Halogen Bond-Assisted Self-assembly of Gold Nanoparticles in Solution and on a Planar Surface

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Electronic Supplementary Information

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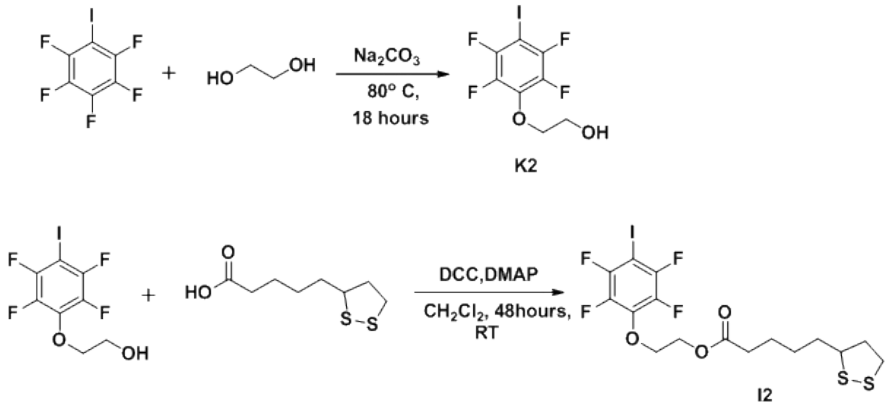
S.1. Synthesis of Ligands

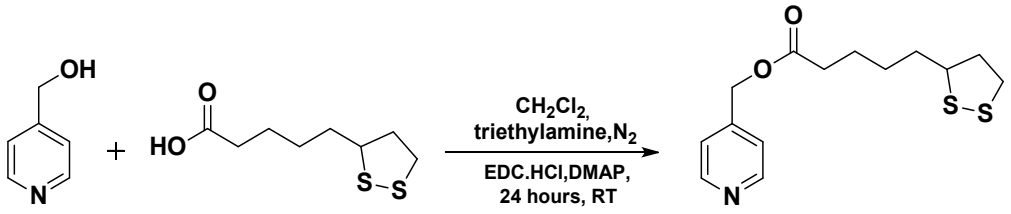
S.1.1. *Synthesis of XB donor ligand (I2)*



*2-(2,3,5,6-tetrafluoro-4-iodophenoxy)ethanol (**K2**):* Iodopentafluorobenzene (34 mmol), ethylene glycol (340 mmol), and Na_2CO_3 (37 mmol) were heated to 80 ºC under vigorous stirring for 18 hours. The product was purified by column chromatography using hexane:ethyl acetate as solvent, varying the polarity from 8:2 to 1:1 mixture. Colorless oil, yield: 5.3 g (47 %), ^{1}H NMR (500 MHz, $CDCl_3$) δ = 4.36 (t, *J*= 15 Hz, 2H), 3.92-3.95 (m, 2 H), 2.01 (t, *J*= 10 Hz, 1 H). ^{19}F NMR (500 MHz, $CDCl_3$) δ = -121.92 (2 F), -155.39 (2 F). MS: $[M]^+$ 336, $[M+ Na]^+$ 359.

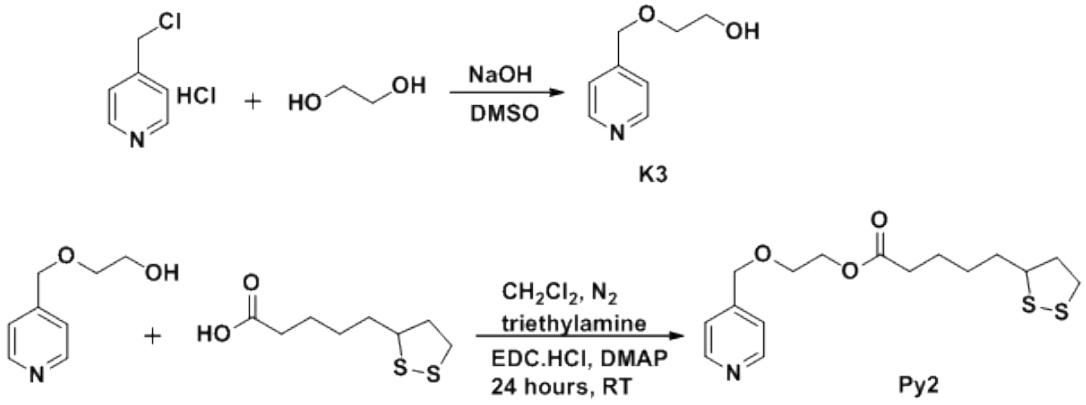
*2-(2,3,5,6-tetrafluoro-4-iodophenoxy)ethyl 5-(1,2-dithiolan-3-yl)pentanoate (**I2**)*: 2-(2,3,5,6-tetrafluoro-4-iodophenoxy)ethanol (13.39 mmol), thioctic acid (13.39 mmol), dicyclohexylcarbodiimide (14.73 mmol) and dimethylaminopyridine (0.044 mmol) were dissolved in dry dichloromethane (100 mL) and stirred at room temperature for 48 hours. The precipitate was filtered off and the filtrate was washed with 5 % (200 mL) aqueous acetic acid, the organic layer was separated and evaporated. Crude sample was purified by column using hexane/ethyl acetate (8:2). Yellow oil, yield: 3.6 g (53 %), ^{1}H NMR (400 MHz, $CDCl_3$) δ = 4.42 (d, *J*= 4 Hz, 4H), 3.53-3.60 (m, 1H), 3.08-3.21 (m, 2H), 2.42-2.50 (m, 1H), 2.35 (t, *J*= 8 Hz, 2H), 1.87-1.95 (m, 1H), 1.61-1.72 (m, 4H), 1.40-1.53 (m, 2H) ppm.^{19}F NMR (500 MHz, $CDCl_3$) δ = -120.9 (2 F), -154.6 (2 F) ppm. ^{13}C NMR (500 MHz, $CDCl_3$): 173.3, 147.3, 140.8, 137.9, 72.8, 62.9, 56.4, 40.4, 38.6, 34.7, 34.0, 29.8, 28.8, 24.7 ppm. MS: $[M]^+$ 524, $[M+ Na]^+$ 547. Elem. Anal. Calculated for $C_{16}H_{17}F_4I_1O_3S_2$: C, 38.9; H, 3.2; F, 14.5; S 12.2; Found: C, 36.6; H, 3.37; F, 14.42; S, 11.4.

S.1.2. *Synthesis of XB acceptor ligand (Py1)*



*Pyridin-4-ylmethyl 5-(1,2-dithiolan-3-yl)pentanoate (**Py1**)*: Thioctic acid (54 mmol) and EDC·HCl (54 mmol) were dissolved in 125 mL of CH_2Cl_2, then added triethylamine (64 mmol) under nitrogen atmosphere and the mixture was stirred for 10 minutes, 4-pyridylcarbinol (46 mmol) and 4-(dimethylamino)pyridine (9 mmol) were added, and was stirred overnight at room temperature. The organic phase was washed with 8 % $NaHCO_3$ solution (3 × 60 mL) and water (2 × 30 mL); the CH_2Cl_2 fraction was then dried over Na_2SO_4, filtered, and evaporated. The residue was purified by column chromatography on silica gel using dichloromethane: ethyl acetate 1:1 as solvent mixture to give yellow oil as the product. Yield: 6.5 g, 48 %. ^{1}H NMR ($CDCl_3$, 400 MHz) δ = 8.61 (dd, J = 6, 2.3 Hz, 2H), 7.27 (d, J = 4 Hz, 2H), 5.15 (s, 2H), 3.52-3.59 (m, 1H), 3.07-3.20 (m, 2H), 2.41-2.48 (m, 3H), 1.85-1.93 (m, 1H), 1.66-1.74 (m, 4H), 1.41-1.55 (m, 2H) ppm. ^{13}C NMR ($CDCl_3$, 400 MHz) δ = 171.8, 148.2, 144.9, 121.1, 63, 55.2, 39.2, 37.5, 33.5, 32.8, 27.7, 23.6 ppm. FTIR (cm^{-1}, selected bands): 2926.6, 2850.6, 1732.9, 1603.1, 1562, 1416.3, 1239, 1156.7, 992, 795.7, 732.4, 580.4. ESI-MS: m/z 298.

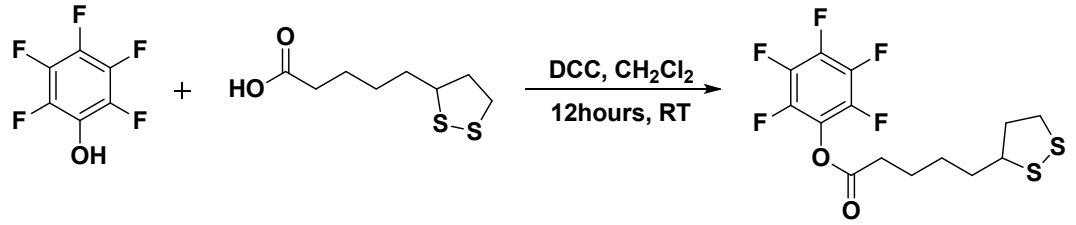
S.1.3. ***Synthesis of XB acceptor ligand (Py2)***



*2-(pyridin-4-ylmethoxy) ethanol (**K3**):* 4-(Chloromethyl)pyridine hydrochloride (18.3 mmol) was suspended in DMSO (5 mL) and then a solution of ethylene glycol (91 mmol) in DMSO (5 mL) was added. The mixture was sonicated and heated to 40 °C until the solid dissolves completely. A solution of sodium hydroxide (55 mmol) was added to the DMSO solution and the reaction mixture was then heated to 100 °C and stirred for 20 hours. The reaction mixture was quenched into 50 mL of a water/ice mixture and the resulting solution was extracted three times with ethyl acetate. The combined organic fractions were dried over sodium sulfate, filtered and concentrated under reduced pressure. The crude product was purified twice by column chromatography on silica (ethyl acetate/ethanol 10:1) to give the title compound (0.8 g, 35 %) as a white solid. ^{1}H NMR (CD_3OD, 400 MHz) δ = 8.44 (d, J = 4 Hz, 2H), 7.41 (d, J = 4.8 Hz, 2H), 4.5 (s, 2H), 3.70 (t, J = 8 Hz, 2H), 3.58 (t, J = 12 Hz, 2H) ppm. ESI-MS: m/z 153 [M+ Na^+] 176.

