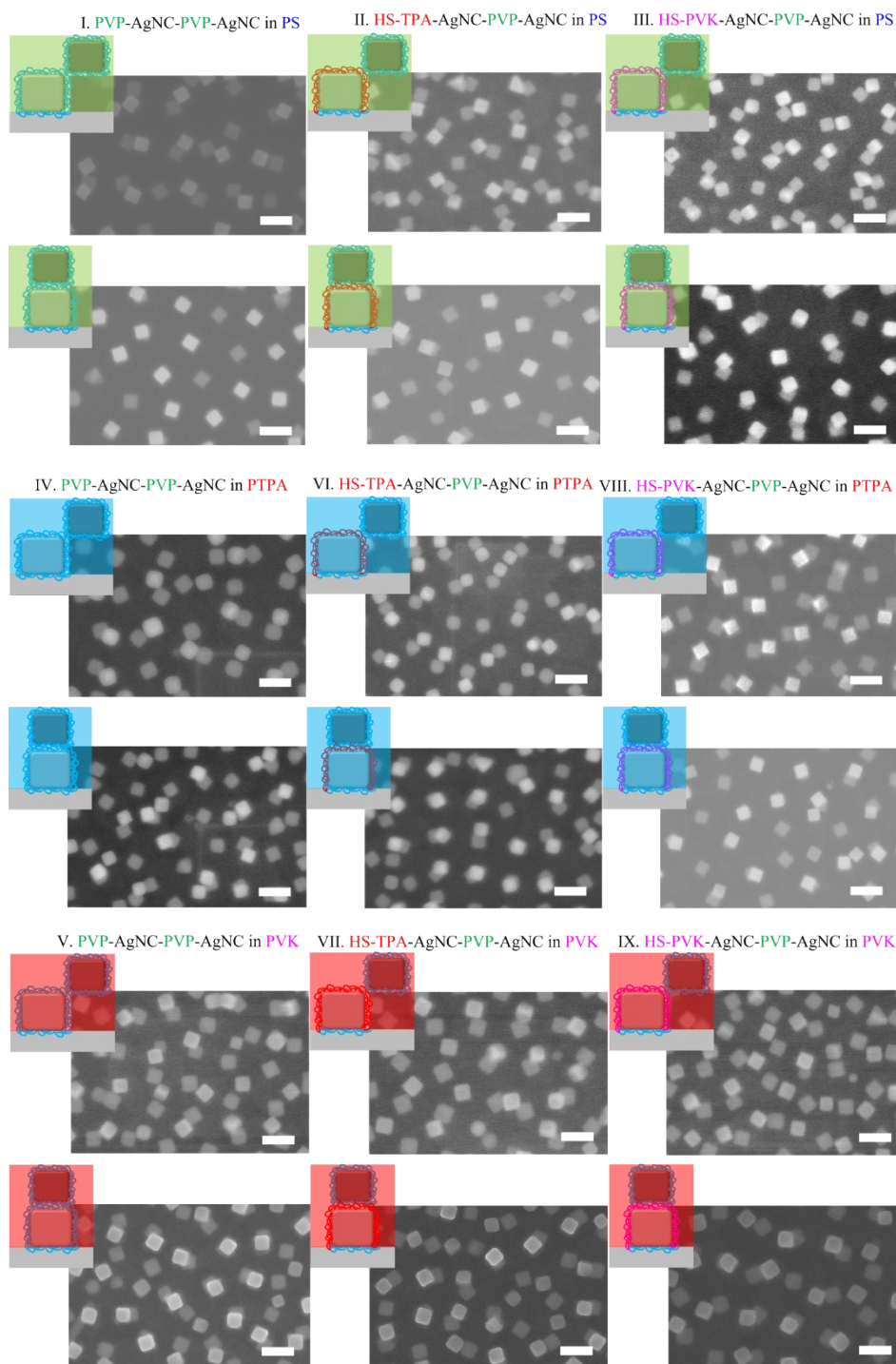**S1 The molecular weight and PDI of polymers used as ligands on AgNC and polymer matrices for the fabrication of dimer nanojunctions nanocomposite.** Black curve: PVK as polymer matrix; red curve: HS-PVK as ligand; blue curve: PTPA as polymer matrix; and purple curve: HS-TPA as ligand.

