Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supporting Information

Controlling the Emission Color of Graphene Nanoribbon Emitters Based on Spatially Excited Topological Boundary States

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Spatial distributions of HOMO and LUMO of a pristine 6-AGNR

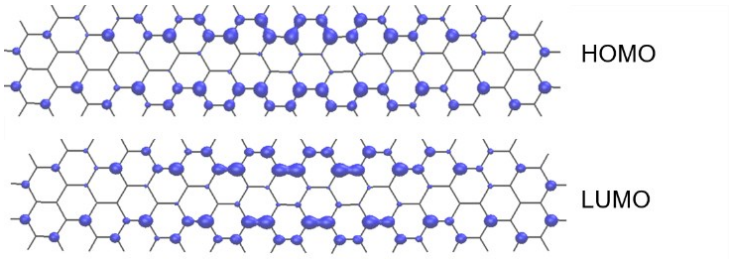

Figure S1 HOMO and LUMO of 6-AGNR.

Spatial distributions of HOMO and LUMO of 6/8-*n*/6-AGNR heterojunctions

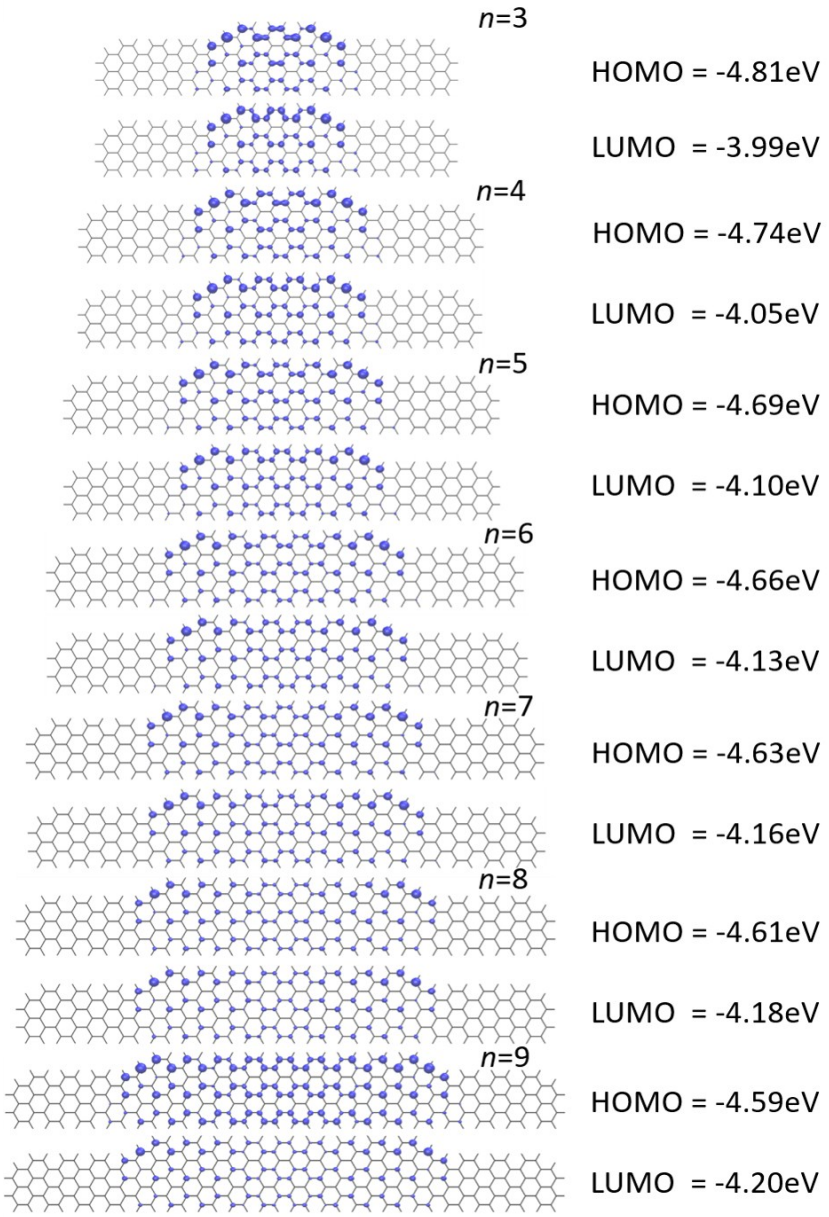

Figure S2 HOMOs and LUMOs of 6/8 -*n*/6-AGNR heterojunctions for *n* equals to 3 to 9.

Atomic structure and density of states (DOS) of the 7/14/7-AGNR heterojunction

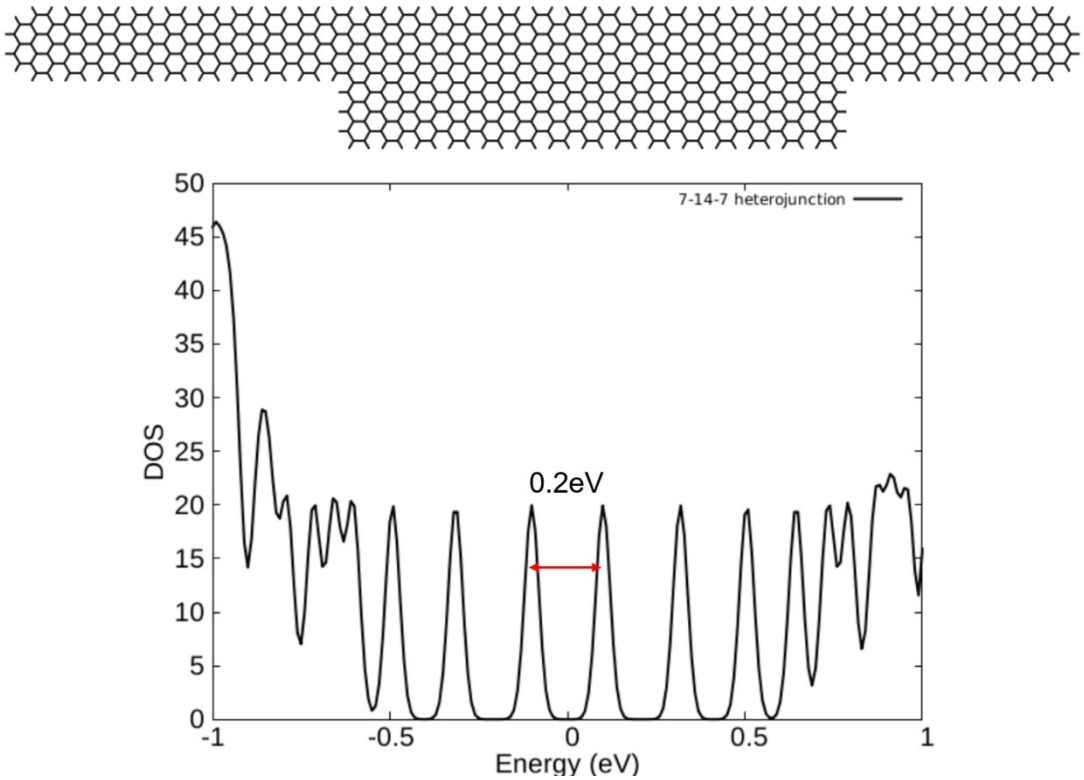

Figure S3 Structure and density of states (DOS) of the 7/14/7-AGNR heterojunction.

