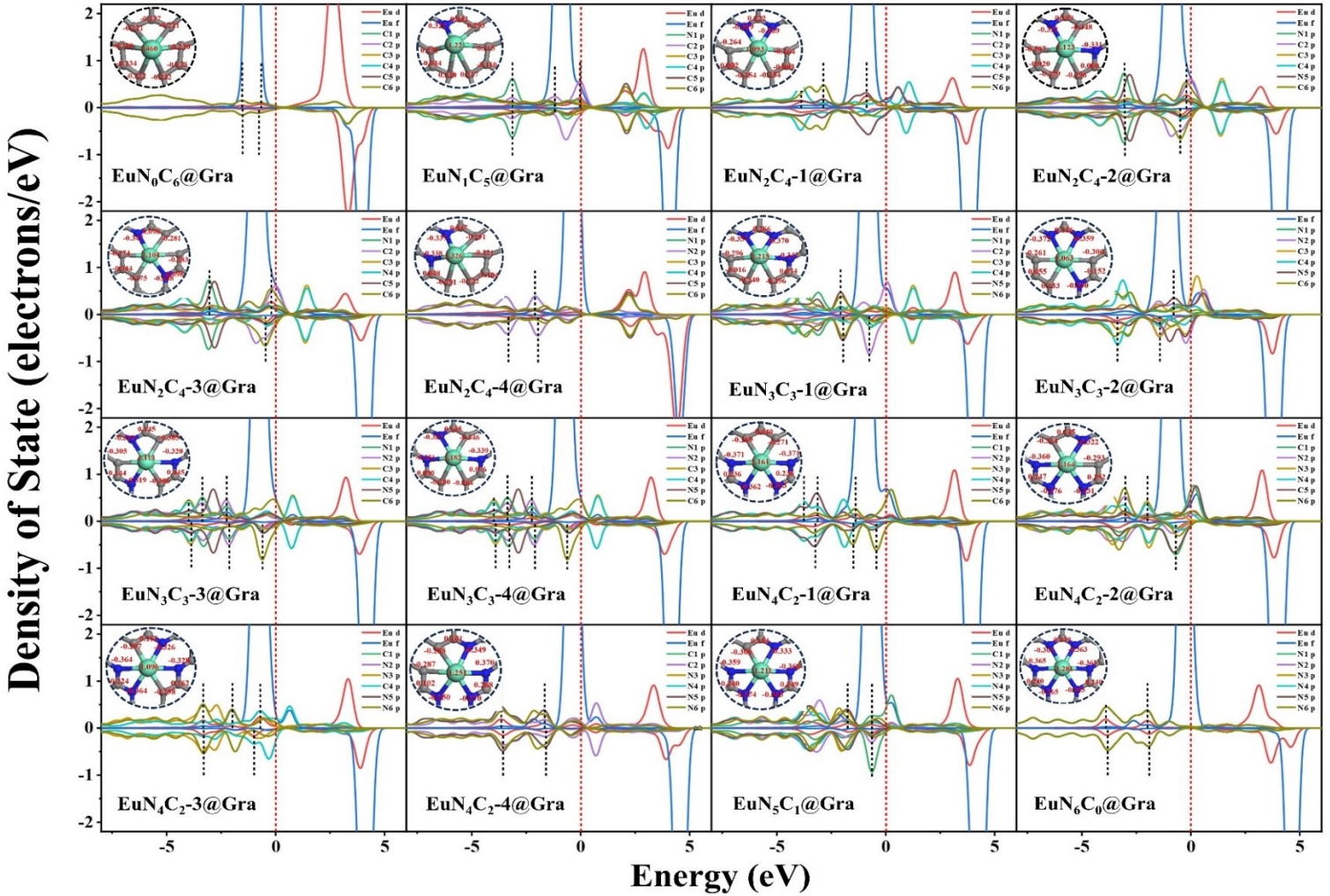
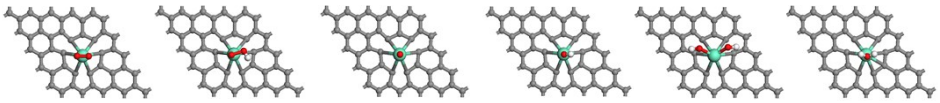
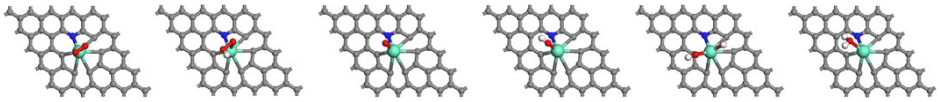
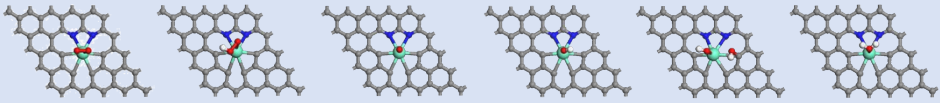
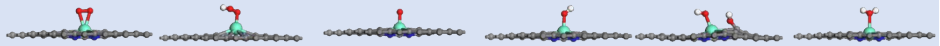
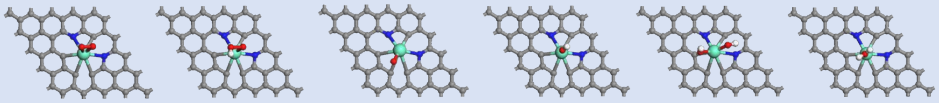
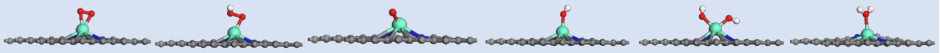
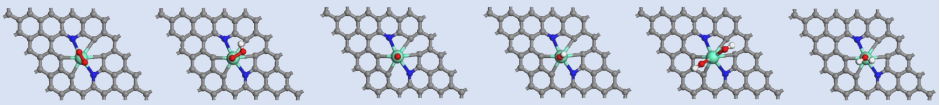
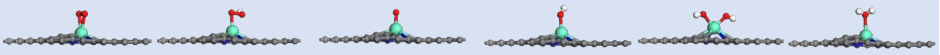
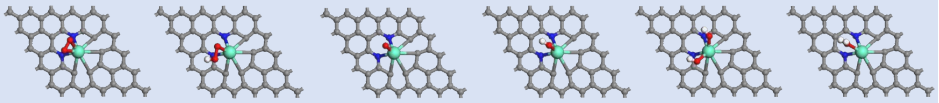
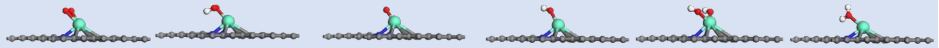
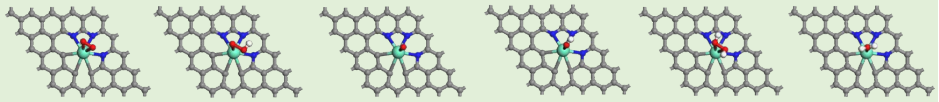
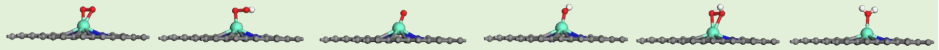
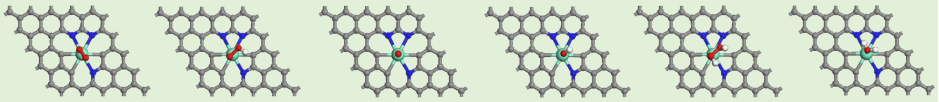
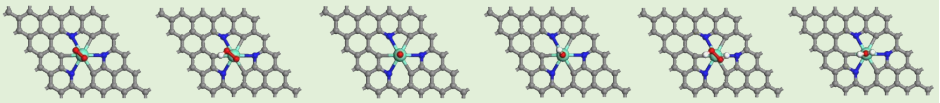