I. PVP-AgNC-PVP-AgNC in PS

II. HS-TPA-AgNC-PVP-AgNC in PS

III. HS-PVK-AgNC-PVP-AgNC in PS

IV. PVP-AgNC-PVP-AgNC in PTPA

VI. HS-TPA-AgNC-PVP-AgNC in PTPA

VIII. HS-PVK-AgNC-PVP-AgNC in PTPA

V. PVP-AgNC-PVP-AgNC in PVK

VII. HS-TPA-AgNC-PVP-AgNC in PVK

IX. HS-PVK-AgNC-PVP-AgNC in PVK

S2 The dimer conformations, horizontal dimers and vertical dimers, were formed in different nanocomposites. (A) the nanocomposites consisted of PVP, HS-poly-*p*-TPA, or HS-PVK coated AgNC and PS matrix. (B) the nanocomposites consisted of PVP, HS-poly-*p*-TPA, or HS-PVK coated AgNC and PTPA matrix. (C) the nanocomposites consisted of PVP, HS-poly-*p*-TPA, or HS-PVK coated AgNC and PVK matrix. The overlapping area is used to distinguish the two dimer nanojunctions. For vertical dimer nanojunctions, the overlapping area of dimer nanojunctions is greater than 50% of the projected area of AgNC. For horizontal dimer nanojunctions, the overlapping area of dimer nanojunctions is less than 50% of the projected area of AgNC. And all samples were measured by > 150 dimer nanojunctions, and the configurations of dimer nanojunctions were named by the majority in the statistical analysis results.
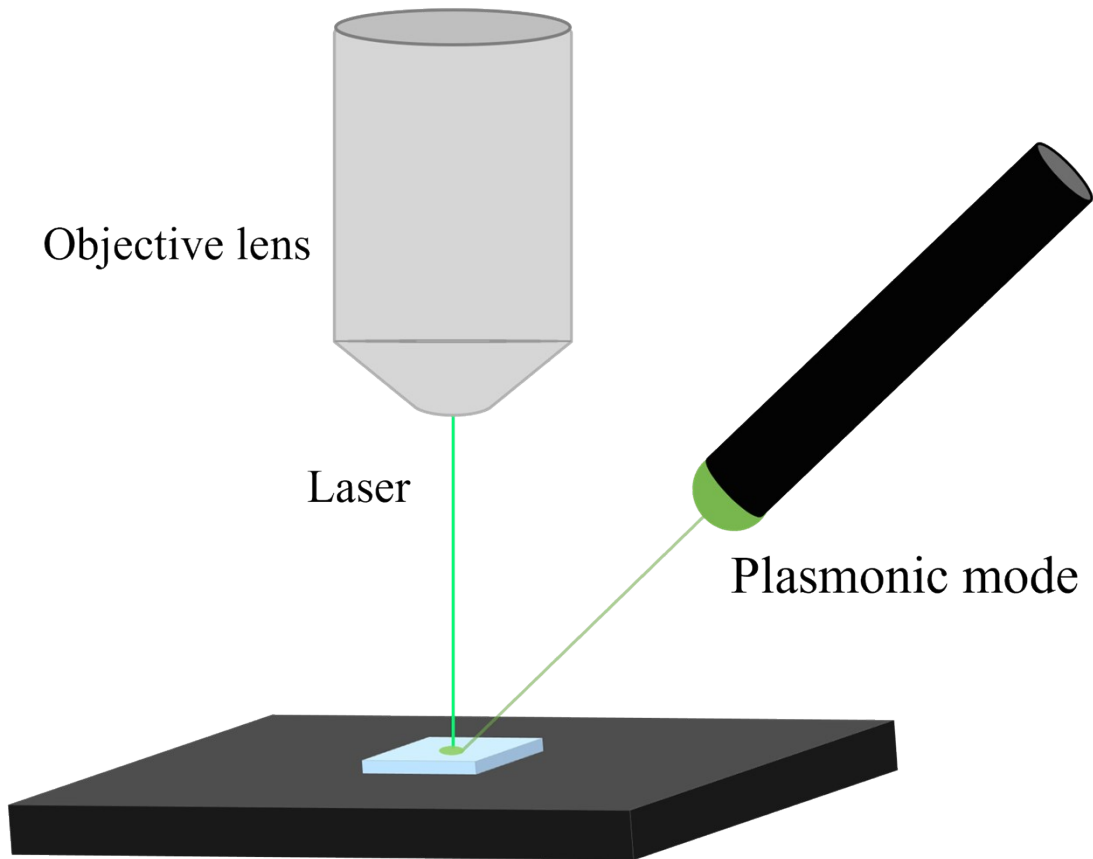