Electron-plasmon interactions

The spectra density of plasmon mode is given as[1,2]:

$$J_p(\omega) = F \times V_p \frac{\omega_p^2}{(2\pi)^3 c^3 2\pi} \frac{1}{(\omega - \omega_p)^2 - \left(\frac{\Gamma_p}{2}\right)^2} \Gamma_p$$

Here, $\omega_p = 0.9\ eV$ is the resonance frequency of the plasmon mode. F is the field enhancement factor caused by the STM cavity effect and it is found to be on the order of 10^4.[3,4] V_p is the effective volume of the nanogap, which is set as 1 nm^3. Γ_p is the decay rate of the plasmon mode, which describes the radiative and non-radiative decay of the plasmon. Based on the experimental results[5], we set the value of Γ_p as 0.2 eV.

Finally, the electron-plasmon interaction Hamiltonian $H_{ep} = \frac{e}{m}\hat{A}_p \cdot \hat{p}$ is included to describe the coupling of the junction to the STM plasmon mode. Here, $\hat{A}_p$ is the vector potential of the plasmon mode and $\hat{p}$ is the momentum operator of the system. The vector potential for the nanocavity plasmon used in this work is given by[2]

$$A_p(r,t) = \left(\frac{\hbar}{2\epsilon_0 \omega_p V_p}\right)^{\frac{1}{2}} a_p U_p(r)(b e^{-i\omega_p t} + b^\dagger e^{i\omega_p t})$$

where ϵ_0 is the vacuum permittivity. ω_p is the plasmon frequency and a_p defines the polarization direction of the plasmon mode. $U_p(r)$ gives the spatial distribution of the plasmon mode. b and $b^\dagger$ are the annihilation and creation operators of plasmon mode.

The spatial distribution of the plasmon mode is given as:

$$U_p(r) = e^{-\alpha[(r_y - r_{y,D})^2 + (r_z - r_{z,D})^2]} e^{-\beta|r_x - r_{x,D}|}$$

where r_D is the position where the maximum field enhancement is located and is set 3 Å below the tip apex. The parameters specifying the plasmon mode are summarized in Table S1.

In our simulations, electrons are injected from the tip and tunnel through the AGNR

inelastically by losing energy to a plasmon in the junction. Here, majority of the electrons tunnel through the system to the substrate without being scattered. The quantum yield corresponds to the efficiency of exciting a plasmon by inelastic tunneling process. The plasmon is then assumed to decay into far-field photons.

Table S1. Parameters for the Nanogap Plasmon

Parameter	Value	explanation
α	$0.31 Å^{-2}$	Spatial extent in y-z plane
β	$0.15 Å^{-1}$	for $r_x < r_{x,D}$
	$0.22 Å^{-1}$	for $r_x > r_{x,D}$

References

(1) Duan, S.; Tian, G.; Ji, Y.; Shao, J.; Dong, Z.; Luo, Y. Theoretical Modeling of Plasmon-Enhanced Raman Images of a Single Molecule with Subnanometer Resolution. J. Am. Chem. Soc. 2015, 137, 9515-9518.

(2) Wu, X.; Wang, R.; Zhang, Y.; Song, B.; Yam, C. Controllable Single-Molecule Light Emission by Selective Charge Injection in Scanning Tunneling Microscopy. J. Phys. Chem. C 2019, 123, 15761-15768.

(3) Koenderink, A. F. On the use of Purcell factors for plasmon antennas. Opt. Lett. 2010, 35, 4208-4210.

(4) Trautmann, S.; Aizpurua, J.; Götz, I.; Undisz, A.; Dellith, J.; Schneidewind, H.; Rettenmayr, M.; Deckert, V. A classical description of subnanometer resolution by atomic features in metallic structures. Nanoscale 2017, 9, 391-401.

(5) Dong, Z.; Zhang, X.; Gao, H.; Luo Y.; Zhang, C.; Chen, L.; Zhang, R.; Tao, X.; Zhang, Y.; Yang, J., Generation of molecular hot electroluminescence by resonant nanocavity plasmons. Nature Photonics 2010, 5, 50-54.