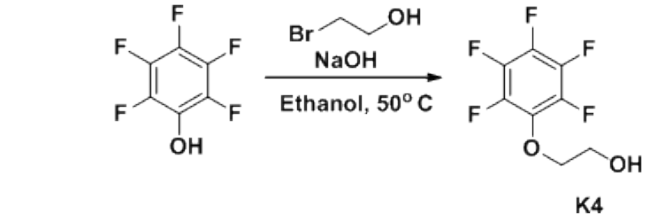
*2-(pyridin-4-ylmethoxy)ethyl 5-(1,2-dithiolan-3-yl)pentanoate (**Py2**):* Thioctic acid (3 mmol) and EDC·HCl (3.4 mmol) were dissolved in 80 mL of CH_2Cl_2, then triethylamine (3.4 mmol) was added under nitrogen atmosphere and the reaction mixture was stirred for 10 minutes. After this period, 2-(pyridin-4-ylmethoxy)ethanol (2.5 mmol) and 4-(dimethylamino)pyridine (0.49 mmol) were added to the mixture and stirred overnight at room temperature. The organic phase was washed with 8 % $NaHCO_3$ solution (3 × 20 mL) and water (2 × 10 mL); the CH_2Cl_2 fraction was then dried over Na_2SO_4, filtered, and evaporated. The crude product was purified by column chromatography using dichloromethane:ethyl acetate 1:1 as solvent mixture resulting yellow oil as the product. Yield: 0.2 g, 50 %. ^{1}H NMR (CD_3OD, 400 MHz) δ = 8.54 (d, J = 8 Hz, 2H), 7.45 (d, J = 4 Hz, 2H), 4.69 (s, 2H), 4.35 (t, J = 8 Hz, 2H), 3.82 (t, J = 8 Hz, 2H), 3.55-3.62 (m, 1H), 3.10-3.23 (m, 2H), 2.45-2.52 (m, 1H), 2.42 (t, J = 8 Hz, 2H), 1.87-1.96 (m, 1H), 1.62-1.78 (m, 4H), 1.46-1.56 (m, 2H) ppm. ^{13}C NMR (400 MHz, CD_3OD) δ = 175.2, 150.6, 150.0, 123.4, 72.0, 70.0, 64.5, 57.5, 41.3, 39.3, 35.7, 34.8, 29.7, 25.8 FTIR (cm^{-1}, selected bands): 2920.8, 2852.1, 1730.2, 1604.6, 1455.9, 1413.2, 1257.8, 1173.5, 1106.6, 796.3, 727.2. ESI-MS: m/z 342 [M+ Na$^+$] 365.

S.1.4. *Synthesis of XB incapable ligand (F1)*

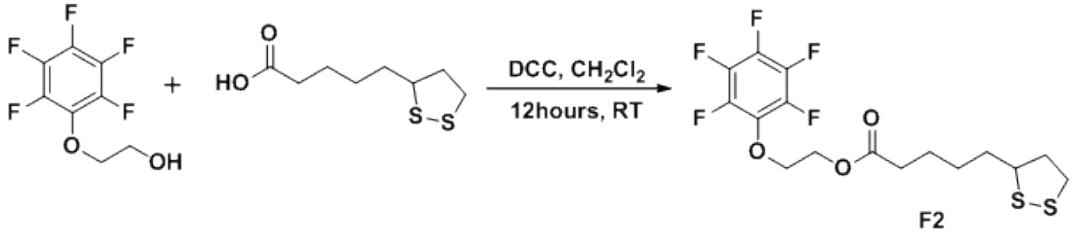


*Perfluorophenyl 5-(1,2-dithiolan-3-yl)pentanoate (**F1**)*: Thioctic acid (16.3 mmol) was dissolved in 30 mL of dichloromethane in a round-bottom flask equipped with a magnetic stirring bar. N,N′-dicyclohexylcarbodiimide (16.3 mmol) was slowly added to the mixture and continued stirring for 15 minutes. Pentafluorophenol (16.3 mmol) dissolved in 30 mL of dichloromethane was then slowly added to the mixture and stirred at ambient temperature overnight. The mixture was filtered and quenched with 60 mL of water, and the product was extracted with dichloromethane. The combined organic layer were further washed with brine, dried over sodium sulfate, filtered, and concentrated under reduced pressure. Purification by column chromatography (9:1 hexane: ethyl acetate) yielded a yellow oil (4.85 g, 90 % yield). ^{1}H NMR ($CDCl_3$, 400 MHz) δ = 3.56-3.63 (m, 4H), 3.09-3-22 (m, 2H), 2.68 (t, J= 16 Hz, 2H), 2.44-2.52 (m, 1H), 1.89-1.97 (m, 1H), 1.80-1.86 (m, 2H), 1.71-1.78 (m, 2H), 1.54-1.63 (m, 2H) ppm. ^{19}F NMR ($CDCl_3$, 500 MHz) δ = -162.52 (2F), -158.27 (1F), 152.89 (2F) ppm. ^{13}C NMR ($CDCl_3$, 400 MHz): δ = 168.9, 148.4, 145.8, 141.4, 139, 129.6, 68.8, 56.1, 40.1, 38.5, 34.4, 33.1, 28.4, 24.5 ppm. FTIR (cm^{-1}, selected bands): 2932.9, 2860.3, 1786.8, 1517.6, 1096.5, 988.9, 887.6, 558.3. MS: [M]$^+$ 372, [M+ Na] $^+$ 395.

S.1.5. ***Synthesis of XB incapable ligand (F2)***



K4



F2

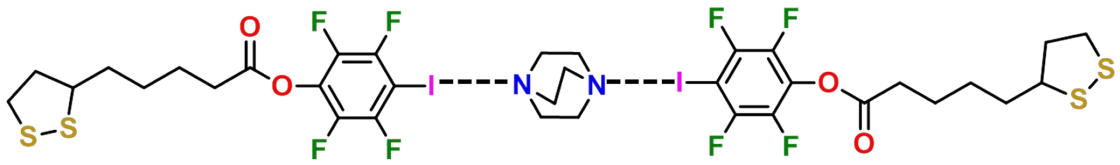
*2-(perfluorophenoxy)ethanol (**K4**):* 2,3,4,5,6-Pentafluorophenol (33 mmol) in ethanol (40 mL) was taken in a round bottom flask, nitrogen gas was bubbled through this mixture for 10 minutes. NaOH (65 mmol) was then added and dissolved by stirring at 50 °C for 20 hours. 2-bromoethanol (49 mmol) in 5 mL of ethanol was added drop wise to the reaction mixture. Further, the mixture was refluxed for 20 hours under nitrogen atmosphere. The reaction mixture was then cooled to room temperature and the solvent was removed under vacuum. The resulting crude product was dissolved in 100 mL of $CHCl_3$ and washed with 10 % NaOH and then with 50 mL of water. The organic layer was dried over Na_2SO_4, filtered and concentrated under reduced pressure. The crude product was purified by column chromatography using hexane:ethyl acetate (1:1) as solvent mixture. Yellow viscous oil, yield: 4.6 g (62 %), viscous liquid. ^{1}H NMR ($CDCl_3$, 400 MHz), δ = 4.26 (t, *J*= 8 Hz, 2H), 3.91 (t, *J*= 12 Hz, 2H), 2.45 (s, 1H) ppm. ^{19}F NMR ($CDCl_3$, 400 MHz) δ = -157.11 (2 F), -163.34 (3 F). ^{13}C NMR ($CDCl_3$, 400 MHz) δ = 148.91, 143.83, 138.63, 129.8, 68.53, 61.70 ppm. MS: $[M]^+$ 228, $[M+ Na]^+$ 251.