S3 Experimental set up for measurement of Raman spectrum of different dimer nanojunctions under the plasmon-induced electromagnetic field. The laser power for measurement of the Raman spectrum was kept constant and the intensities of irradiation light were tuned for creating the different strengths of the electromagnetic field around dimer nanojunctions. A diode-pumped laser was used as the excitation source (532 nm) and the laser power was maintained at 2.5 mW for all spectral acquisitions. The spectra were collected using 20 scans and the duration of each scan was 1 second. And the point source of purple irradiation (LED source) was used as an external stimulus to excite the plasmon-induced electromagnetic field (I_0 = 2.475 W).
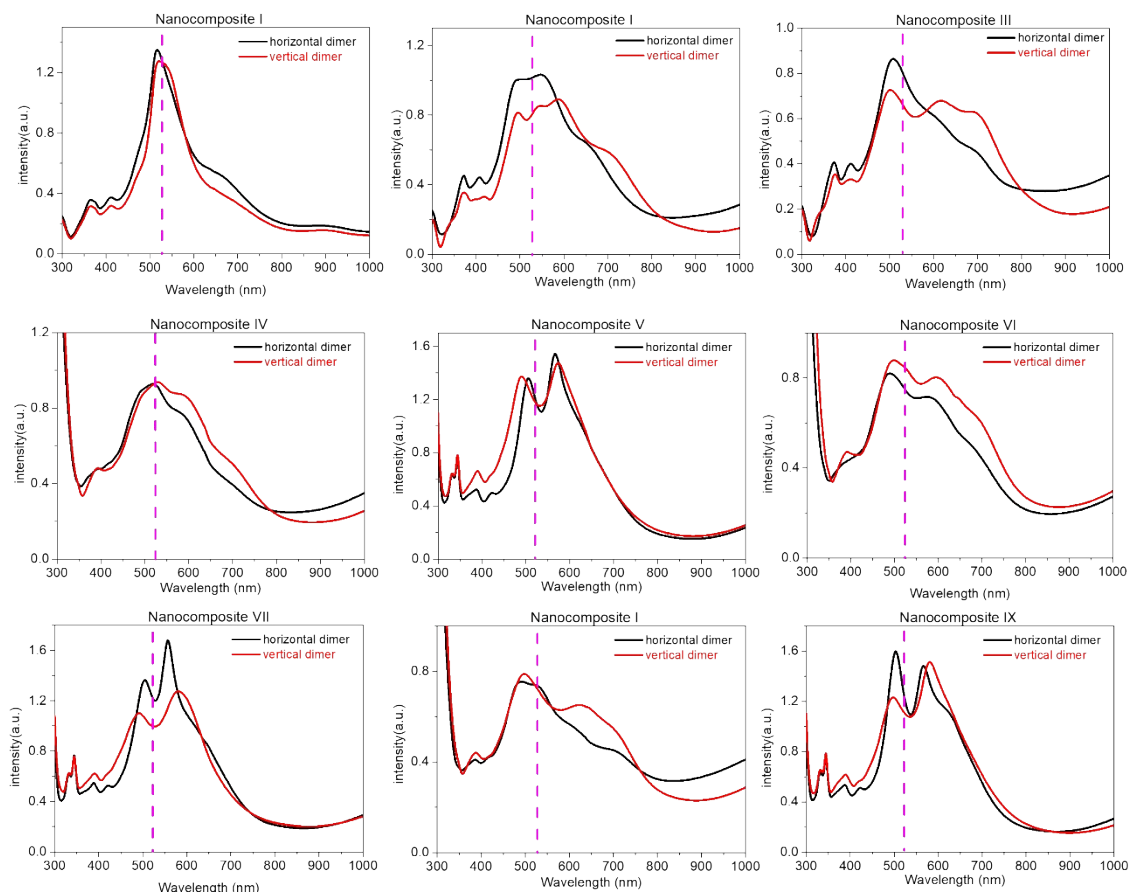
S4 Extinction spectra of horizontal and vertical dimer nanojunctions in nine different nanocomposites. The black solid cures were the extinction spectra of horizontal dimer nanojunctions in nanocomposites (nanocomposite I to IX) composed of different ligands coated AgNC and different polymer matrices. The red solid cures were the extinction spectra of vertical dimer nanojunctions in nanocomposites (nanocomposite I to IX) composed of different ligands coated AgNC and different polymer matrices. The purple dashed lines corresponding to the irradiation wavelength triggered the plasmon-induced electromagnetic field. The extinction spectra of the dimer nanojunctions in nanocomposites at wavelengths below 350nm are caused by scattering or absorption from the rough edges of the glass substrate, which are negligible.