Cartesian coordinates of the GNR heterojunction emitter

C	12.405	15.347	73.354
C	13.815	15.347	73.354
C	11.700	16.568	73.354
C	12.405	17.789	73.354
C	13.815	17.789	73.354
C	14.520	16.568	73.354
C	11.700	19.010	73.354
C	12.405	20.231	73.354
C	13.815	20.231	73.354
C	14.520	19.010	73.354
C	14.520	21.453	73.354
C	16.635	15.347	73.354
C	18.045	15.347	73.354
C	15.930	16.568	73.354
C	16.635	17.789	73.354
C	18.045	17.789	73.354
C	18.750	16.568	73.354
C	15.930	19.010	73.354
C	16.635	20.231	73.354
C	18.045	20.231	73.354
C	18.750	19.010	73.354
C	15.930	21.453	73.354
C	18.750	21.453	73.354
C	20.865	15.347	73.354
C	22.275	15.347	73.354
C	20.160	16.568	73.354
C	20.865	17.789	73.354
C	22.275	17.789	73.354
C	22.980	16.568	73.354
C	20.160	19.010	73.354
C	20.865	20.231	73.354
C	22.275	20.231	73.354
C	22.980	19.010	73.354
C	20.160	21.453	73.354
C	22.980	21.453	73.354
C	25.095	15.347	73.354
C	26.505	15.347	73.354
C	24.390	16.568	73.354
C	25.095	17.789	73.354
C	26.505	17.789	73.354
C	27.210	16.568	73.354
C	24.390	19.010	73.354
C	25.095	20.231	73.354
C	26.505	20.231	73.354
C	27.210	19.010	73.354
C	24.390	21.453	73.354
C	27.210	21.453	73.354
C	29.325	15.347	73.354
C	30.735	15.347	73.354
C	28.620	16.568	73.354
C	29.325	17.789	73.354
C	30.735	17.789	73.354
C	31.440	16.568	73.354
C	28.620	19.010	73.354
C	29.325	20.231	73.354

C	30.735	20.231	73.354
C	31.440	19.010	73.354
C	28.620	21.453	73.354
C	29.325	22.674	73.354
C	30.735	22.674	73.354
C	31.440	21.453	73.354
C	31.440	23.895	73.354
C	33.555	15.347	73.354
C	34.965	15.347	73.354
C	32.850	16.568	73.354
C	33.555	17.789	73.354
C	34.965	17.789	73.354
C	35.670	16.568	73.354
C	32.850	19.010	73.354
C	33.555	20.231	73.354
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C	35.670	19.010	73.354
C	32.850	21.453	73.354
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C	34.965	22.674	73.354
C	35.670	21.453	73.354
C	32.850	23.895	73.354
C	35.670	23.895	73.354
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C	37.080	21.453	73.354
C	37.785	22.674	73.354
C	39.195	22.674	73.354
C	39.900	21.453	73.354
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C	43.425	17.789	73.354
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C	103.350	16.568	73.354
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C	103.350	19.010	73.354
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C	123.795	20.231	73.354
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C	121.680	21.453	73.354
C	124.500	21.453	73.354
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C	128.730	16.568	73.354
C	125.910	19.010	73.354
C	126.615	20.231	73.354
C	128.025	20.231	73.354
C	128.730	19.010	73.354
C	125.910	21.453	73.354
C	128.730	21.453	73.354
C	130.845	15.347	73.354
C	132.255	15.347	73.354
C	130.140	16.568	73.354
C	130.845	17.789	73.354
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C	132.960	16.568	73.354
C	130.140	19.010	73.354
C	130.845	20.231	73.354
C	132.255	20.231	73.354
C	132.960	19.010	73.354
C	130.140	21.453	73.354
H	11.835	14.360	73.354
H	14.385	14.360	73.354
H	10.560	16.568	73.354
H	10.560	19.010	73.354
H	11.835	21.219	73.354
H	13.950	22.440	73.354
H	16.065	14.360	73.354
H	18.615	14.360	73.354
H	16.500	22.440	73.354
H	18.180	22.440	73.354
H	20.295	14.360	73.354
H	22.845	14.360	73.354
H	20.730	22.440	73.354
H	22.410	22.440	73.354
H	24.525	14.360	73.354