*2- (Perfluorophenoxy)ethyl 5-(1,2-dithiolan-3-yl) pentanoate (**F2**)*: 2-(perfluorophenoxy) ethanol (13 mmol), thioctic acid (13 mmol), dicyclohexylcarbodiimide (14.5 mmol) and dimethylaminopyridine (0.64 mmol) were dissolved in dry dichloromethane (90 mL) and stirred at ambient temperature for 18 hours. The precipitate was filtered off and the filtrate was washed with 5 % (180 mL) aqueous acetic acid, the organic layer was separated and evaporated. The crude sample was purified by chromatography column using dichloromethane/ethyl acetate (1:1), yielding a Yellow Oil, Yield: 4.6 g (84 %), ^{1}H NMR (400 MHz, $CDCl_3$) δ = 4.34-4.41 (m, 4H), 3.53-3.60 (m, 1H), 3.08-3.21 (m, 2H), 2.42-2.50 (m, 1 H), 2.36 (t, *J*= 8 Hz, 2H), 1.87-1.95 (m, 1H), 1.63-1.73 (m, 4H), 1.41-1.53 (m, 2H) ppm. ^{19}F NMR (500 MHz, $CDCl_3$) δ = -156.5 (2 F), -162.7 (1 F), -163.0 (2 F) ppm. ^{13}C NMR (400 MHz, $CDCl_3$) δ = 173.2, 143.2, 140.7, 136.9, 133.5, 73.2, 62.8, 56.4, 40.3, 38.6, 34.7, 33.9, 28.8,

24.6. FTIR (cm^{-1}, selected bands): 2936.3, 1733.1, 1479.8, 1096.7, 973.2, 799.1.MS: $[M]^+$ 416, $[M+Na]^+$ 439.

S.2. Co-crystallization of I1 ligand with the ditopic acceptor 1b

S.2.1 *Synthesis of complex I1·1b*



The formation of the **I1·1b** was performed by mixing the **I1**-ligand with XB acceptor moiety 1,4-diazabicyclo[2.2.2]octane (**1b**) in chloroform in a 2:1 molar ratio. After 3 days at room temperature, pale yellow block crystals were formed. Melting point: 123-125 °C, FTIR of pure 1,4-Diazabicyclo[2.2.2]octane (**1b**) (cm^{-1}, selected bands): 2936.8, 1454.9, 1315.5, 1056.2, 991.6, 904.1, 835, 770.9, 747.9, 589.9. FTIR of **I1·1b** (cm^{-1}, selected bands): 2932.6, 1788.8, 1478.8, 1382.7, 1086.4, 968.2, 892, 801.7, 774.6 and 791.5.

S.3. Single crystal X-ray diffraction studies

Single crystals suitable to X-ray diffraction analysis for the co-crystals were grown by slow isothermal evaporation from a $CHCl_3$ solution containing a 2:1 mixture of the XB donor ligand **I1** and the acceptor **1b** at room temperature. Crystal data, data collection and structure refinement details for ligand **I1** and cocrystal **I1·1b** are summarized in Table S.1.

Table S.1 Crystallographic information and refinement table for **I1·1b**

Compound	**I1.1b**
Chemical formula	$2(C_{14}H_{13}F_4IO_2S_2)\bullet C_6H_{12}N_2$
Formula weight	1072.70
CCDC number	1945416
Temperature (K)	296(3)
Crystal system	Triclinic
Space group	*P-1*
a (Å)	11.2731(19)
b (Å)	12.217(2)
c (Å)	15.984(3)
α (°)	96.052(9)
β (°)	92.734(9)
γ (°)	114.183(8)
Volume (Å^3)	1986.8(6)
Z	2
Density (gcm^{-3})	1.981
μ (mm^{-1})	1.882
F (000)	1184
No. of measured, independent and observed [I > 2σ(I)] reflections	41885, 12091, 8815
Rint	0.031
(sin θ/λ)max (Å^{-1})	0.716
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.054, 0.145, 1.04
No. of parameters	534
No. of restraints	44
Δρmax, Δρmin (e Å^{-3})	4.52, −2.62

S.3.1. Electrostatic potential maps on molecular surfaces

All calculations were carried out with the Gaussian 09 software.[1] The B3LYP functional was used with 6-311G** basis set.[2–4] The ESP maps were visualized using GaussView 4.1 software[5] and traced over electron density surfaces with an isodensity of 0.02 a.u. (electron bohr^{-}3).

S.4. Synthesis of AuNPs

S.4.1. XB function cleavage by $NaBH_4$

Tetraoctylammonium bromide (TOAB) was dissolved in trifluorotoluene, ligand (**I1**) was added and stirred vigorously for 10 mins and the reaction mixture was cooled to 0 ºC. $NaBH_4$ dissolved in mQW was dropwise added in continued stirring at 0 °C for 3 hours. Organic layer was separated and characterized using ^{19}F NMR.

^{19}F NMR spectrum of the organic sample showed two sets of tetrafluoro benzene rings. One is related to the iodine replaced ligand **I1** and the other is tetra-fluorophenol, that appears from the Retro-aldol reaction. It is well known that sodium borohydride is the good reducing agent and it can cleave the C-O bond. Iodine replaced ligand **I1**: -145.3, -154.1 ppm (disappearance of peak at -119.9 ppm and the appearance of new peak at-145.3 ppm indicates replacement of iodine in the iodo-tetrafluoro ring by hydrogen atom). Tetrafluoro phenol -140.1, -164.9 ppm

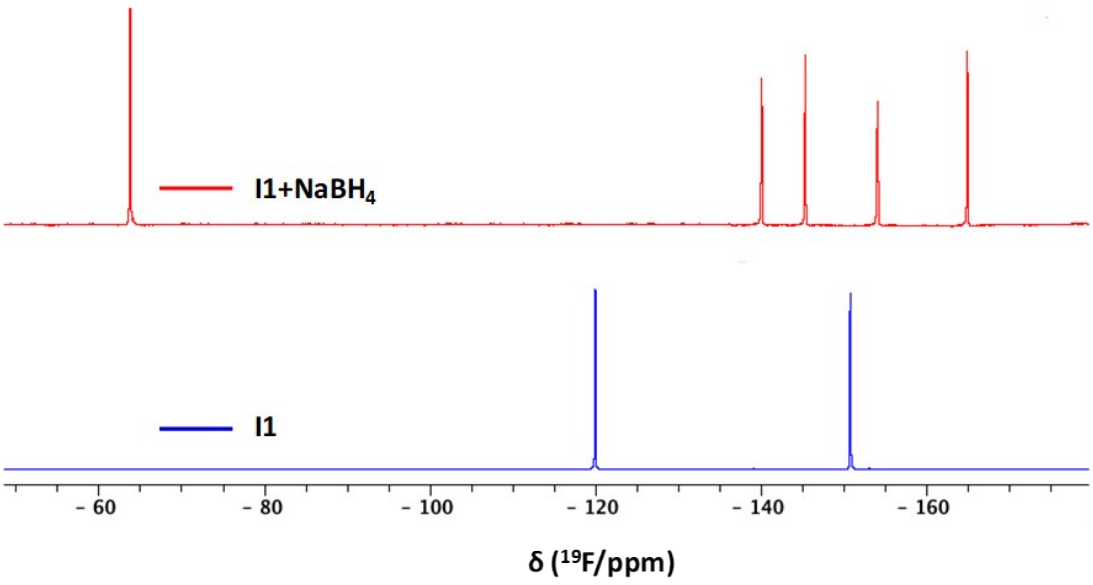
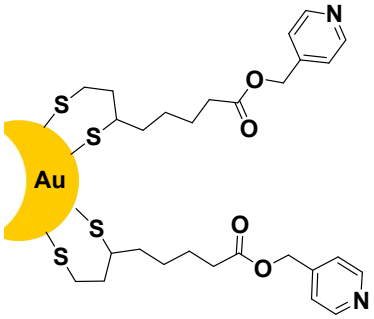


Figure S.1. ^{19}F NMR of **I1+$NaBH_4$** in trifluorotoluene (red line) and ^{19}F NMR of **I1** (blue line).

S.4.2. ***Synthesis of AuNP-Py1via direct method***



AuNP-Py1

Synthetic procedure: An aqueous solution of $HAuCl_4.H_2O$ in mQW (50 mg, 6.5 mL) and a solution of TOAB in toluene (172 mg, 22 mL) were shaken in a funnel until the yellow aqueous layer turns colorless and toluene layer turns red. The aqueous phase was discarded and 15 mg of **Py1**-ligand were added to the organic phase and vigorously stirred. After 10 min a freshly prepared solution of $NaBH_4$ in 1.3 mL of mQW (48 mg, 1.5 mL) was added to the organic solution, which became purple. After four hours of stirring the aqueous layer was removed by extraction and the organic layer was collected. During extraction it was observed that the particles were insoluble in toluene. To avoid precipitation, we removed the toluene under reduced pressure and re-dissolved the NPs in THF.

The THF fraction was taken into a falcon tube, precipitated on adding cold ethanol and the solid residue was recovered by centrifuging at 9500 rpm for 20 minutes. This step was repeated for several times in order to get rid of excess free ligand from the solution. The obtained particles were re-dissolved in THF and filtered through 0.2 μm pores membrane filter and used for further characterization.

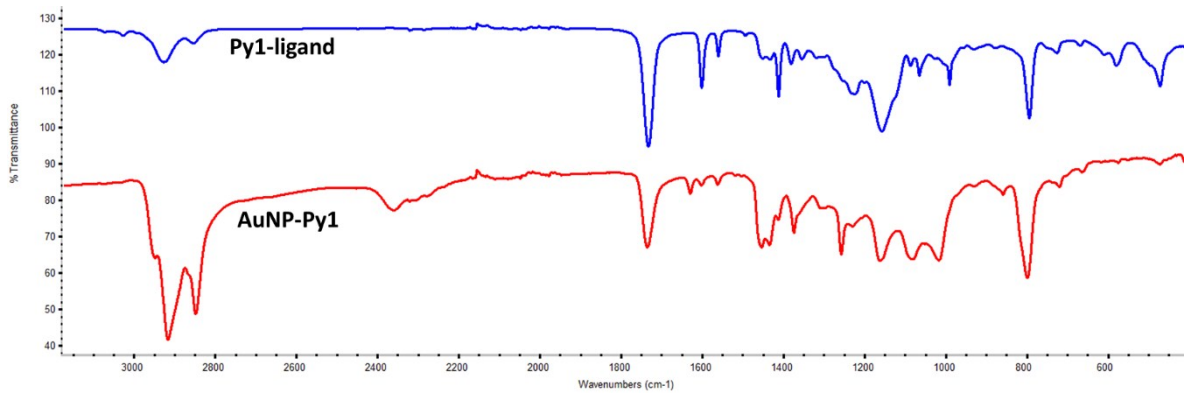


Figure S.2. Comparison between FTIR spectra of the pure ligand **Py1** (Top, blue) and the synthesized AuNP-**Py1** (Bottom, red).