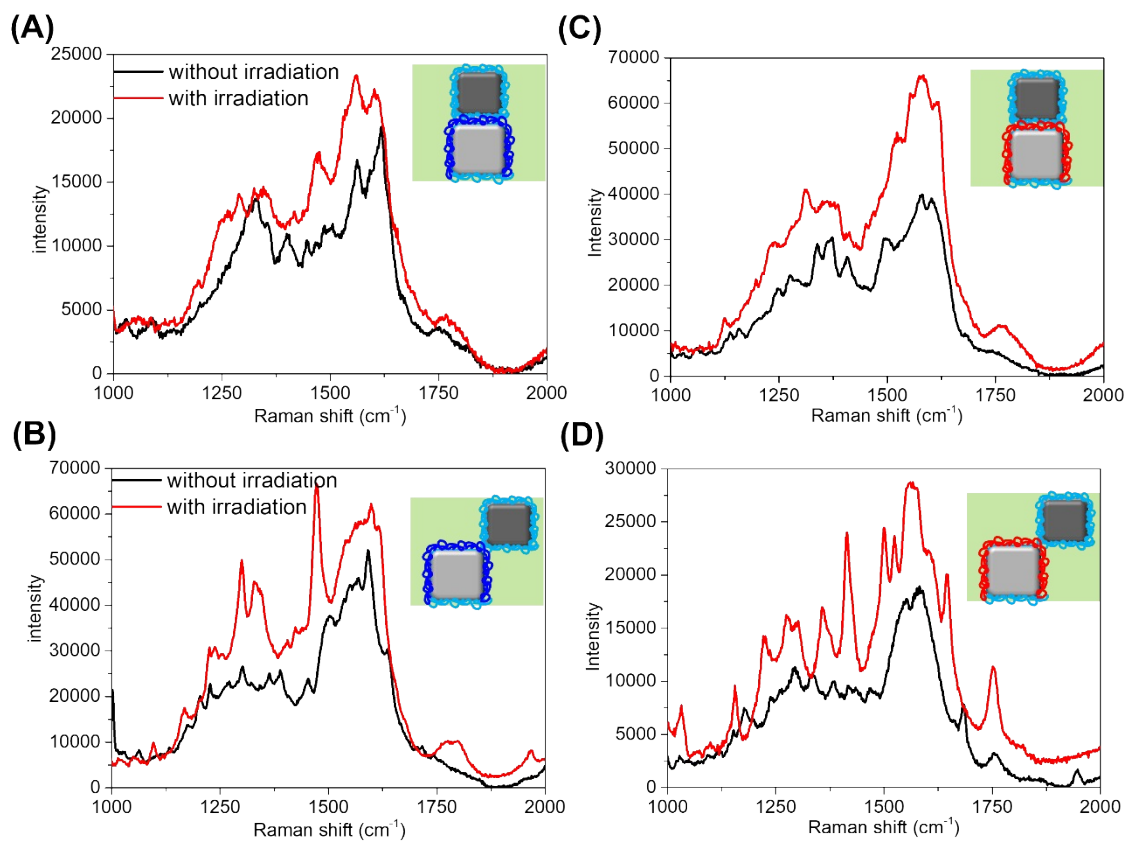
S5 Raman spectra of dimer nanojunctions in different nanocomposites. **(A)** The vertical dimer nanojunctions consisted of HS-poly-*p*-TPA coated AgNCs and PS matrix. **(B)** The horizontal dimer nanojunctions consisted of HS-poly-*p*-TPA coated AgNCs and PS matrix. **(C)** The vertical dimer nanojunctions consisted of HS-PVK coated AgNCs and PS matrix. **(D)** The horizontal dimer nanojunctions consisted of HS-PVK coated AgNCs and PS matrix.
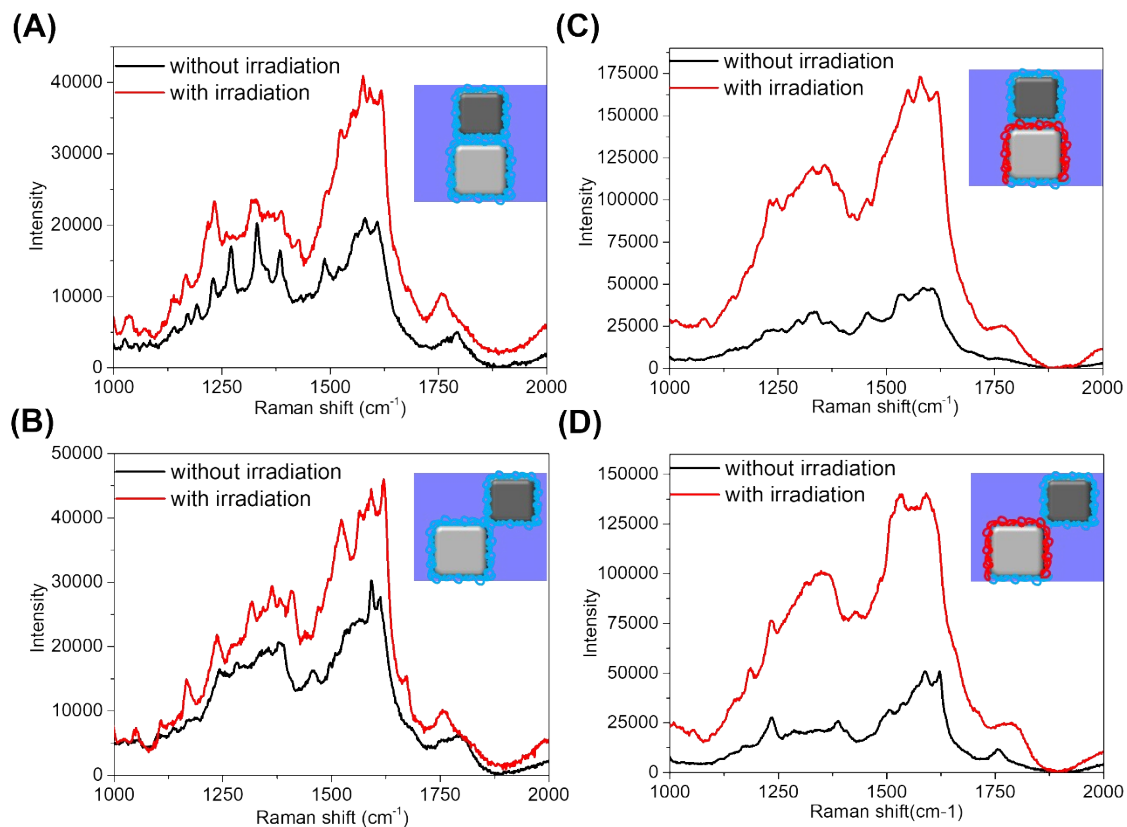
S6 Raman spectra of dimer nanojunctions in different nanocomposites. (A) The vertical dimer nanojunctions consisted of PVP-coated AgNCs and PTPA matrix. **(B)** The horizontal dimer nanojunctions consisted of PVP-coated AgNCs and PTPA matrix. **(C)** The vertical dimer nanojunctions consisted of HS-PVK coated AgNCs and PTPA matrix. **(D)** The horizontal dimer nanojunctions consisted of HS-PVK coated AgNCs and PTPA matrix.
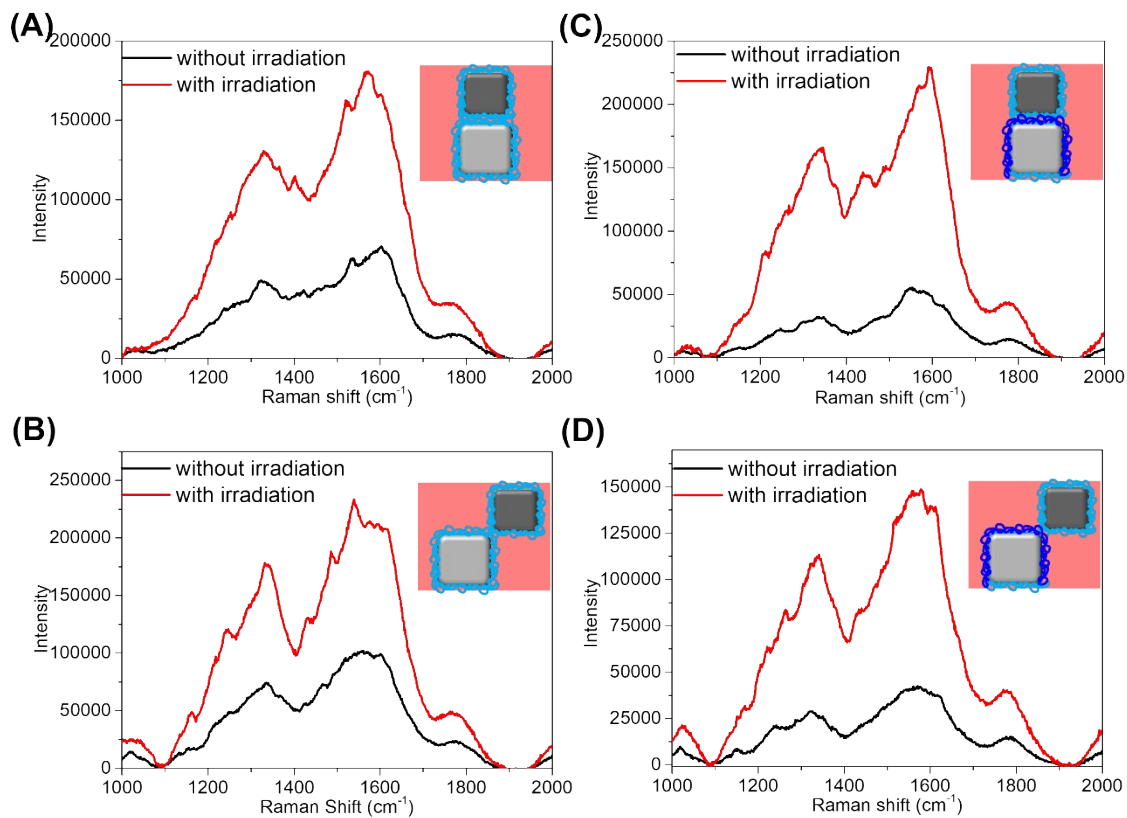
S7 Raman spectra of dimer nanojunctions in different nanocomposites. (A) The vertical dimer nanojunctions consisted of PVP-coated AgNCs and PVK matrix. **(B)** The horizontal dimer nanojunctions consisted of PVP-coated AgNCs and PVK matrix. **(C)** The vertical dimer nanojunctions consisted of HS-poly-*p*-TPA coated AgNCs and PVK matrix. **(D)** The horizontal dimer nanojunctions consisted of HS-poly-*p*-TPA coated AgNCs and PVK matrix.

