Low-dimensional Carbon Spacers in Surface Plasmon-Coupled Emission with Femtomolar Sensitivity and 1000-fold Fluorescence Enhancements.

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Supplementary Information

Materials and Methods:

Fullerenes (C60 and C70), carbon nanotubes (CNT), nano-diamonds (ND) were purchased from PlasmaChem GmbH, Berlin. Silver nitrate (AgNO3), Rhodamine 6G (Rh6G), poly vinyl alcohol (PVA) were procured from Sigma-Aldrich. Graphene was procured from Graphene Supermarket, USA. Graphene oxide (GO) was prepared from graphene by Hummer's method[S1]. Carbon dots (CD) were synthesized by microwave assisted method[S2]. Silver and gold nanoparticles decorated carbon dots (AgCD and AuCD) were synthesized by a modified procedure[S3], by taking silver and gold salts in the presence of CD at different concentrations and irradiating with 265nm UV light for 20 minutes in Heber multi-lamp photo reactor. Pyrex slides coated with 50nm silver thin film and 5 nm silica top layer were purchased from EMF Corp, USA.

The carbon allotropes (graphene, GO, CNT C60 and C70) of 1 mg/ml concentration and 0.1 % solution of ND and CD dispersed in 1% PVA were used for spacer layer engineering. The fabrication of RC1 and RC2 formats containing the low-dimensional carbon, involved the use of silver slides that were spin-coated at 3000 rpm for 60 seconds to obtain a 30 nm thick layer of PVA. The thus fabricated multilayer SPCE substrates were attached to a hemi-cylindrical prism that was mounted on a rotating stage. The substrates were illuminated with a 532 nm c.w. laser (5mW). The emission was passed through a 550 nm filter, before collecting into a fiber coupled to Ocean Optics USB 2000+ fiber optic spectrometer. The angularity and enhancements were measured with the help of a rotating stage. Polarization measurements were carried out by placing a sheet polarizer between the prism and the collection fiber. Commercially available Lumerical FDTD solutions and TfCalc softwares were used for complimenting the experimental results with the simulation studies.

SPCE angularity studies with CNT, Graphene, GO and C60:

To elucidate the predominant interaction between Rh6G and π- conjugated systems like CNT, GO, graphene and C60 were taken in the RC1 format and the emission at different SPCE angles were recorded. We found that in the case of GO and CNT (that were O-functionalized), there was a change in the emission wavelength maxima when observed at different SPCE angles. However, in the case of graphene and C60, there was no change in the emission wavelength maxima with the observation angle (Figure S1). We could hence conclude that the coulombic interactions were responsible for the aggregation of Rh6G into dimers and trimers in the case of CNT and GO.

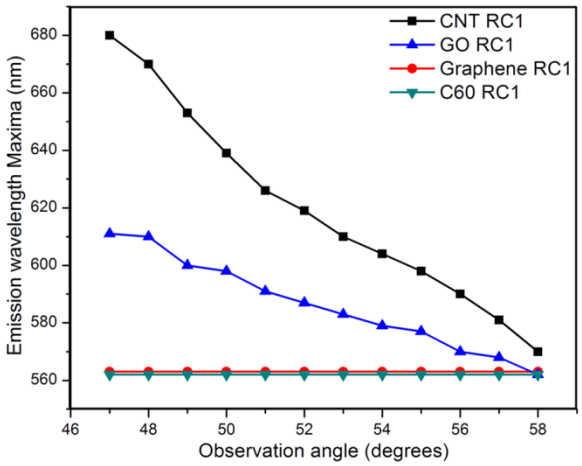

Figure S1. Rh6G emission at different SPCE observation angles for CNT, GO, graphene and C60.