Fig. S1 The projected density of states (PDOS) and the Mulliken population analysis of EuN_xC_{6-x}-Gra.

Table S1 The optimal adsorption configurations of $*O_2$, *OOH, *O, *OH, *2OH and $*H_2O$ on EuN_xC_{6-x}-Gra.

EuN_0C_6-Gra	$*O_2$ (side-on)	*OOH	*O	*OH	*2OH	$*H_2O$
Top						
Side						
ΔE_{*ads}/eV	-1.33	-1.44	-2.77	0.46	-5.13	1.25
EuN_1C_5-Gra	$*O_2$ (side-on)	*OOH	*O	*OH	*2OH	$*H_2O$
Top						
Side						
ΔE_{*ads}/eV	-1.20	-1.87	-2.60	-3.06	-5.25	-0.64
EuN_2C_4-1-Gra	$*O_2$ (side-on)	*OOH	*O	*OH	*2OH	$*H_2O$
Top						
Side						
ΔE_{*ads}/eV	-0.60	-1.37	-1.75	-2.43	-5.98	-0.60
EuN_2C_4-2-Gra	$*O_2$ (side-on)	*OOH	*O	*OH	*2OH	$*H_2O$
Top						
Side						
ΔE_{*ads}/eV	-0.84	-1.44	-2.16	-2.47	-4.60	-0.54
EuN_2C_4-3-Gra	$*O_2$ (side-on)	*OOH	*O	*OH	*2OH	$*H_2O$
Top						