FTIR of **Py1** (cm^{-1}, selected bands): 2927.2, 2853.3, 1734.7, 16.13.5, 1414, 1383.6, 1226.5, 1159.7,

1066.4, 989.6, 796.2, 578.4, 474.1

FTIR of AuNP-**Py1** (cm^{-1}, selected bands): 2920.3, 2850.6, 1739.3, 1631.6, 1457.5, 1378.3, 1261.2, 1163, 1083.9, 1017.4, 802.1

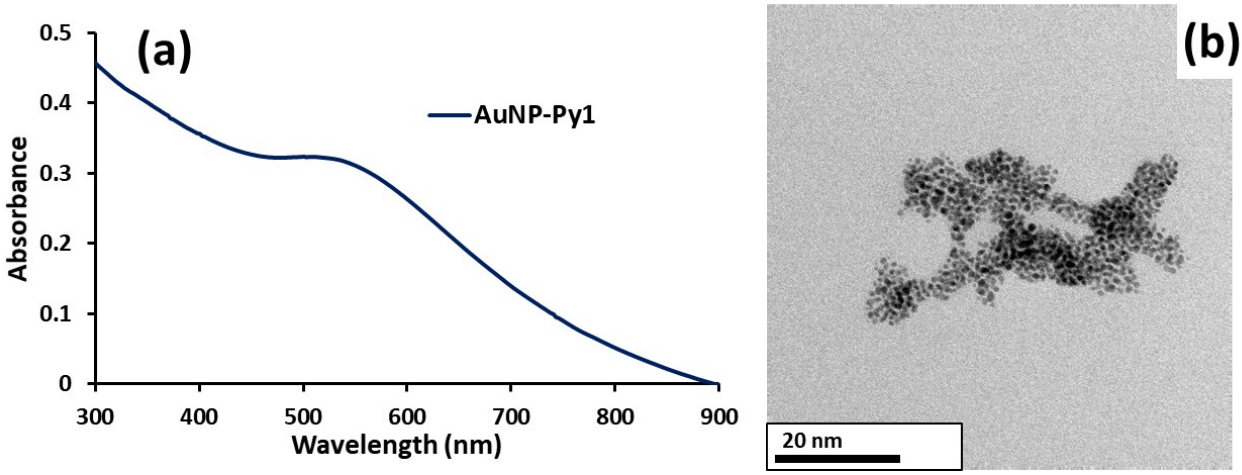


Figure S.3. (a) UV-Vis spectra of AuNP-**Py1** dispersion showing a broadening of the surface plasmon peak. (b) Representative TEM image of AuNP-**Py1** showing aggregation of particles.

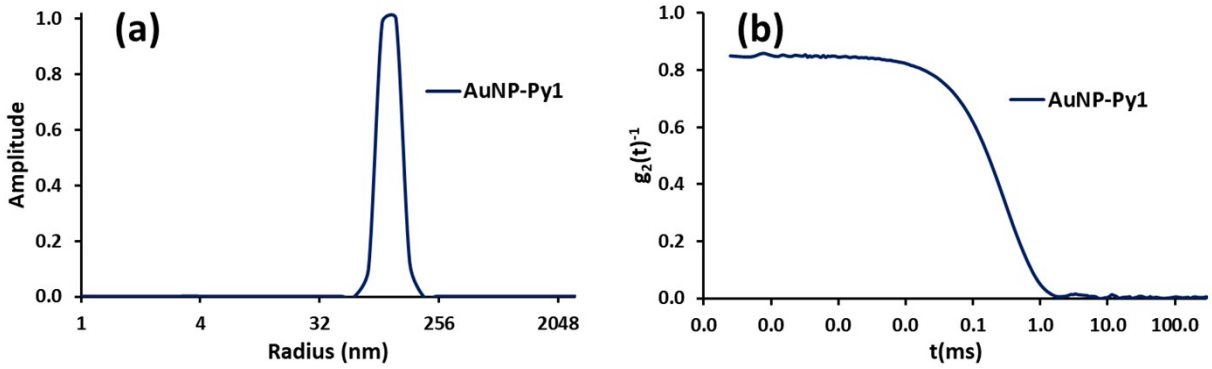
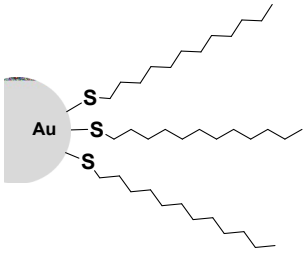


Figure S.4. (a) Intensity weighted NP size distribution obtained by DLS for AuNP-**Py1** dispersion in THF obtained through CONTIN analysis. (b) Scattered intensity auto-correlation functions of AuNP-**Py1** dispersions in THF.

S.4.3. *Synthesis of AuNP-DT*



AuNP-DT

TOAB in toluene (135 mL, 6.8 mM) was added to an aqueous solution of $HAuCl_4.3H_2O$ (42 mL, 1.3 mM). The mixture was stirred until the tetrachloroaurate was transferred into the organic phase. The two phases were separated and a freshly prepared solution of sodium borohydride ($NaBH_4$) in mQW (42 mL, 14.7 mM) was slowly added to the organic layer under vigorous stirring. The organic phase became dark purple. After one hour of stirring, excess of $NaBH_4$ was eliminated by washing with hydrochloric acid (42 mL, 0.01 M), sodium hydroxide (42 mL, 0.01 M) and three times with mQW (20 mL). The organic phase was left stirring for one day, **DT** (16.7 mL, 70 mM) was added and the mixture was then incubated at 65 °C for two hours. The reaction mixture was cooled to room temperature; larger aggregates were removed by centrifugation. Particles were precipitated by adding methanol and centrifuged to remove the excess DT. This procedure was repeated for 4-6 times in order to get rid of free ligand. The **DT**-coated AuNPs were dissolved in toluene and filtered using 0.22 μm membrane filters.

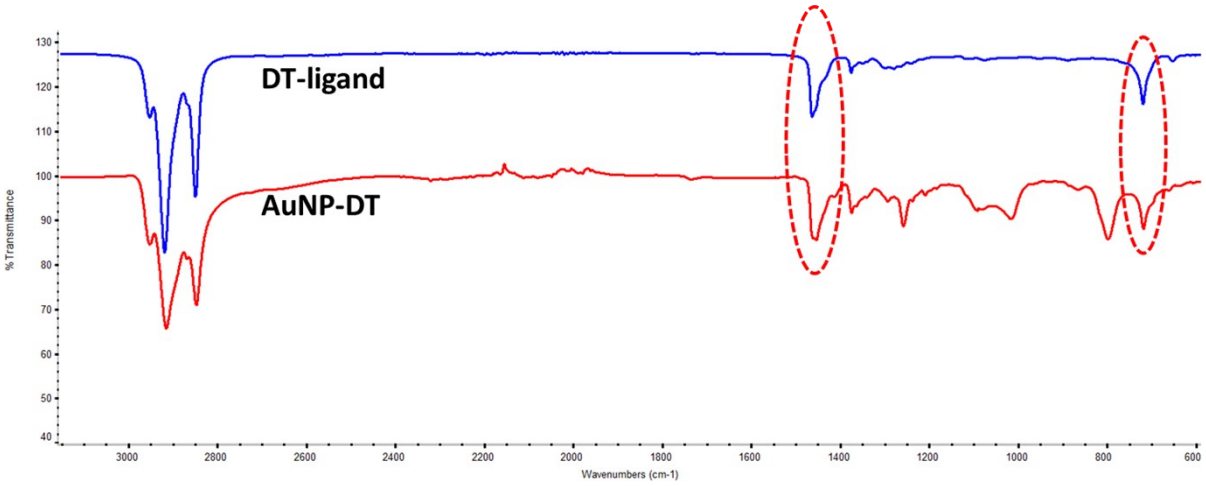


Figure S.5. FTIR spectra of pure **DT** (Top, blue) and AuNP-**DT** (Bottom, red), the particles in toluene were drop casted on diamond and the spectrum was recorded after solvent evaporation.