TableS1 Enhancement factor of chemical vibration modes of PVP, PS, PTPA, and PVK in Raman spectra

Bottom layer-Top layer in Matrix	Dimer	polymer	Enhancement factor (%)	Error bar
I：PVP-AgNC-PVP-AgNC in PS	horizontal	PVP	0.11	2.444
		PS	1.77	3.185
	vertical	PVP	-2.73	2.488
		PS	-3.49	2.583
II：HS-TPA-AgNC-PVP-AgNC in PS	horizontal	PVP	29.01	10.204
		PS	56.03	19.466
		PTPA	27.09	11.549
	vertical	PVP	42.60	3.646
		PS	17.07	8.340
		PTPA	43.69	14.464
III：HS-PVK-AgNC-PVP-AgNC in PS	horizontal	PVP	58.46	36.565
		PS	78.70	2.262
		PVK	43.47	10.117
	vertical	PVP	72.62	9.137
		PS	44.16	15.772
		PVK	62.72	10.379

Bottom layer-Top layer in Matrix	Dimer	polymer	Enhancement factor (%)	Error bar
IV：PVP-AgNC-PVP-AgNC in PTPA	horizontal	PVP	64.68	33.495
		PTPA	74.84	4.971
	vertical	PVP	99.83	3.997
		PTPA	56.31	8.245
V：PVP-AgNC-PVP-AgNC in PVK	horizontal	PVP	126.11	4.648
		PVK	135.02	13.014
	vertical	PVP	177.19	18.810
		PVK	164.83	21.833
VI：HS-TPA-AgNC-PVP-AgNC in PTPA	horizontal	PVP	152.35	5.510
		PTPA	173.39	2.046
	vertical	PVP	251.24	26.194
		PTPA	216.43	16.248
VII：HS-TPA-AgNC-PVP-AgNC in PVK	horizontal	PVP	206.11	16.379
		PTPA	273.36	24.502
		PVK	199.42	14.726
	vertical	PVP	301.51	36.123
		PTPA	245.15	22.631
		PVK	286.33	24.001

