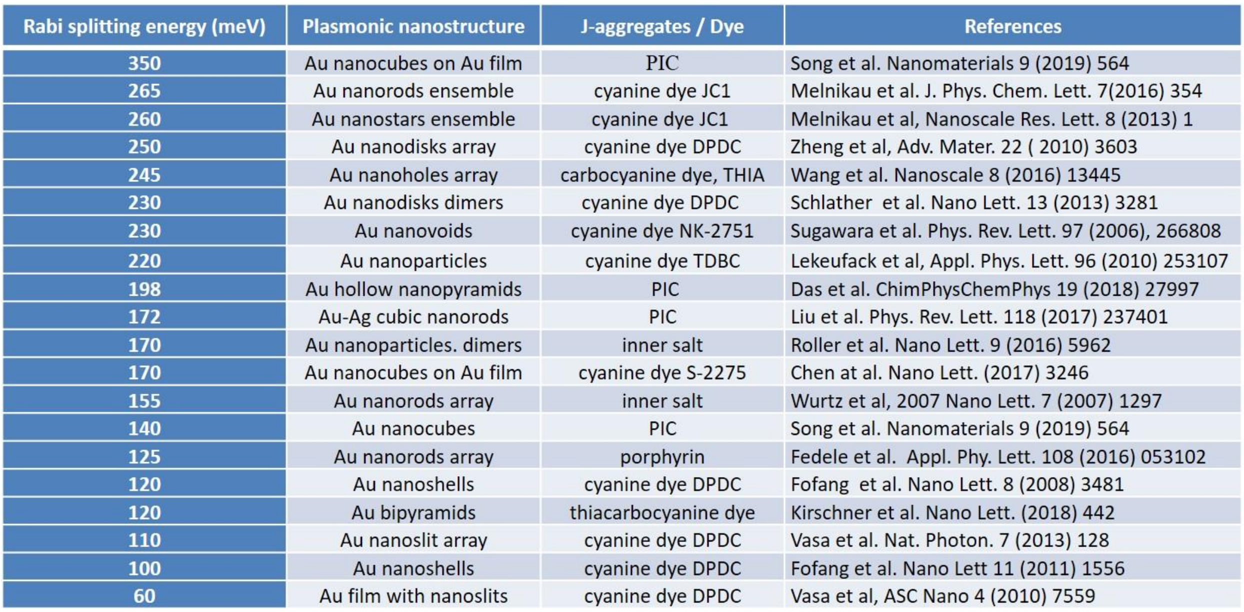
Electronic Supplementary Material (ESI) for Nanoscale.

Supporting information

Strongly coupled exciton-plasmon nanohybrids reveal extraordinary resistance to harsh environmental stressors: temperature, pH and irradiation

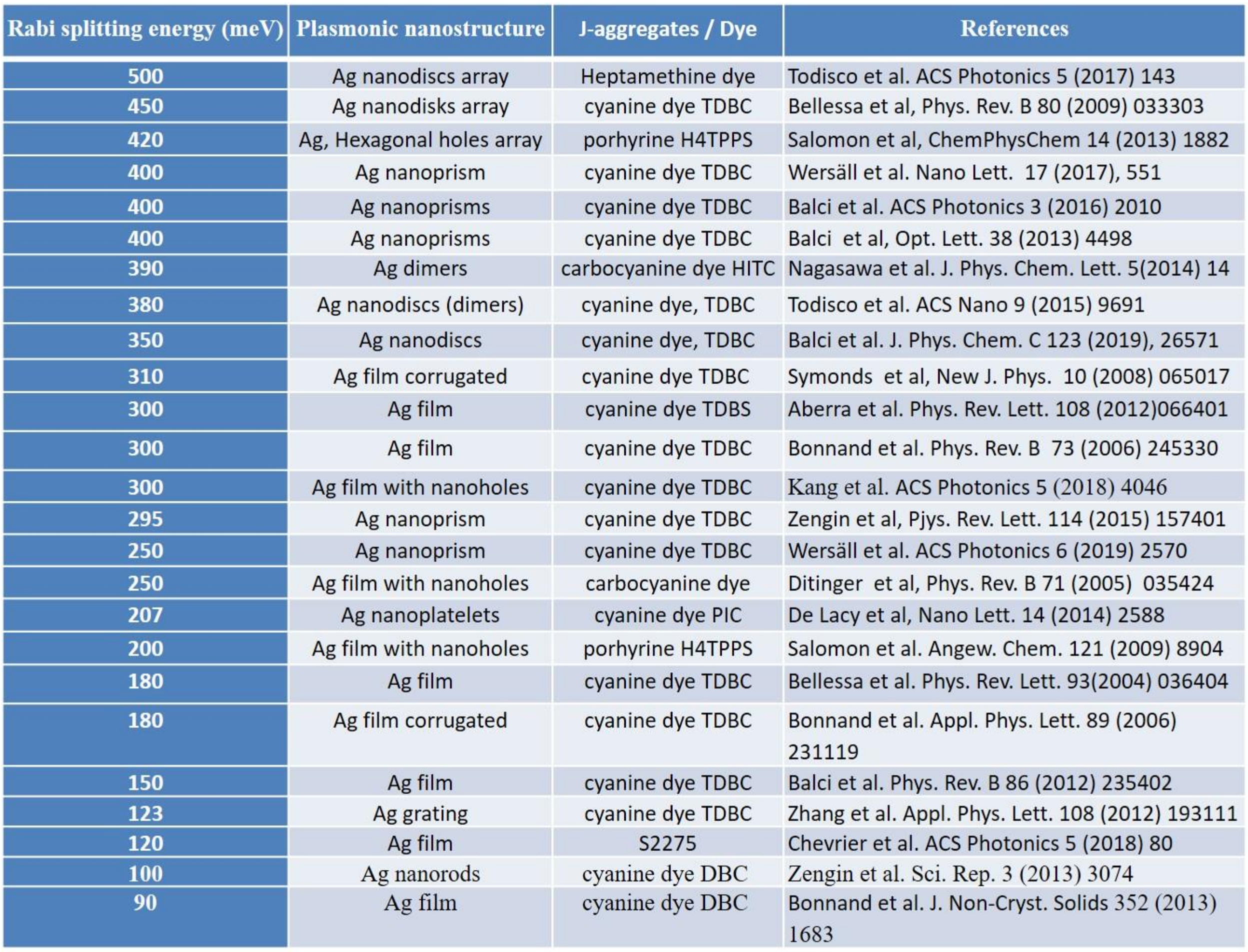
*Thomas Hendel, Victor Krivenkov, Ana Sánchez-Iglesias, Marek Grzelczak, Yury P. Rakovich**