Table S1: Spacer materials and their SPCE enhancements in different formats

Spacer materials	Format	Free Space region*(a.u)	SPCE region* (a.u)	Fluorescence Enhancements*‡	% p-Polarization*‡
Graphene	RC1	249 (±5.26)	3176(±178.70)	13 (±0.77)	97 (±0.76)
	RC2	515(±7.20)	13845(±151.20)	27 (±0.48)	96 (±1.00)
GO	RC1	247(±4.49)	6132(±102.79)	25 (±0.62)	94 (±1.04)
	RC2	275(±4.88)	5485(±84.04)	20 (±0.47)	98 (±0.28)
CNT	RC1	223(±4.50)	6241(±119.18)	28 (±0.78)	96 (±0.76)
	RC2	289(±5.57)	6167(±87.74)	21 (±0.51)	98 (±0.57)
C60	RC1	214(±3.66)	5536(±98.65)	25 (±0.57)	96 (±1.00)
	RC2	238(±6.62)	11971(±39.60)	50 (±0.83)	99 (±0.50)
C70	RC1	610(±7.43)	13160(±92.55)	22 (±0.30)	97 (±0.76)
	RC2	643(±5.43)	33325(±87.23)	52 (±0.46)	96 (±1.04)
ND	RC1	368(±4.33)	4415(±67.99)	12 (±0.23)	96 (±0.28)
	RC2	376(±6.18)	4180(±92.01)	11 (±0.31)	95 (±0.57)
CD	RC1	367(±4.94)	64824(±114.35)	177 (±2.40)	97 (±0.76)
	RC2	327(±4.76)	24401(±106.50)	75 (±1.13)	94 (±0.28)
AgCD	RC1†	55(±2.22)	64779(±89.25)	1178 (±47.47)	98 (±0.57)
	RC2	226(±4.60)	12723(±86.52)	56 (±1.21)	98 (±0.76)
AuCD	RC1	601(±4.26)	30904(±79.57)	51 (±0.39)	96 (±0.76)
	RC2	610(±7.56)	12934(±121.71)	21 (±0.33)	94 (±0.57)

* Mean values obtained from triplicate studies of the sample. ‡ Standard deviation in parenthesis. †High fluorescence intensities required the use of an aperture, to reduce the illumination area of the sample.

SPCE based bio-tagging application:

Trichoderma harzianum rifai (TH) and *Aspergillus oryzae* (AO) grown in a nutrient medium containing CD were coated on silver thin films as spacers. Figure S2 and S3 show the enhancement and polarization of plasmon-coupled fluorescence in the presence of CD tagged TH and AO respectively.

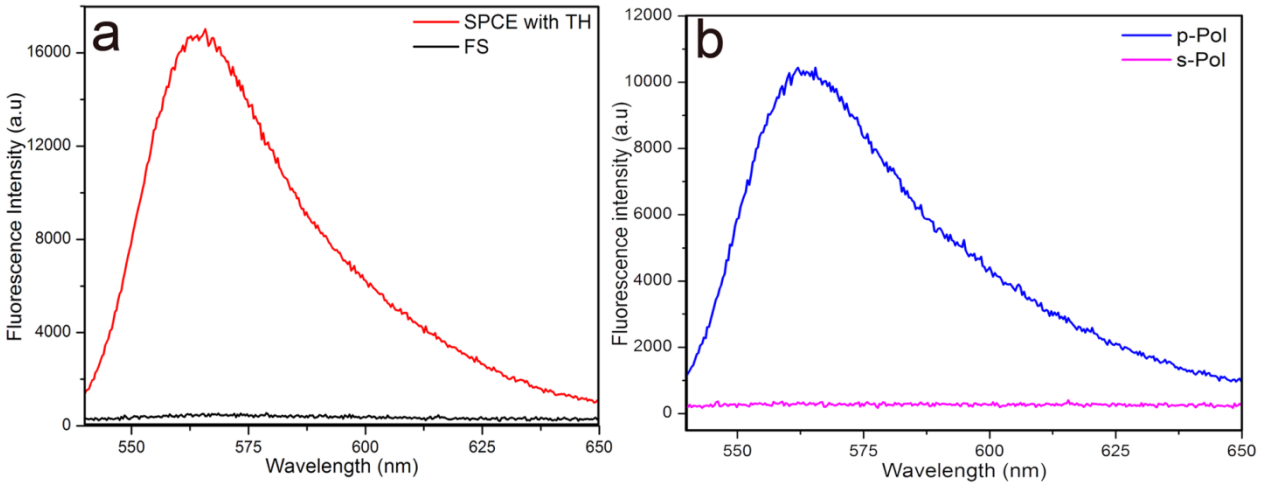

Figure S2. (a) Free space and plasmon-enhanced emission with TH, (b) Polarization of the enhanced emission.