FTIR of pure **DT** (cm^{-1}, selected bands): 2954.7, 2921.2, 2851.8, 1465.3, 1377.4, 721.13;

FTIR of **AuNP-DT** (cm^{-1}, selected bands): 2954.2, 2917.6, 2849.9, 1456.3, 1376.5, 1259.9, 1085, 1017, 800, 720

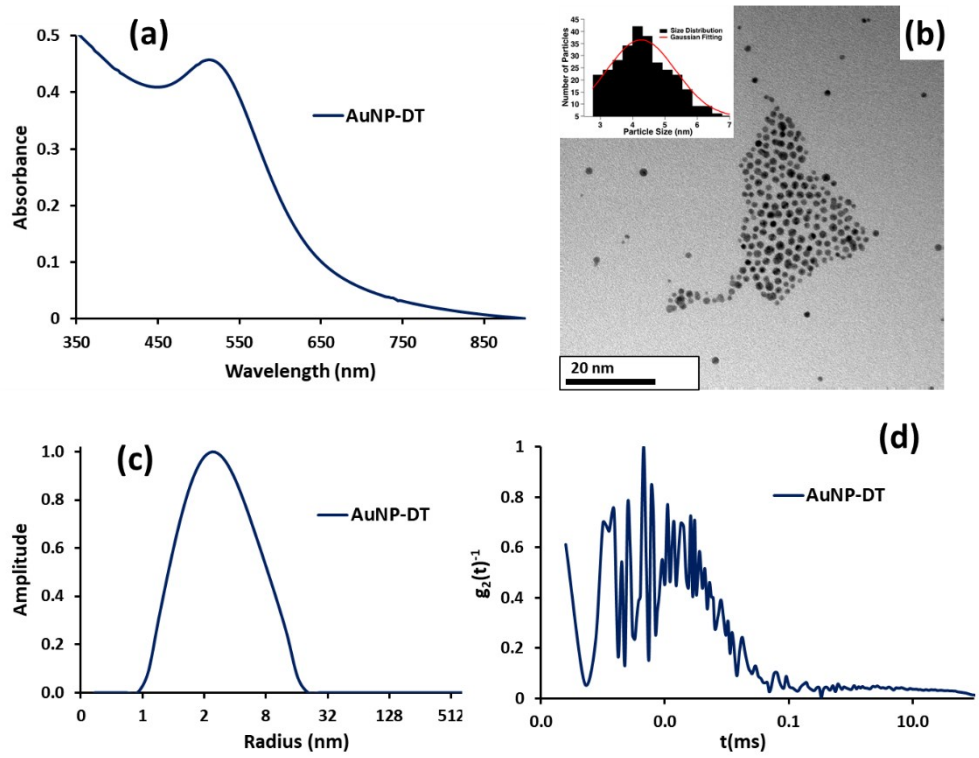


Figure S.6. (a) UV-Vis spectra of AuNP-**DT**. (b) TEM image of AuNP-**DT** showing the NPs size distribution (inset) resulting in NPs averaged diameter of about 4 nm. (c) Intensity weighted NP size distributions obtained by DLS for AuNP-**DT** dispersion in toluene at 90º obtained through CONTIN analysis. (d) Scattered intensity auto-correlation functions of AuNP-**DT** dispersion in toluene.

S.4.4. *General procedure for the synthesis of AuNP-I1, AuNP-I2, AuNP-F1, AuNP-F2, AuNP-Py2 (via exchange reactions) and their characterization.*

A solution of the chosen ligand in toluene (100 mM) was added to 5 mL of AuNP-**DT** solution (5.1 x 10^{15} NPs/mL) and the obtained mixture was vigorously stirred for 18 hours at room temperature. The reaction mixture was precipitated by addition of methanol and the precipitate was recovered by centrifuging at 9500 rpm for 20 minutes. The precipitate was dissolved in toluene and cold methanol was added to precipitate NPs. The NPs were separated by centrifugation. This step was repeated several times to remove the excess of free ligand from the solution. The exchanged NPs were then filtered using a 0.22 μm pores membrane filter and used for further studies.

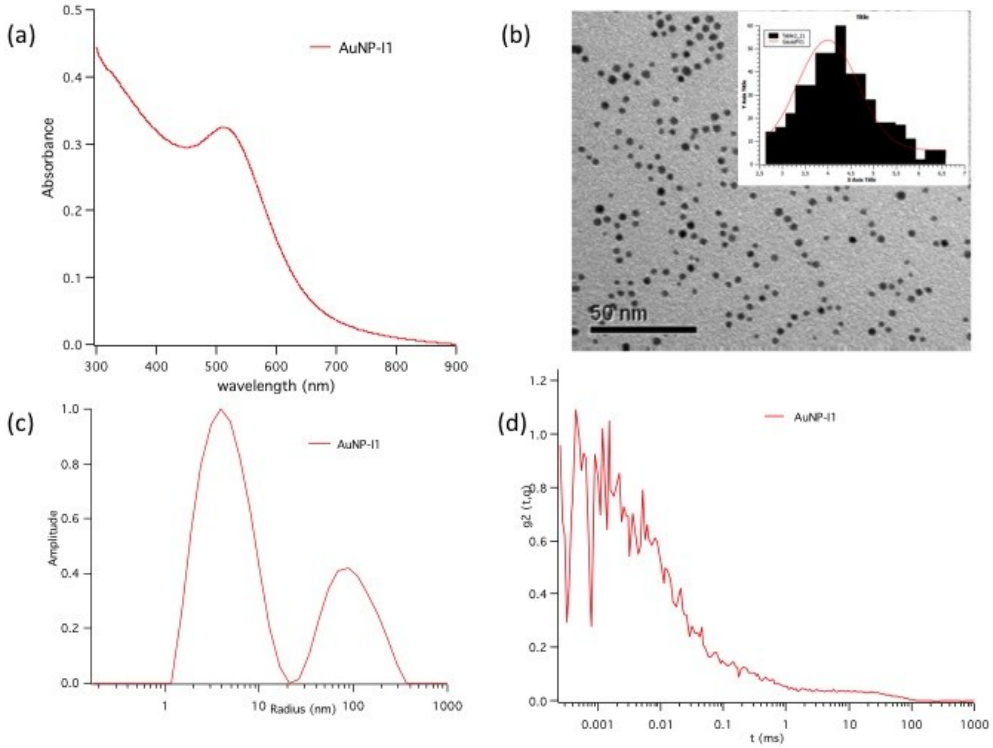


Figure S.7. Characterization of AuNP-**I1** obtained via exchange reaction: (a) UV-Vis spectra of AuNP-**I1**. (b) TEM image of AuNP-**I1** showing the NPs size distribution (inset) with an averaged diameter of about 4 nm. (c) Intensity weighted NP size distributions obtained by DLS for AuNP-**I1** dispersion in toluene at 90º obtained through CONTIN analysis of the auto-correlation function showed in (d). (d) Scattered intensity auto-correlation functions of AuNP-**I1** dispersion in toluene at 90º.

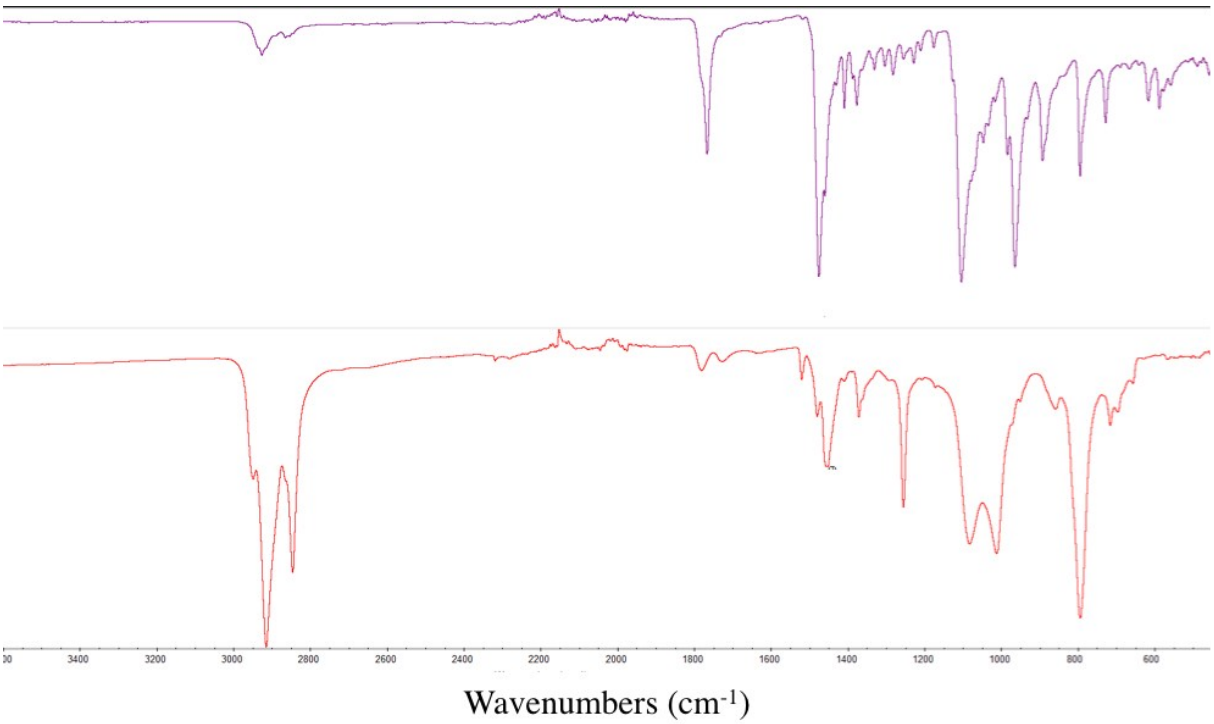


Figure S.8. FTIR spectra of ligand **I1** (above) and AuNP-**I1** (below).

FTIR of **I1**-ligand (cm^{-1}, selected bands): 2929.7, 1771.5, 1480.5, 1379.8, 1285.5, 1108.9, 969.4, 897.4, 799.1, 733.9

FTIR AuNP-**I1** (cm^{-1}, selected bands): 2919.2, 2850.7, 1783.2, 1480.3, 1258. 9, 1080.1, 1037.6, 1015.1, 975.9, 801.6, 717.3.