S1. Rabi splitting energies in Au/J-aggregates –based hybrid nanostructures



Rabi splitting energy (meV)	Plasmonic nanostructure	J-aggregates / Dye	References
350	Au nanocubes on Au film	PIC	Song et al. Nanomaterials 9 (2019) 564
265	Au nanorods ensemble	cyanine dye JC1	Melnikau et al. J. Phys. Chem. Lett. 7(2016) 354
260	Au nanostars ensemble	cyanine dye JC1	Melnikau et al, Nanoscale Res. Lett. 8 (2013) 1
250	Au nanodisks array	cyanine dye DPDC	Zheng et al, Adv. Mater. 22 (2010) 3603
245	Au nanoholes array	carbocyanine dye, THIA	Wang et al. Nanoscale 8 (2016) 13445
230	Au nanodisks dimers	cyanine dye DPDC	Schlather et al. Nano Lett. 13 (2013) 3281
230	Au nanovoids	cyanine dye NK-2751	Sugawara et al. Phys. Rev. Lett. 97 (2006), 266808
220	Au nanoparticles	cyanine dye TDBC	Lekeufack et al, Appl. Phys. Lett. 96 (2010) 253107
198	Au hollow nanopyramids	PIC	Das et al. ChimPhysChemPhys 19 (2018) 27997
172	Au-Ag cubic nanorods	PIC	Liu et al. Phys. Rev. Lett. 118 (2017) 237401
170	Au nanoparticles. dimers	inner salt	Roller et al. Nano Lett. 9 (2016) 5962
170	Au nanocubes on Au film	cyanine dye S-2275	Chen at al. Nano Lett. (2017) 3246
155	Au nanorods array	inner salt	Wurtz et al, 2007 Nano Lett. 7 (2007) 1297
140	Au nanocubes	PIC	Song et al. Nanomaterials 9 (2019) 564
125	Au nanorods array	porphyrin	Fedele et al. Appl. Phy. Lett. 108 (2016) 053102
120	Au nanoshells	cyanine dye DPDC	Fofang et al. Nano Lett. 8 (2008) 3481
120	Au bipyramids	thiacarbocyanine dye	Kirschner et al. Nano Lett. (2018) 442
110	Au nanoslit array	cyanine dye DPDC	Vasa et al. Nat. Photon. 7 (2013) 128
100	Au nanoshells	cyanine dye DPDC	Fofang et al. Nano Lett 11 (2011) 1556
60	Au film with nanoslits	cyanine dye DPDC	Vasa et al, ASC Nano 4 (2010) 7559