Bottom layer-Top layer in Matrix	Dimer	polymer	Enhancement factor (%)	Error bar
VIII：HS-PVK-AgNC-PVP-AgNC in PTPA	horizontal	PVP	239.38	4.438
		PTPA	239.26	6.377
		PVK	289.37	23.482
	vertical	PVP	352.97	9.059
		PTPA	372.54	29.524
		PVK	319.44	22.365
IX：HS-PVK-AgNC-PVP-AgNC in PVK	horizontal	PVP	452.52	18.200
		PVK	484.36	13.394
	vertical	PVP	519.94	25.816
		PVK	475.50	25.799

PS: Enhancement factor = $\dfrac{I_{PIEF} - I_{NoN-PIEF}}{I_{NoN-PIEF}}$

I_{PIEF}: the mean intensity of Raman signals of the analyte under the plasmon-induced electromagnetic field

$I_{NoN-PIEF}$: the mean intensity of Raman signals of the analyte without the plasmon-induced electromagnetic field

TableS2 Enhancement factor of chemical vibration modes of PVP and PS in Raman spectra

Bottom layer-Top layer in Matrix	Power (%)	polymer	enhancement factor(%)	Error bar
Ⅰ：**PVP**-AgNC-**PVP**-AgNC in **PS** (horizontal)	0	PVP	0	1.00E-07
		PS	0	1.00E-07
	25	PVP	0.02	0.838
		PS	0.99	2.498
	50	PVP	-2.35	3.862
		PS	0.17	0.639
	75	PVP	-2.34	3.285
		PS	1.64	1.822
	100	PVP	0.11	2.445
		PS	1.77	3.185
Ⅱ：**PVP**-AgNC-**PVP**-AgNC in **PS** (vertical)	0	PVP	0	1.00E-07
		PS	0	1.00E-07
	25	PVP	-3.54	2.667
		PS	-5.92	3.046
	50	PVP	-3.15	1.134
		PS	-1.50	4.989
	75	PVP	-4.41	0.464
		PS	-1.54	2.323
	100	PVP	-2.73	2.488
		PS	-3.49	2.583

Table S3 Enhancement factor of chemical vibration modes of PVP and PTPA in Raman spectra

Bottom layer-Top layer in Matrix	Power (%)	polymer	Enhancement factor(%)	Error bar
Ⅲ：**SH-TPA**-AgNC-**PVP**-AgNC in **PTPA** (horizontal)	0	PVP	0	1.00E-07
		PTPA	0	1.00E-07
	25	PVP	34.00	7.796
		PTPA	38.41	6.704
	50	PVP	72.64	1.753
		PTPA	89.36	3.145
	75	PVP	112.18	4.813
		PTPA	145.12	7.272
	100	PVP	152.35	5.510
		PTPA	216.43	16.248
Ⅳ：**SH-TPA**-AgNC-**PVP**-AgNC in **PTPA** (vertical)	0	PVP	0	1.00E-07
		PTPA	0	1.00E-07
	25	PVP	45.99	12.376
		PTPA	50.00	0.642
	50	PVP	94.88	21.240
		PTPA	81.59	0.384
	75	PVP	151.34	13.349
		PTPA	132.20	2.883
	100	PVP	251.24	26.194
		PTPA	173.39	2.046

Table S4 Enhancement factor of chemical vibration modes of PVP and PVK in Raman spectra

Bottom layer-Top layer in Matrix	Power (%)	polymer	Enhancement factor(%)	Error bar
V：SH-PVK-AgNC-PVP-AgNC in PVK (horizontal)	0	PVP	0	1.00E-07
		PVK	0	1.00E-07
	25	PVP	53.67	12.477
		PVK	63.14	5.707
	50	PVP	216.07	15.020
		PVK	266.80	10.214
	75	PVP	348.15	13.213
		PVK	379.85	36.343
	100	PVP	452.52	18.201
		PVK	484.36	13.394
VI：SH-PVK-AgNC-PVP-AgNC in PVK (vertical)	0	PVP	0	1.00E-07
		PVK	0	1.00E-07
	25	PVP	89.61	2.639
		PVK	73.22	7.190
	50	PVP	222.57	16.133
		PVK	162.43	37.816
	75	PVP	379.03	35.142
		PVK	277.34	42.960
	100	PVP	519.94	25.816
		PVK	475.50	25.799

Table S5 The relationship between the enhancement factor of chemical vibration mode and irradiation intensity

Sample	Fitting formula：$y=y_0+A*exp(R_0X)$			
	Y_0	A	R_0	R-square
PVP-AgNC-PVP-AgNC in PS (horizontal)	-3.51E-15	3.50E-18	0.380	-0.9956
PVP-AgNC-PVP-AgNC in PS (vertical)	-4.17	4.17	-1298.7	0.9710
SH-TPA-AgNC-PVP-AgNC in PTPA (horizontal)	-611.14	611.14	0.00224	0.9999
SH-TPA-AgNC-PVP-AgNC in PTPA (vertical)	-138.56	138.56	0.01012	0.9954
SH-PVK-AgNC-PVP-AgNC in PVK (horizontal)	-255.53	255.53	0.01077	0.9742
SH-PVK-AgNC-PVP-AgNC in PVK (vertical)	-253.75	253.75	0.01176	0.9930