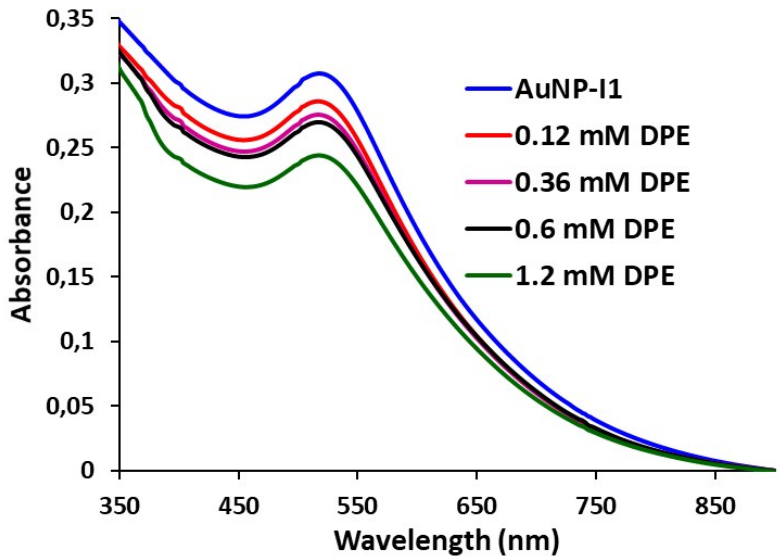


Figure S.9. UV-Vis spectra of AuNP-**I1** compared upon incremental addition of 1,2-Di(4-pyridyl)ethylene. Obtained data show no changes in the SPR bands even when an excess of the XB acceptor system is present. AuNP-I1 were not used to prepare XB driven AuNPs assemblies as they

did not show any binding due to the length of the chain between the thioctic moiety and functional group.

FTIR Spectra of *AuNP-I2, AuNP-F2, AuNP-Py2.*

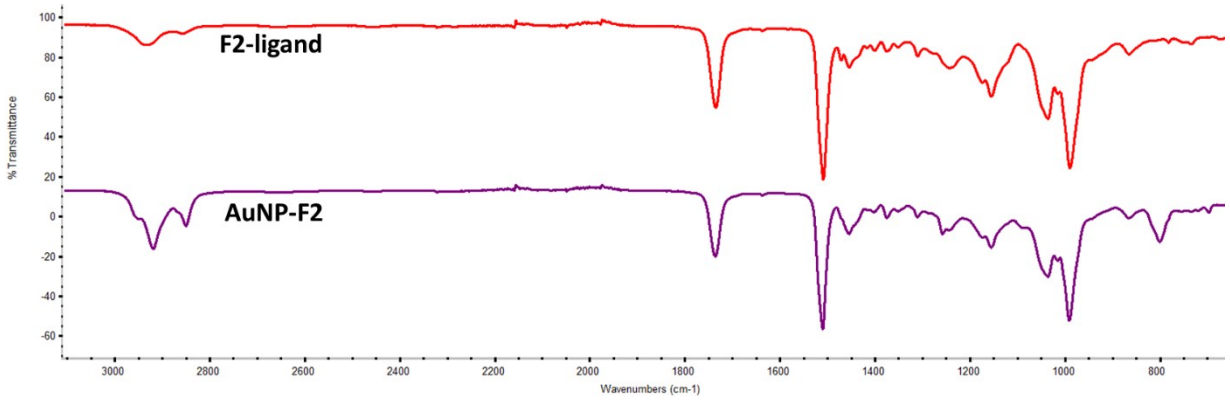


Figure S.10. Comparison FTIR spectra of pure ligand **F2** (Top, red) and the exchanged AuNP-**F2** (Bottom, magenta). The particles in toluene were drop casted on diamond and spectra was recorded after solvent evaporation.

FTIR of **F2-**ligand (cm^{-1}, selected bands): 2936.4, 1737, 1473, 1456.3, 1376.8, 1312.4, 1245.2, 1156.9, 1038.1, 991.8, 867.5, 498.6.

FTIR of AuNP-**F2** (cm^{-1}, selected bands): 2921.6, 2852.3, 1738, 1511.8, 1456.4, 1377, 1312.6, 1259.7, 1157.5, 1038.2, 992.8, 802.6, 498**.**

NMR of AuNP-**F2:** ^{1}H NMR (400 MHz, $PhCH_3$-d_8) δ = 4.14 (bs, 2H), 3.92 (bs, 2H), 2.85 (bs, 3H), 2.26 (bs, 2H). ^{19}F NMR (500 MHz, $PhCH_3$-d_8) δ = -157.3 (2 F), -163.6 (1 F), -163.8 (2 F).

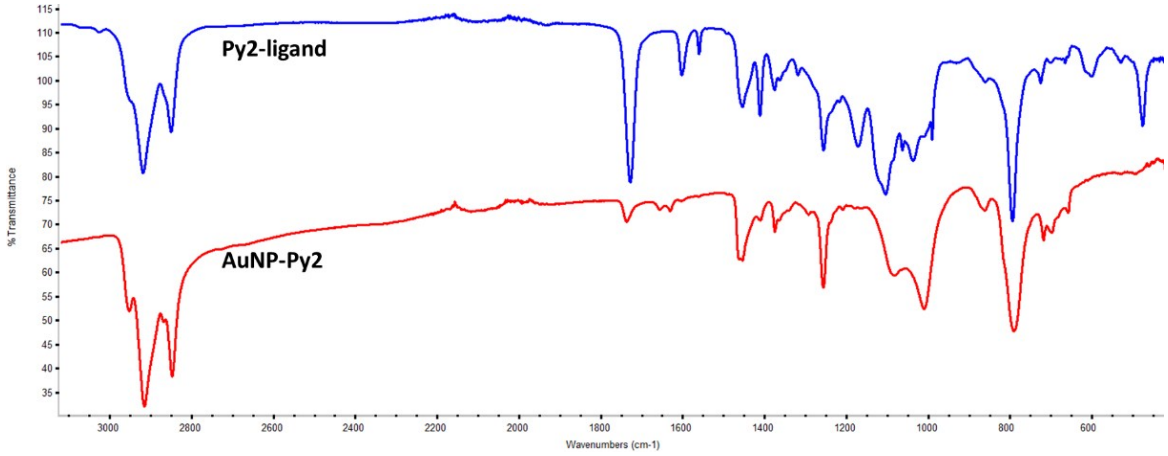


Figure S.11. Comparison FTIR spectra of pure ligand **Py2** (Top, blue) and the exchanged AuNP-**Py2** (Bottom, red). The particles in toluene were drop-casted on diamond and spectrum was recorded after solvent evaporation.

FTIR of **Py2-**ligand (cm^{-1}, selected bands): 2920, 2852.1, 1730.2, 1604.6, 1455.9, 1413.2, 1257.8, 1173.5, 1106.6, 796.3, 727.2.

FTIR of AuNP-**Py2** (cm^{-1}, selected bands): 2954, 2917, 2849, 1739, 1456, 1376, 1258, 1085, 1012, 792, 720**.**

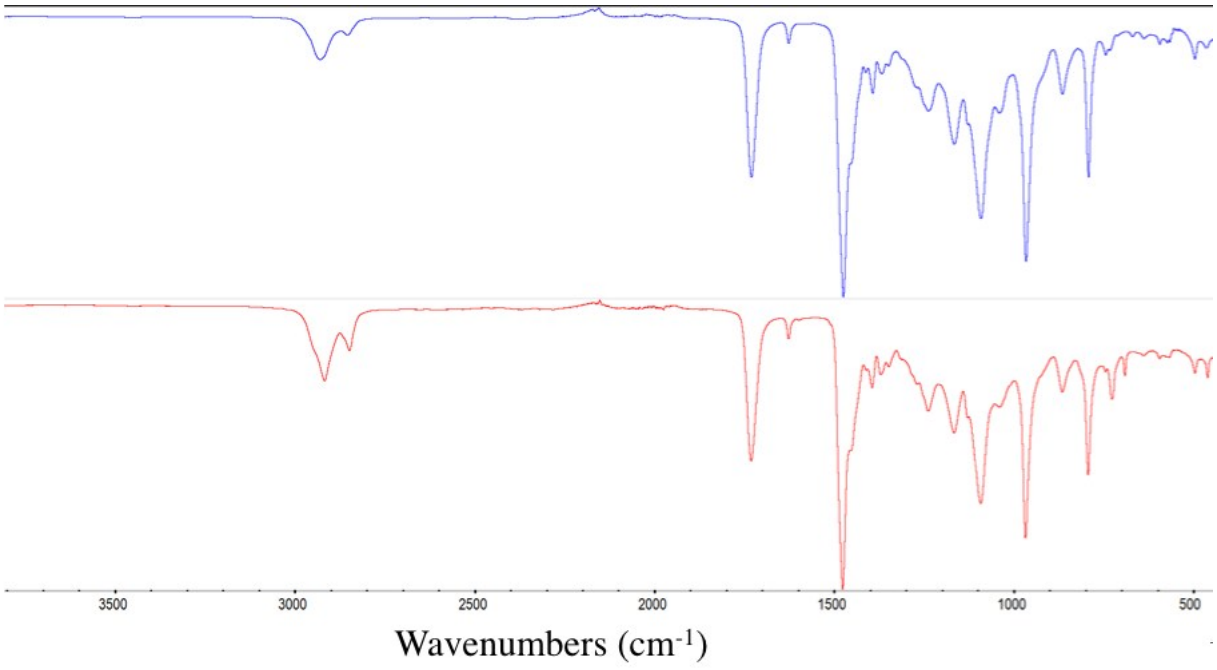


Figure S.12. Comparison FTIR spectra of pure ligand **I2** (Top, blue) and the exchanged AuNP-**I2** (Bottom, red). The particles in toluene were drop-casted on diamond and spectrum was recorded after solvent evaporation.