H	27.075	14.360	73.354
H	24.960	22.440	73.354
H	26.640	22.440	73.354
H	28.755	14.360	73.354
H	31.305	14.360	73.354
H	28.755	23.661	73.354
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H	35.100	24.882	73.354
H	37.215	14.360	73.354
H	39.765	14.360	73.354
H	39.765	23.661	73.354
H	37.650	24.882	73.354
H	41.445	14.360	73.354
H	43.995	14.360	73.354
H	41.880	22.440	73.354
H	43.560	22.440	73.354
H	45.675	14.360	73.354
H	48.225	14.360	73.354
H	46.110	22.440	73.354
H	47.790	22.440	73.354
H	49.905	14.360	73.354
H	52.455	14.360	73.354
H	50.340	22.440	73.354
H	52.020	22.440	73.354
H	54.135	14.360	73.354
H	56.685	14.360	73.354
H	54.570	22.440	73.354
H	56.250	22.440	73.354
H	58.365	14.360	73.354
H	60.480	13.139	73.354
H	58.800	22.440	73.354
H	60.480	22.440	73.354
H	62.595	11.918	73.354
H	65.145	11.918	73.354
H	63.030	22.440	73.354
H	64.710	22.440	73.354
H	66.825	11.918	73.354
H	69.375	11.918	73.354
H	67.260	22.440	73.354
H	68.940	22.440	73.354
H	71.055	11.918	73.354
H	73.605	11.918	73.354
H	71.490	22.440	73.354
H	73.170	22.440	73.354
H	75.720	13.139	73.354
H	77.835	14.360	73.354
H	75.720	22.440	73.354
H	77.400	22.440	73.354
H	79.515	14.360	73.354
H	82.065	14.360	73.354
H	79.950	22.440	73.354
H	81.630	22.440	73.354
H	83.745	14.360	73.354
H	86.295	14.360	73.354
H	84.180	22.440	73.354

H	85.860	22.440	73.354
H	87.975	14.360	73.354
H	90.525	14.360	73.354
H	88.410	22.440	73.354
H	90.090	22.440	73.354
H	92.205	14.360	73.354
H	94.755	14.360	73.354
H	92.640	22.440	73.354
H	94.320	22.440	73.354
H	96.435	14.360	73.354
H	98.985	14.360	73.354
H	96.435	23.661	73.354
H	98.550	24.882	73.354
H	100.665	14.360	73.354
H	103.215	14.360	73.354
H	101.100	24.882	73.354
H	102.780	24.882	73.354
H	104.895	14.360	73.354
H	107.445	14.360	73.354
H	105.330	24.882	73.354
H	107.010	24.882	73.354
H	109.125	14.360	73.354
H	111.675	14.360	73.354
H	109.560	24.882	73.354
H	111.240	24.882	73.354
H	113.355	14.360	73.354
H	115.905	14.360	73.354
H	115.905	23.661	73.354
H	113.790	24.882	73.354
H	117.585	14.360	73.354
H	120.135	14.360	73.354
H	118.020	22.440	73.354
H	119.700	22.440	73.354
H	121.815	14.360	73.354
H	124.365	14.360	73.354
H	122.250	22.440	73.354
H	123.930	22.440	73.354
H	126.045	14.360	73.354
H	128.595	14.360	73.354
H	126.480	22.440	73.354
H	128.160	22.440	73.354
H	130.275	14.360	73.354
H	132.825	14.360	73.354
H	134.100	16.568	73.354
H	132.825	21.219	73.354
H	134.100	19.010	73.354
H	130.710	22.440	73.354