Table S6 The relationship between the enhancement factor of chemical vibration mode and irradiation intensity

Sample	Fitting formula：$y=y_0+A*exp(R_0X)$			
	Y_0	A	R_0	R-square
PVP-AgNC-PVP-AgNC in PS (horizontal)	-0.35	0.19	0.023	-1.7250
PVP-AgNC-PVP-AgNC in PS (vertical)	-3.49	3.49	-1223.2	0.5113
SH-TPA-AgNC-PVP-AgNC in PTPA (horizontal)	-168.84	168.84	0.00838	0.9993
SH-TPA-AgNC-PVP-AgNC in PTPA (vertical)	-776.60	776.60	0.00203	0.9922
SH-PVK-AgNC-PVP-AgNC in PVK (horizontal)	-357.13	357.13	0.00884	0.9383
SH-PVK-AgNC-PVP-AgNC in PVK (vertical)	-171.56	171.56	0.01332	0.9971
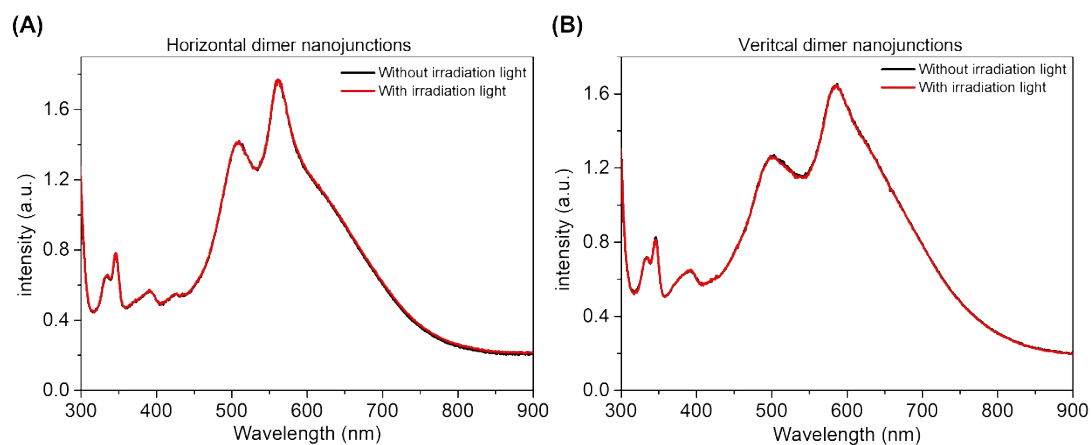
S8 Extinction spectra of HS-PVPK coated AgNC-PVP coated AgNC in PVK matrix with and without plasmon-induced electromagnetic field. The plasmonic response of horizontal and vertical dimer nanojunctions exhibited no significant change under the plasmon-induced electromagnetic field, as shown in (A) and (B), respectively.
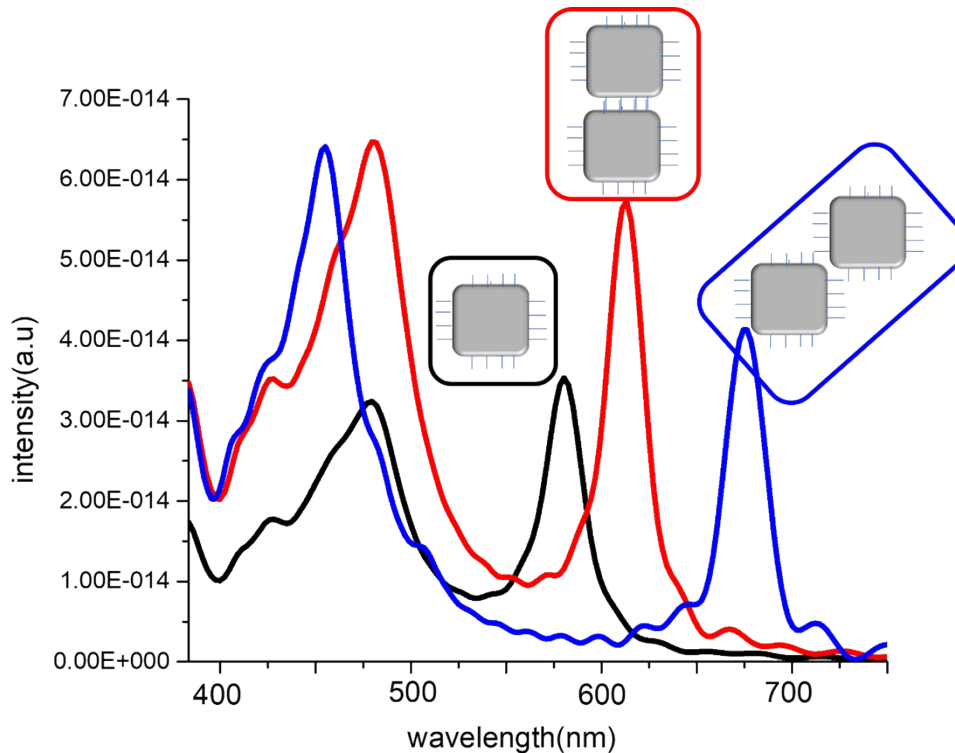
S9 Simulation of extinction spectra: An individual AgNC on the glass substrate (black curve); vertical dimer nanojunction on the glass substrate (red curve); and horizontal dimer nanojunction on the glass substrate (blue curve).