FTIR of **I2** (cm^{-1}, selected bands): 2936.3, 2863.5, 1733.1, 1479.8, 1245.5, 1172.7, 1096.7, 973.2, 865.6, 799.1.

FTIR of AuNP-**I2** (cm^{-1}, selected bands): 2922.2, 2853, 1735.5, 1481, 1243.6, 1171.5, 1096, 971.6, 869.6, 797.4

NMR of AuNP-**I2**: ^{1}H NMR (400 MHz, $PhCH_3$-d_8) δ = 4.15 (bs, 2H), 4.00 (bs, 2H), 2.82-2.90 (m, 3H), 2.25 (bs, 2H).^{19}F NMR (400 MHz, $PhCH_3$-d_8) δ = -121.5 (2 F), -154.4 (2 F).

ICP-AES Results and AuNP concentration calculation

ICP-AES was employed to quantify the amount of Au and estimate the NP concentration in each AuNP sample. Each measurement was repeated in triplicates.

To evaluate the NP concentration, first the volume of one AuNP was calculated considering the NP as a sphere and applying the formula

$$V = \frac{4\pi r^3}{3}$$

in which the radius (r) was set 2 nm (AuNP size obtained by TEM is 4 nm in diameter) for all the synthesized AuNPs, and the obtained volume (V) of one AuNP resulted equal to $3.35103*10^{-20}$ cm^3.

Knowing that the density (d) of Au = 19 g/cm^3, the weight of a AuNP (W_{AuNP}) was calculated, according to the formula

$$W = d*V = 6.36696*10^{-19}\ g$$

The AuNPs concentration C_{AuNP} was then obtained dividing the Au concentration value obtained from ICP-AES experiments by the weight of one AuNP, according to the following formula

$$C_{AuNP} = C_{Au} / W_{AuNP}$$

The Au content obtained by ICP-AES and the calculated AuNP concentrations, for representative batches of AuNP samples used in this work, are reported in Table S.2.

Table S.2. ICP-AES results and calculated AuNPs concentration for the synthesized stock samples.

Sample	Au concentration (mg/L)	AuNP concentration AuNPs/mL
AuNP-**DT**	5178	$8,13*10^{15}$
AuNP-**F1**	1602	$2,52*10^{15}$
AuNP-**F2**	2863	$4,50*10^{15}$
AuNP-**I1**	3229	$5,10*10^{15}$
AuNP-**I2**	3068	$4,85*10^{15}$
AuNP-**Py2**	4001	$6,28*10^{15}$

ICP-AES analysis was also performed to quantify the amount of I in the samples AuNP-**I1** and AuNP-**I2** reported in Table S.2 obtaining values of 198,4 ppm mg/L (i.e. 0.1984 mg/mL) and 210,4 mg/L (i.e. 0.2104 mg/mL), respectively. From these values, [I] was calculated equal to 9.45×10^{17} atoms/mL and $9,45 \times 10^{17}$ atoms/mL, respectively. Dividing the number of I atom/mL by the number of AuNPs/mL the amount of iodinated ligand per AuNP could be extrapolated, considering that each ligand molecule hosts 1 I atom and assuming a statistic ligand distribution among the AuNPs.

$(9,45\times10^{17})$ I atoms/mL / (5.1×10^{15}) NPs/mL = 185 molecules **I1** ligand/AuNP.

(9.96×10^{17}) I atoms/mL / (4.85×10^{15}) NPs/mL = 207 molecules **I2** ligand/AuNP.

Calculating the total available surface of a NP (assuming the area of a sphere) and extrapolating the area occupied by a ligand from the crystal structure (i.e. approximating the ligand to a cylinder with diameter of the cylinder base of 4.24 Å), we determined the remaining area occupied by DT molecules and extrapolated an exchange yield of about 65% for **I1** and 80% for **I2**.

S.5. Self-assembly of AuNPs in solution

S.5.1. ***General procedure for the AuNPs self-assembly in solution:*** AuNP-**I2** was mixed with AuNP-**Py2** in 1:1 molar ratio (the calculation were made based on the ICP analysis).

The assembly behavior of AuNP-**I2** and AuNP-**Py2** were confirmed by UV-Vis spectroscopy, DLS

and TEM. These dispersions showed precipitation of large superstructures over time. This process also involves a gradual color change of the dispersions from purple to blue.

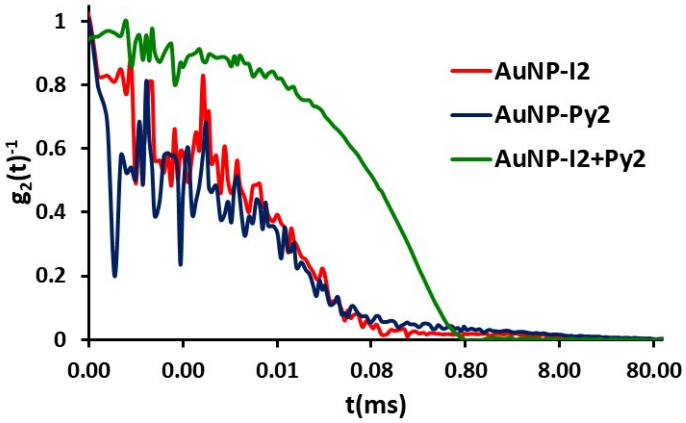


Figure S.13. Auto-correlation functions of the fresh dispersions of AuNP-**I2**, AuNP-**Py2** and AuNP-**I2+Py2** in toluene at the same NP concentration.

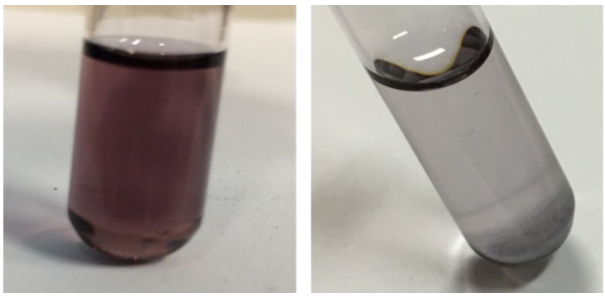


Figure S.14. Images of the fresh (left) and one-month aged (right) AuNP**I2**+**Py2** sample in toluene.

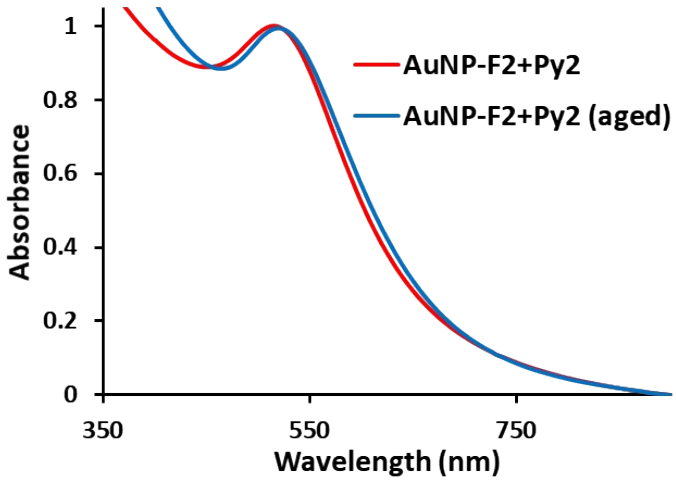


Figure S.15. UV-Vis spectra of AuNP-**F2+Py2**: freshly prepared (Red line) and one month aged mixture (Blue line).

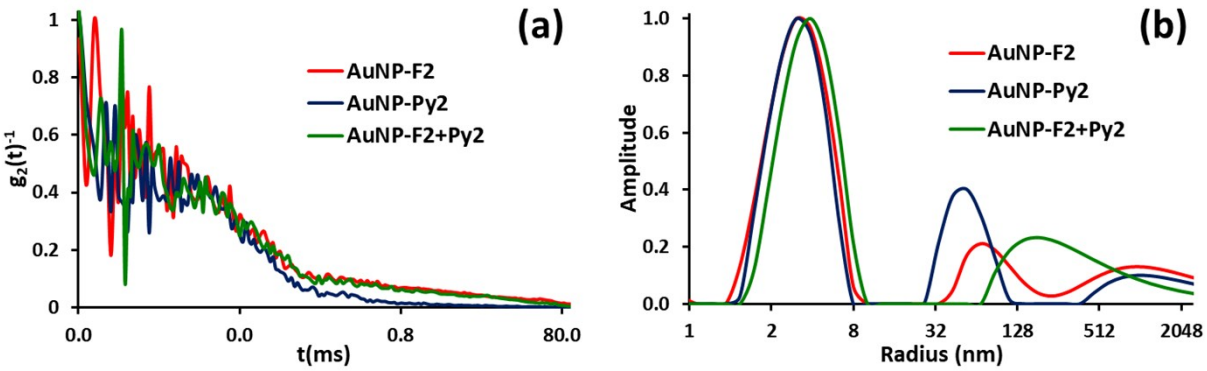


Figure S.16 (a) Scattered intensity auto-correlation functions of AuNP mixture dispersions in toluene AuNP-**F2,** AuNP-**Py2 and** AuNP-**F2+Py2** after 1 month. (b) Intensity weighted NP size distributions obtained by DLS for AuNP-**F2,** AuNP-**Py2 and** AuNP-**F2+Py2** dispersions 1 month aged in toluene at 90º obtained through CONTIN analysis.