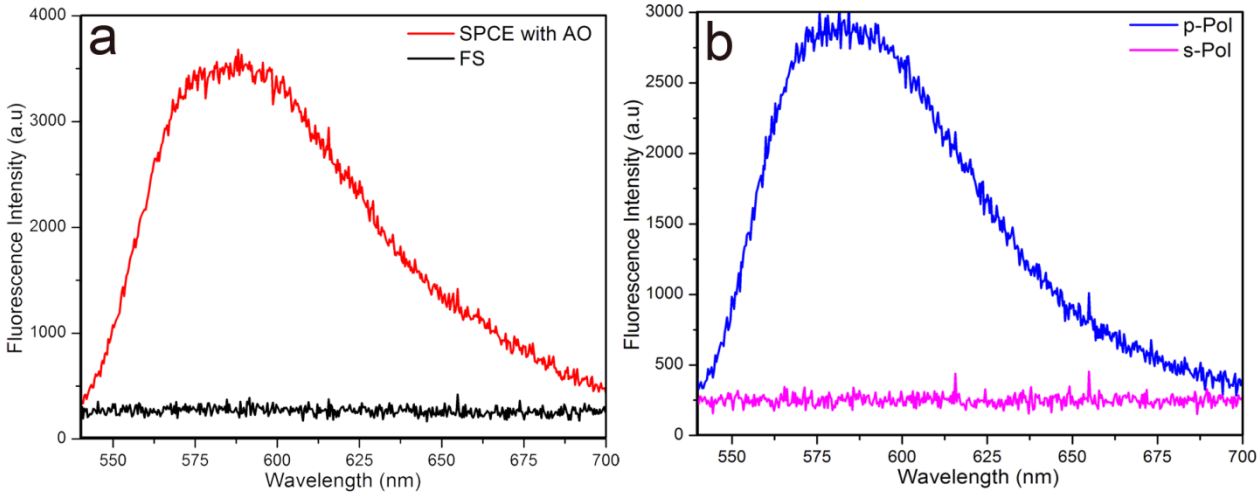

Figure S3. (a) Free space and plasmon-enhanced emission with AO, (b) Polarization of the enhanced emission.

AuCD as spacer in SPCE studies:

AuCD showed lesser enhancements than bare CD. This is in line with our previous work[4] where we reported that gold nanoparticles act as quencher for Rh6G emission. However, this material could be used to tune the SPCE enhancements for sensing applications.

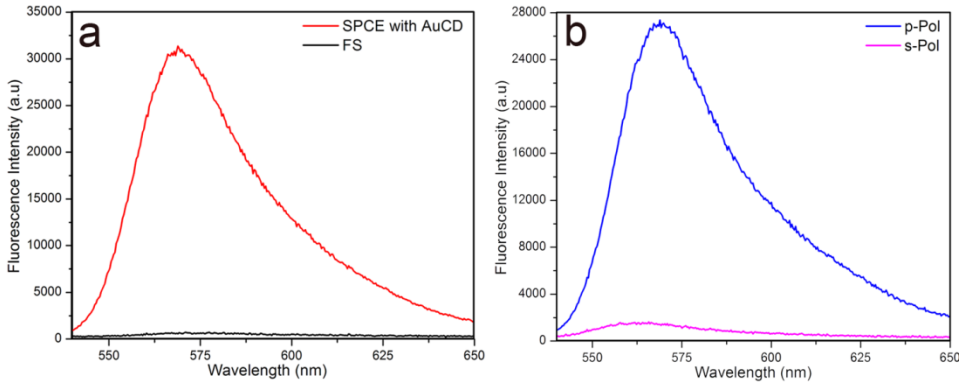

Figure S4. Enhanced emission of Rh6G in the presence of AuCD in RC1 format, (b) Polarization of the enhanced emission.

AgCD: a unique spacer

AgCD in RC1 format yielded >1000 fold enhancement in fluorescence emission. However, to confirm the unique SPCE enhancements achieved with AgCD alone, we carried out similar SPCE studies by taking a physical mixture of silver nanoparticles (AgNPs) and CD in RC1 format. We found that the spacer generated using a physical mixture of AgNPs and CD did not show similar enhancements in fluorescence like AgCD (FigureS5). Consequently the decoration of CD with AgNPs is a prerequisite to attain high SPCE enhancements.

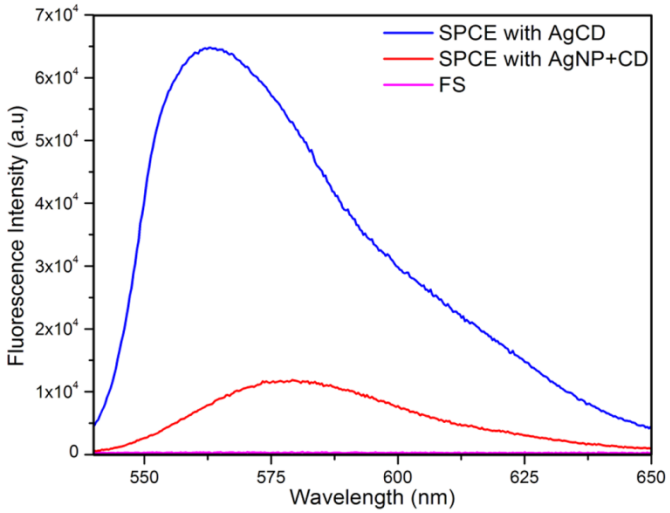

Figure S5. Different SPCE enhancements obtained with the use of AgCD and a physical mixture of AgNPs and CD in RC1 format.