S2. Rabi splitting energies in Ag/J-aggregates –based hybrid structures



Rabi splitting energy (meV)	Plasmonic nanostructure	J-aggregates / Dye	References
500	Ag nanodiscs array	Heptamethine dye	Todisco et al. ACS Photonics 5 (2017) 143
450	Ag nanodisks array	cyanine dye TDBC	Bellessa et al, Phys. Rev. B 80 (2009) 033303
420	Ag, Hexagonal holes array	porhyrine H4TPPS	Salomon et al, ChemPhysChem 14 (2013) 1882
400	Ag nanoprism	cyanine dye TDBC	Wersäll et al. Nano Lett. 17 (2017), 551
400	Ag nanoprisms	cyanine dye TDBC	Balci et al. ACS Photonics 3 (2016) 2010
400	Ag nanoprisms	cyanine dye TDBC	Balci et al, Opt. Lett. 38 (2013) 4498
390	Ag dimers	carbocyanine dye HITC	Nagasawa et al. J. Phys. Chem. Lett. 5(2014) 14
380	Ag nanodiscs (dimers)	cyanine dye, TDBC	Todisco et al. ACS Nano 9 (2015) 9691
350	Ag nanodiscs	cyanine dye, TDBC	Balci et al. J. Phys. Chem. C 123 (2019), 26571
310	Ag film corrugated	cyanine dye TDBC	Symonds et al, New J. Phys. 10 (2008) 065017
300	Ag film	cyanine dye TDBS	Aberra et al. Phys. Rev. Lett. 108 (2012)066401
300	Ag film	cyanine dye TDBC	Bonnand et al. Phys. Rev. B 73 (2006) 245330
300	Ag film with nanoholes	cyanine dye TDBC	Kang et al. ACS Photonics 5 (2018) 4046
295	Ag nanoprism	cyanine dye TDBC	Zengin et al, Pjys. Rev. Lett. 114 (2015) 157401
250	Ag nanoprism	cyanine dye TDBC	Wersäll et al. ACS Photonics 6 (2019) 2570
250	Ag film with nanoholes	carbocyanine dye	Ditinger et al, Phys. Rev. B 71 (2005) 035424
207	Ag nanoplatelets	cyanine dye PIC	De Lacy et al, Nano Lett. 14 (2014) 2588
200	Ag film with nanoholes	porhyrine H4TPPS	Salomon et al. Angew. Chem. 121 (2009) 8904
180	Ag film	cyanine dye TDBC	Bellessa et al. Phys. Rev. Lett. 93(2004) 036404
180	Ag film corrugated	cyanine dye TDBC	Bonnand et al. Appl. Phys. Lett. 89 (2006) 231119
150	Ag film	cyanine dye TDBC	Balci et al. Phys. Rev. B 86 (2012) 235402
123	Ag grating	cyanine dye TDBC	Zhang et al. Appl. Phys. Lett. 108 (2012) 193111
120	Ag film	S2275	Chevrier et al. ACS Photonics 5 (2018) 80
100	Ag nanorods	cyanine dye DBC	Zengin et al. Sci. Rep. 3 (2013) 3074
90	Ag film	cyanine dye DBC	Bonnand et al. J. Non-Cryst. Solids 352 (2013) 1683

S3. Experimental

Optical extinction spectra were recorded using a Cary 50 spectrometer (Agilent Technologies). For measurement of the pH value a FiveGo F2 pH-meter (Mettler-Toledo) has been used.

To study the pH influence on the hybrid nanostructures small amounts of diluted H_2SO_4 have been added to the samples under vigorous stirring and subsequently pH value and extinction spectra have been measured.

The temperature influence on the hybrid nanostructures has been investigated recording their extinction spectra with an 8453 spectrophotometer equipped with a Peltier temperature controller 89090A 8 (both Agilent).

Photostability experiments have been carried out using a high intensity illuminator MI-150 (Dolan-Jenner Industries) equipped with a low voltage halogen lamp 13629 (Philips). The irradiance was measured with a PMA2200 photometer (Solar Light). The samples were irradiated directly in a quartz cuvette and extinction spectra were recorded after certain time intervals.

A transmission electron microscopy (TEM) image of nanorods obtained using transmission electron microscope FEG-TEM of type JEOL JEM-2100F UHR.

S4. Chemicals

Cyanine dyes 5,5′,6,6′-Tetrachloro-1,1′,3,3′-tetraethyl-imidacarbocyanine iodide (JC1), tetrachloroauric acid (HAuCl4), sodium borohydride (NaBH4), hexadecyltrimethylammonium bromide (CTAB), benzyldimethylhexadecylammonium chloride (BDAC), silver nitrate (AgNO3), hydrochloric acid (HCl), ascorbic acid (AA) were purchased from Sigma-Aldrich.