Side						
ΔE_{*ads}/eV	-0.73	-1.4	-1.88	-2.54	-4.54	-0.58
EuN_2C_4-4-Gra	**$*O_2$ (side-on)**	***OOH**	***O**	***OH**	***2OH**	**$*H_2O$**
Top						
Side						
ΔE_{*ads}/eV	-1.28	-1.93	-2.55	-3.08	-4.86	-0.59
EuN_3C_3-1-Gra	**$*O_2$ (side-on)**	***OOH**	***O**	***OH**	***2OH**	**$*H_2O$**
Top						
Side						
ΔE_{*ads}/eV	-0.91	-1.50	-2.06	-2.68	-4.47	-0.53
EuN_3C_3-2-Gra	**$*O_2$ (side-on)**	***OOH**	***O**	***OH**	***2OH**	**$*H_2O$**
Top						
Side						
ΔE_{*ads}/eV	-0.68	-1.23	-1.52	-2.38	-6.72	-0.60
EuN_3C_3-3-Gra	**$*O_2$ (side-on)**	***OOH**	***O**	***OH**	***2OH**	**$*H_2O$**
Top						
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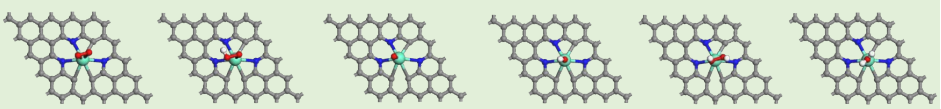
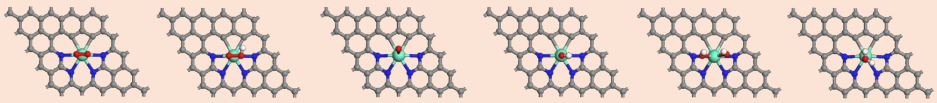
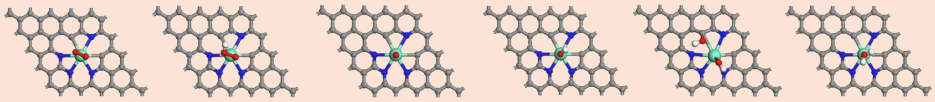
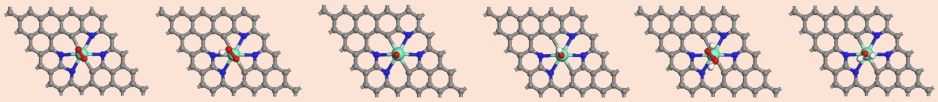
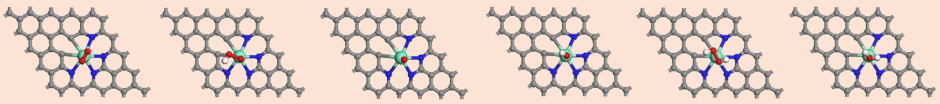
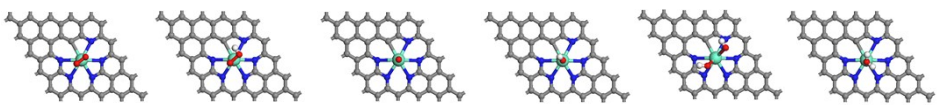
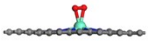
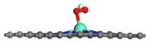
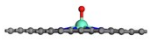
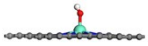
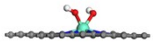
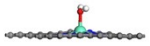
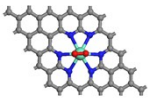
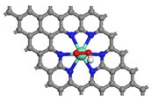
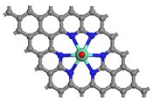
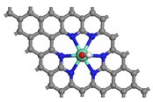
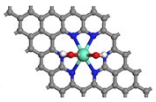
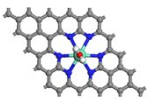
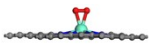
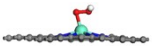
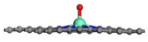
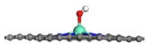
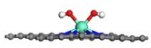
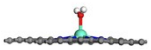
ΔE_{*ads}/eV	-0.71	-1.33	-1.65	-2.47	-4.17	-0.57
EuN_3C_3-4-Gra	**$*O_2$ (side-on)**	***OOH**	***O**	***OH**	***2OH**	**$*H_2O$**
Top						