PS: The effect of the configuration of the dimer structure on the plasmonic response (extinction spectrum) and Raman scattering signal of the dimer nanojunctions

" Horizontal dimers" includes the "face-corner", "corner-corner", and "face-face" configurations. The configuration with the strongest electric field is the "corner-corner" configuration, and the one with the weakest electric field is the "face-face" configuration. As shown in supporting information S10 and the literature report,[1] the electric field strength of the "corner-corner" configuration is approximately 1.35 times that of the "face-face" configuration. And the "face-corner" configuration has the electric strength between the "face-face" and "corner-corner" configuration. The difference in electric field strength between different configurations of "horizontal" dimer nanojunctions is not sufficient to cause a significant difference in plasmonic response (extinction spectrum). However, since the Raman scattering signal is highly sensitive to changes in the "electromagnetic field", this difference in electric field strength between different configurations can lead to significant changes in the intensity of the Raman scattering signal. This makes the "horizontal dimer" (which involved three configurations) have a stronger Raman enhancement factor than the "vertical dimer" (mainly "face-face configuration).

Reference
1. B. Gao, G. Arya and A. R. Tao, Nature Nanotechnology, 2012, 7, 433-437.
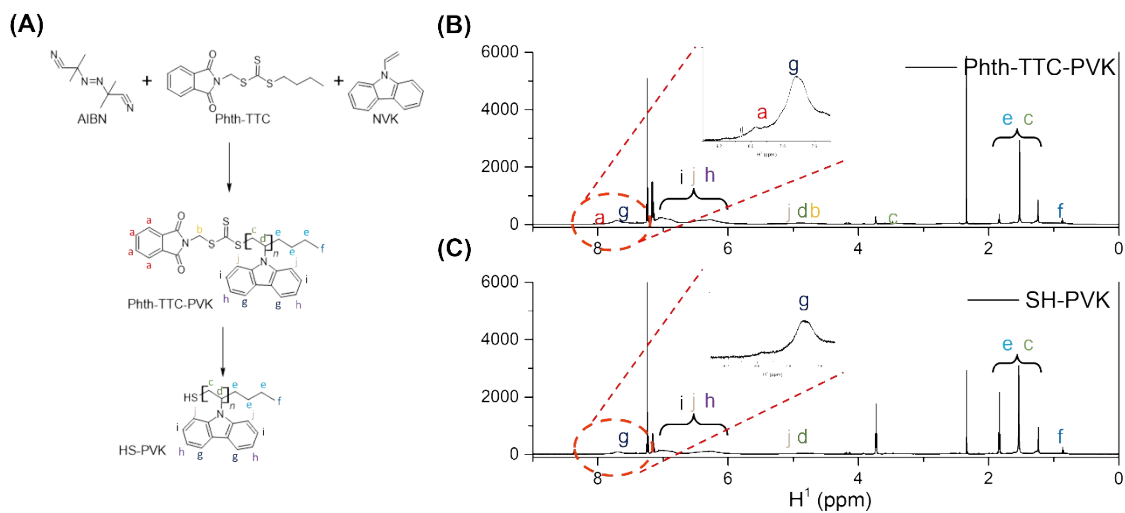
S10 Synthesized of thiol terminated poly(3,6-N-vinylcarbazole) (HS-PVK) by RAFT polymerization (A) For the synthesis of HS-PVK, there are two steps involved: RAFT polymerization and thiolation (more detail can be found in experimental section). (B) The nuclear magnetic resonance (NMR) spectrum of Phth-TTC-PVK monomer. (C) The NMR spectrum of HS-PVK. And the relative chemical shift of H^1 resulted from the corresponded chemical structure as shown in (A) and table S7.

Table S7 Chemical vibration modes of Phth-TTC-PVK and HS-PVK in NMR

Sample	Symbol	Group	Chemical shift
Phth-TTC-PVK	a	Benzene of Phth-TTC	8.05
	b	N-CH_2-S	4.5-5.2
	c	S-CH_2-CH	3.47、1.1-2.0
	d	S-CH$_2$-CH	4.5-5.2
	e	R-(CH_2)$_3$-CH$_3$	1.1-2
	f	R-(CH$_2$)$_3$-CH_3	0.85
	g	Benzene of NVK	7.5-8.0
	h		6.0-7.1
	i		6.0-7.1
	j		4.5-5.2、6.0-7.1
HS-PVK	c	S-CH_2-CH	1.1-2.0
	d	S-CH$_2$-CH	4.5-5.2
	e	R-(CH_2)$_3$-CH$_3$	1.1-2
	f	R-(CH$_2$)$_3$-CH_3	0.85
	g	Benzene of NVK	7.5-8.0
	h		6.0-7.1
	i		6.0-7.1
	j		4.5-5.2、6.0-7.1