Simulations:

We carried out a series of 2D FDTD simulations to study the orientation effect of a radiating dipole with a graphene sheet and its coupling efficiency. The graphene layer was simulated as reported[S4] and the dipole was placed at a 10nm distance from the graphene surface to excite the TM mode SPP wave. The efficiency of coupling with the graphene plasmons was studied at different angles of orientation. The Tf.Calc simulation of the plasmon resonance dips for the monomer, perfect dimer and twisted dimers of Rh6G show that the coupling angles for each of these moieties are different. This correlated well with the observation of the fluorescence emission from these diverse species at different SPCE angles.

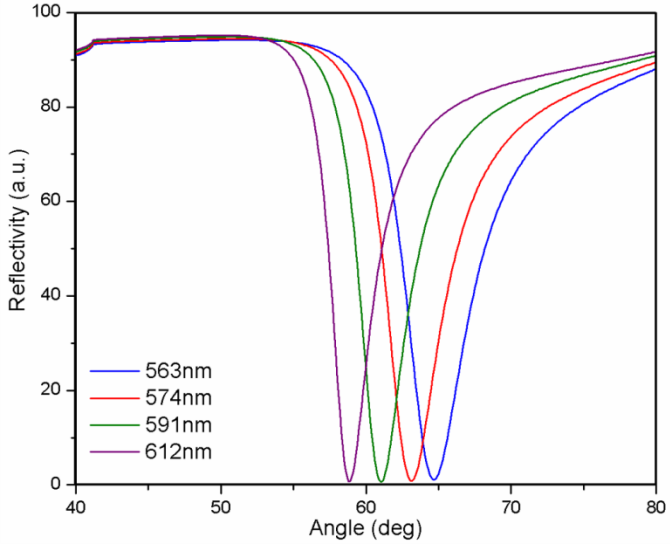

Figure S6. Plasmon resonance dips for different Rh6G moieties on the silver thin film.

Magnitude of fluorescence emission intensities from different Rh6G molecular aggregates:

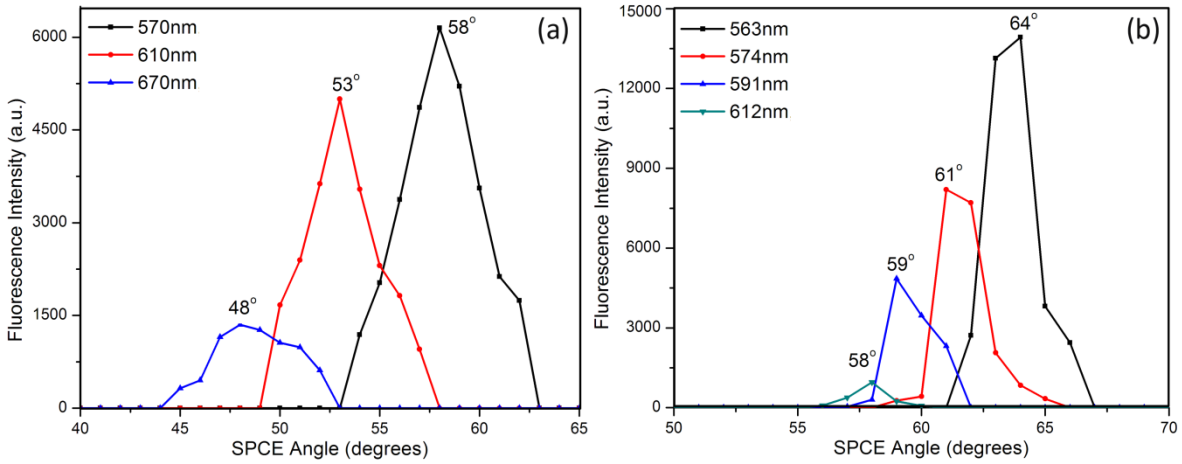

Figure S7. Fluorescence emission of different wavelengths observed at various angles with (a) CNT in RC1, (b) Graphene in RC2 formats.

References:

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