Side						
ΔE_{*ads}/eV	-0.84	-1.40	-1.91	-2.54	-6.69	-0.52
EuN_4C_2-1-Gra	**$*O_2$ (side-on)**	***OOH**	***O**	***OH**	***2OH**	**$*H_2O$**
Top						
Side						
ΔE_{*ads}/eV	-0.76	-1.35	-1.80	-2.48	-3.88	-0.59
EuN_4C_2-2-Gra	**$*O_2$ (side-on)**	***OOH**	***O**	***OH**	***2OH**	**$*H_2O$**
Top						
Side						
ΔE_{*ads}/eV	-0.71	-1.31	-1.73	-2.33	-6.41	-0.34
EuN_4C_2-3-Gra	**$*O_2$ (side-on)**	***OOH**	***O**	***OH**	***2OH**	**$*H_2O$**
Top						
Side						
ΔE_{*ads}/eV	-0.61	-1.16	-1.55	-2.14	-6.46	1.73
EuN_4C_2-4-Gra	**$*O_2$ (side-on)**	***OOH**	***O**	***OH**	***HOOH**	**$*H_2O$**
Top						
Side						
ΔE_{*ads}/eV	-0.87	-1.47	-1.95	-2.58	-4.22	-0.49
EuN_5C_1-Gra	**$*O_2$ (side-on)**	***OOH**	***O**	***OH**	***2OH**	**$*H_2O$**
Top						

Side						
ΔE_{*ads}/eV	-0.71	-1.30	-1.70	-2.42	-3.18	-0.58
EuN_6C_0-Gra	**$*O_2$ (side-on)**	***OOH**	***O**	***OH**	***2OH**	**$*H_2O$**
Top						
Side						
ΔE_{*ads}/eV	-0.84	-1.42	-1.77	-2.52	-3.66	-0.12