S5. Synthesis of gold nanorods

Gold nanorods were prepared using Ag-assisted seeded growth. Seeds were prepared by the reduction of $HAuCl_4$ (5 mL, 0.25 mM) with $NaBH_4$ (0.3 mL, 10 mM) in aqueous CTAB solution (100 mM). An aliquot of seed solution (0.12 mL) was added to a growth solution containing CTAB (50 mL, 100 mM), HAuCl4 (0.5 mL, 50 mM), ascorbic acid

(0.4 mL, 100 mM), $AgNO_3$ (0.6 mL, 10 mM) and HCl (0.95 mL, 1000 mM). The mixture was left undisturbed at 30 ºC for 2 h. The solution was centrifuged twice (8000 rpm, 30 min) and redispersed in BDAC (10 mM) to obtain a final concentration of gold equal to 0.25 mM. The maximum of LSPR of the initial gold nanorods was 860 nm.

S6. Preparation of J-aggregates and formation of hybrid nanostructures

J-aggregates of the JC1 dye form spontaneously upon dissolution of this dye in water at pH8. The production of the hybrid Au@Ag nanorods and J-aggregates system relies upon the electrostatic interactions between the anionic groups of the J-aggregates and the cationic sites of stabilizing agent CTAB at the surface of bare Au nanorods. An aliquot of ethanol solution of JC1 (20 µL, 0.774 mM) was added to the solution of gold nanorods (2 mL, [Au] = 0.5 mM, [CTAB] = 1mM) under stirring, followed by the addition of NaOH (20 µL, 0.1 M). The solution was left stirring for the next 10 minutes. The sample was centrifuged (6000 rpm, 20 minutes) and redispersed in Mili-Q water.

Z-potential studies of Au nanorods reveal positive potential even after their integration with J-aggregates. This implies that surface charge provided by a stabilizer is not compensated by the charge of J-aggregates and prevails in the hybrid system ensuring colloidal stability.

S7. Spectral characterization

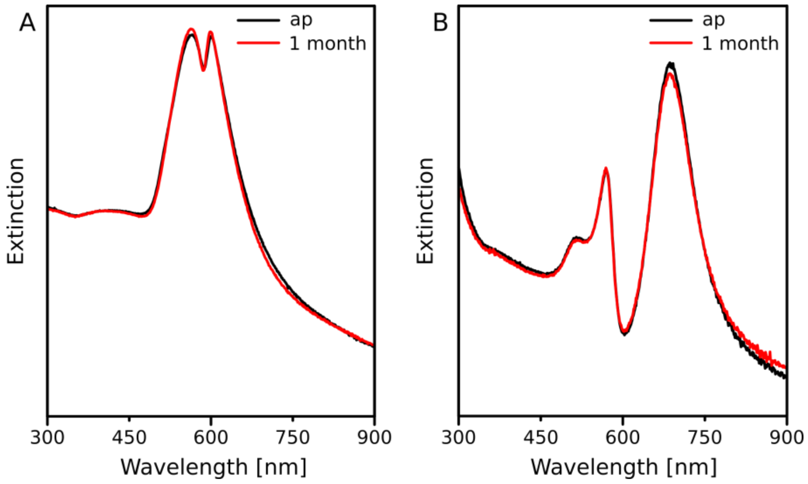


Figure S1. Extinction spectra of as-prepared and aged solutions containing hybrids from JC1-based J-aggregates with gold nanospheres (A) and nanorods (B).

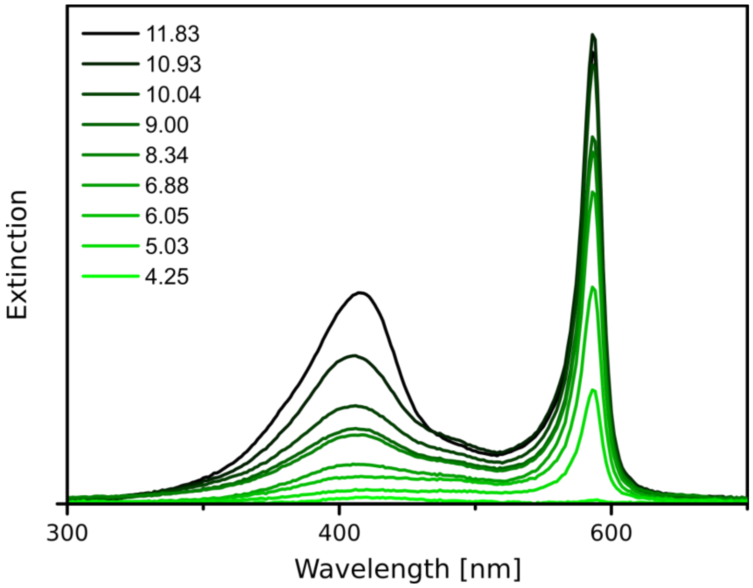


Figure S2. Evolution of extinction spectra of a pure aqueous JC1 solution upon decrease of the pH value.