Determination of monolayer-protected gold nanoparticles' ligand shell morphology via NMR

Xiang Liu[1,2], Miao Yu[1,2], Hyewon Kim[2], Marta Mameli[1] and Francesco Stellacci*[1,2]

[1]*Institute of Materials, École Polytechnique Fédérale de Lausanne, Switzerland*

[2]*Department of Materials Science and Engineering, Massachusetts Institute of Technology, 77 Massachusetts Avenue, Cambridge, MA 02139 (USA)*

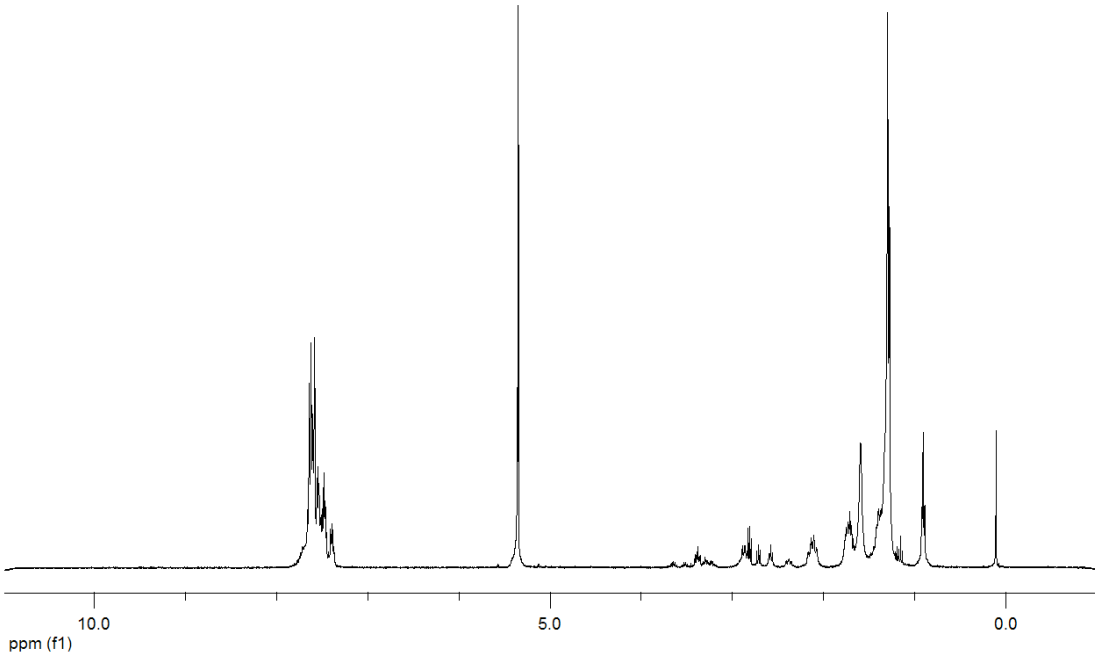


Figure S1. Representative NMR spectrum collected after decomposing the gold core via cyanide etching showing the actual ligand composition on nanoparticles.