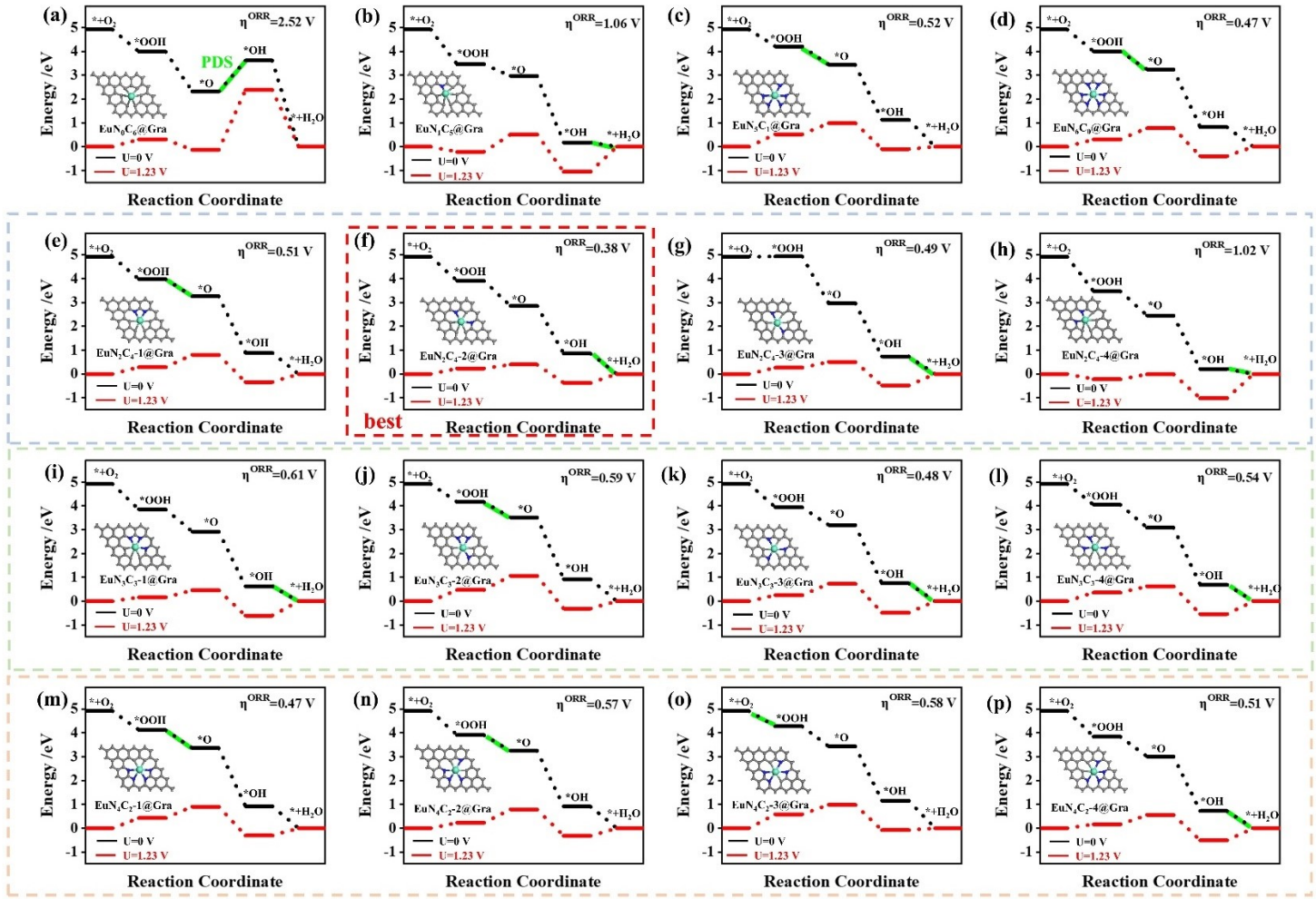


Fig. S2 The free energy diagrams of EuN_xC_{6-x}-Gra electrocatalysts.

Table S2 The adsorption free energy of *OOH, *O, *OH and *2OH and the overpotential of EuN_xC_{6-x}-Gra.

	ΔG_{*OOH}/eV	ΔG_{*O}/eV	ΔG_{*OH}/eV	ΔG_{*2OH}/eV	η^{ORR}/V
EuN_0C_6-Gra	**3.99**	**2.32**	**3.61**	**1.54**	**2.52**
EuN_1C_5-Gra	**3.46**	**2.97**	**0.17**	**1.26**	**1.06**
EuN_2C_4-1-Gra	**3.98**	**3.26**	**0.88**	**0.85**	**0.51**
EuN_2C_4-2-Gra	**3.91**	**2.86**	**0.85**	**2.10**	**0.38**
EuN_2C_4-3-Gra	**3.95**	**2.96**	**0.74**	**2.09**	**0.49**
EuN_2C_4-4-Gra	**3.47**	**2.44**	**0.21**	**1.74**	**1.02**
EuN_3C_3-1-Gra	**3.85**	**2.92**	**0.62**	**2.10**	**0.61**
EuN_3C_3-2-Gra	**4.16**	**3.52**	**0.92**	**0.22**	**0.59**
EuN_3C_3-3-Gra	**3.94**	**3.19**	**0.75**	**2.44**	**0.48**
EuN_3C_3-4-Gra	**4.05**	**3.09**	**0.69**	**0.04**	**0.54**
EuN_4C_2-1-Gra	**4.12**	**3.36**	**0.92**	**2.75**	**0.47**
EuN_4C_2-2-Gra	**3.91**	**3.25**	**0.91**	**0.50**	**0.57**
EuN_4C_2-3-Gra	**4.27**	**3.44**	**1.15**	**0.40**	**0.58**
EuN_4C_2-4-Gra	**3.85**	**3.01**	**0.72**	**2.36**	**0.51**
EuN_5C_1-Gra	**4.21**	**3.44**	**1.12**	**3.81**	**0.52**
EuN_6C_0-Gra	**4.00**	**3.24**	**0.82**	**2.81**	**0.47**

Table S3 The d-band and f-band centers of EuN_xC_{6-x}-Gra.

	ε_f	ε_d		ε_f	ε_d
EuN_0C_6-Gra	**0.41**	**2.27**	**EuN_5C_1-Gra**	**1.40**	**0.80**
EuN_1C_5-Gra	**0.68**	**1.32**	**EuN_6C_0-Gra**	**1.61**	**1.06**
EuN_2C_4-1-Gra	**0.81**	**0.02**	**EuN_2C_4-3-Gra**	**0.88**	**0.19**
EuN_2C_4-2-Gra	**1.00**	**0.19**	**EuN_2C_4-4-Gra**	**0.46**	**2.26**
EuN_3C_3-1-Gra	**1.12**	**0.56**	**EuN_3C_3-3-Gra**	**0.99**	**0.01**
EuN_3C_3-2-Gra	**0.83**	**0.04**	**EuN_3C_3-4-Gra**	**1.14**	**0.72**
EuN_4C_2-1-Gra	**1.08**	**0.48**	**EuN_4C_2-3-Gra**	**1.19**	**0.65**
EuN_4C_2-2-Gra	**1.12**	**0.61**	**EuN_4C_2-4-Gra**	**1.53**	**0.97**

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