S.6. Self-assembly of AuNPs on a planar surface

QCM-D experiments: A Q-Sense E4 instrument (Q-Sense) quartz crystal microbalance with dissipation monitoring (QCM-D) was used to measure the adsorbed mass of AuNPs on QCM gold crystals functionalized with different ligands.

Cleaning of the QCM-D sensors: The QCM-D sensors were first treated for 10 minutes in an UV/ozone chamber and then immersed at 75 °C in a $H_2O/NH_3/H_2O_2$ (5:1:1 v/v) mixture for 10 minutes. The sensors were rinsed thoroughly with mQW and dried with nitrogen. Once again these *QCM-D sensors* were placed in UV/ozone chamber for 10 minutes to remove the contaminants from the surfaces.

Preparation of monolayer's (surface functionalization): Surface functionalization was carried out by immersing clean QCM-D sensors into a 10 mM ligand solution (CH_2Cl_2) overnight. The ligand functionalized sensors were washed with pure CH_2Cl_2 and then with mQW, dried with nitrogen and mounted into the measurement chamber, which was maintained at 21 °C.

General procedure for the formation of AuNP based assemblies on monolayer: Firstly, the pure toluene was fluxed to establish a stable baseline. Then, 1 mL of the AuNP solution at a concentration of 0.02 m^2/mL was fluxed through the measurement chamber using a flow rate of 100 µL min^{-1}. The sensors were then incubated for 15 minutes in zero-flow conditions. Subsequently, 1 mL of the AuNP solution was again flowed through the chambers at a rate of 100 µL min^{-1}, monitoring if there was

further deposition. The sensors were incubated for another 15 minutes in zero-flow conditions and then rinsed for 40 minutes using the pure solvent.

Investigation of deposition of AuNP-I2 on DT functionalized surfaces: The QCM sensor was immersed in a solution of **DT**-ligand (lacking of XB donor moiety and fluorinated core) overnight, at room temperature. The **DT**-functionalized sensors were then washed with dichloromethane, rinsed with mQW and dried under nitrogen. The functionalized sensor was further placed in a QCM chamber and pure solvent was fluxed to establish a stable baseline. The surface modified AuNP solutions such as AuNP-**I2** (0.02 ms^2/mL) were fluxed on QCM senor previously functionalized with **DT** ligand using the same experimental conditions reported for **Py1** ligand functionalized surface. Several cycles of AuNPs were fluxed and the unbound AuNPs were removed by fluxing the pure solvent. The mass of surface-bound material as well as the viscoelastic properties of the adsorbed layer was determined.

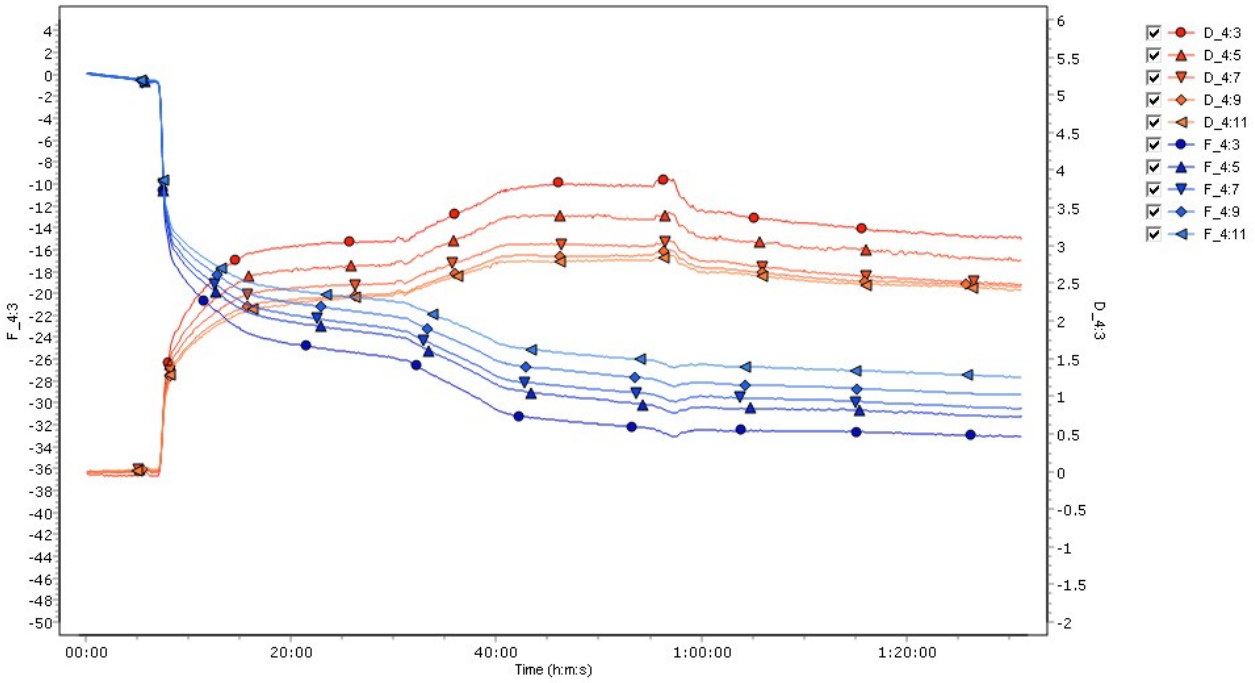


Figure S.17. QCM-D measurement of change in frequency change and the change in dissipation plotted against time upon the adsorption of AuNP-**I2** on the QCM-D sensor coated with **Py1** ligand.

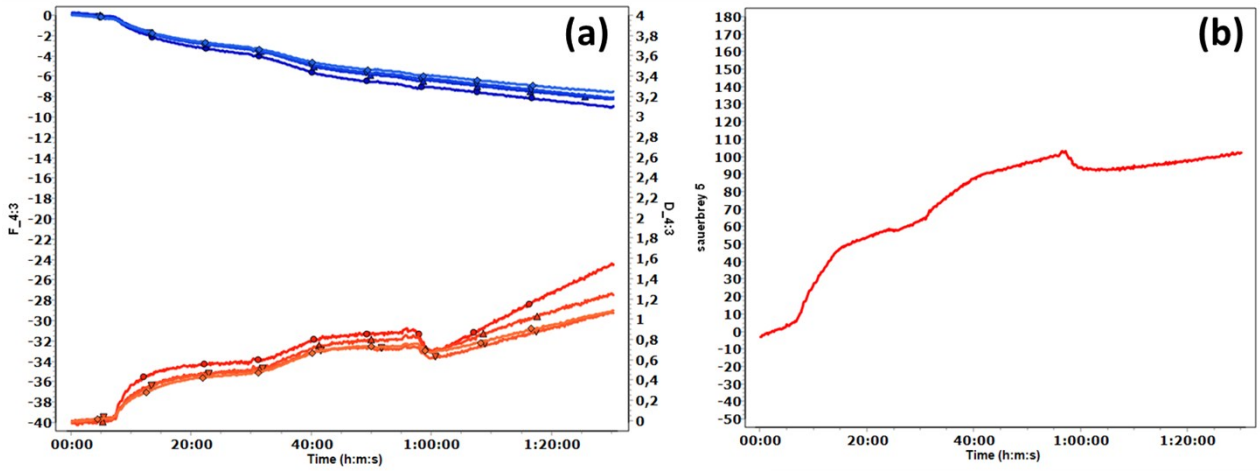


Figure S.18. Deposition of AuNP-**I2** on the surface of QCM-D sensors functionalized with **DT** ligands. (a) Change in frequency and dissipation with time. (b) Mass gain as a function of time.

Contact angle

Water contact angle measurements were performed to investigate the hydrophilic character of grafted surfaces after the different functionalization steps. The data presented in Figure S.19 displays water contact angles for bare Au around 79 ± 2°, as expected for a clean gold surface. Upon the functionalization of XB acceptor ligand **Py1** the water contact angle decreases compared to the clean gold sample with a value of 50 ± 2°. Interestingly, when the **Py1** functionalized sensor absorbs AuNP-**I2**, the water contact angle for increases to 78 ± 2°.

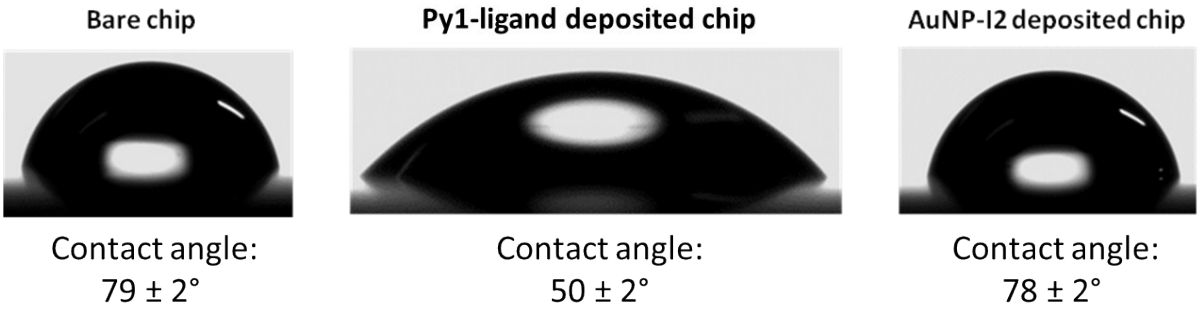


Figure S.19. Static water contact angles of the bare gold sensor (left), functionalized with the XB acceptor ligand (middle) and sensor deposited with AuNP-**I2** on top of the XB acceptor ligand (right).

S.7. References

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