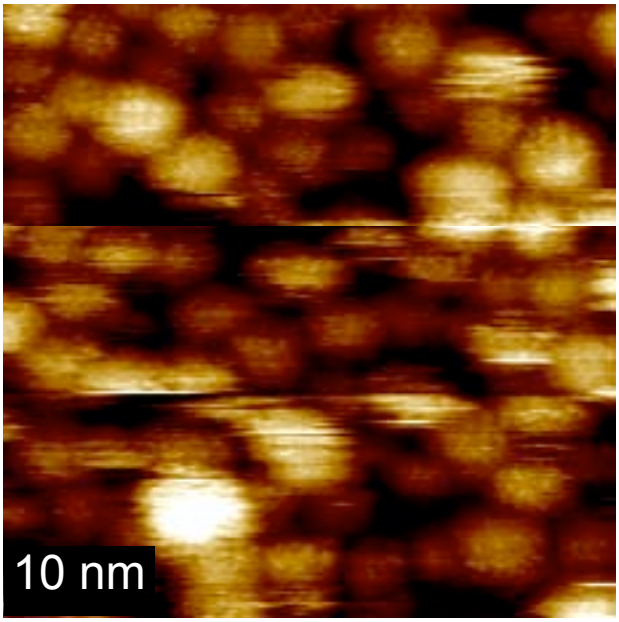


Figure S2. STM images of striped nanoparticles Au-$DPT_{0.58}DDT_{0.42}$

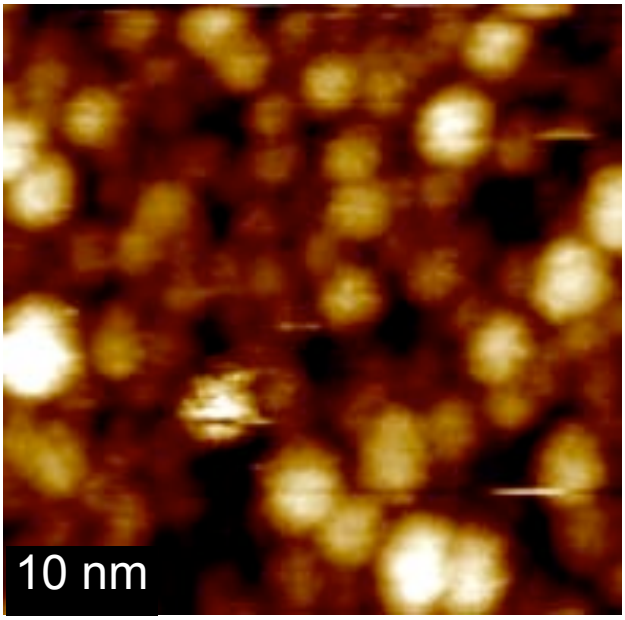


Figure S3. STM images of Janus nanoparticles Au-$DPT_{0.56}DDT_{0.44}$

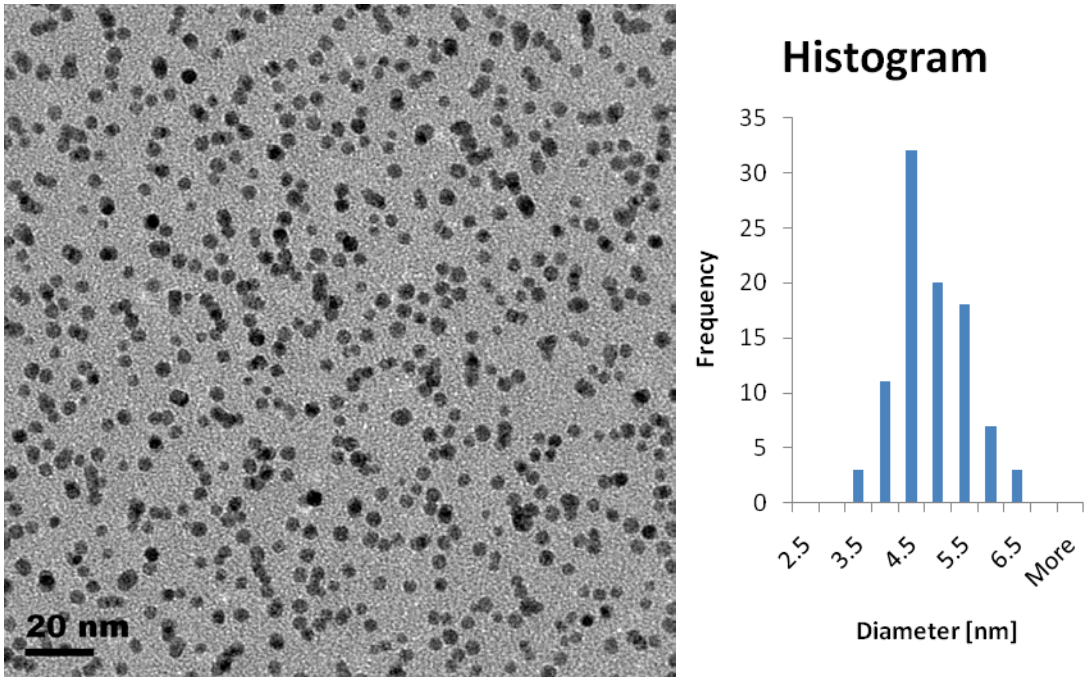


Figure S4a. TEM image of randomly mixed Au-$DPT_{0.22}DMOT_{0.78}$ (D=4.54±0.82 nm)

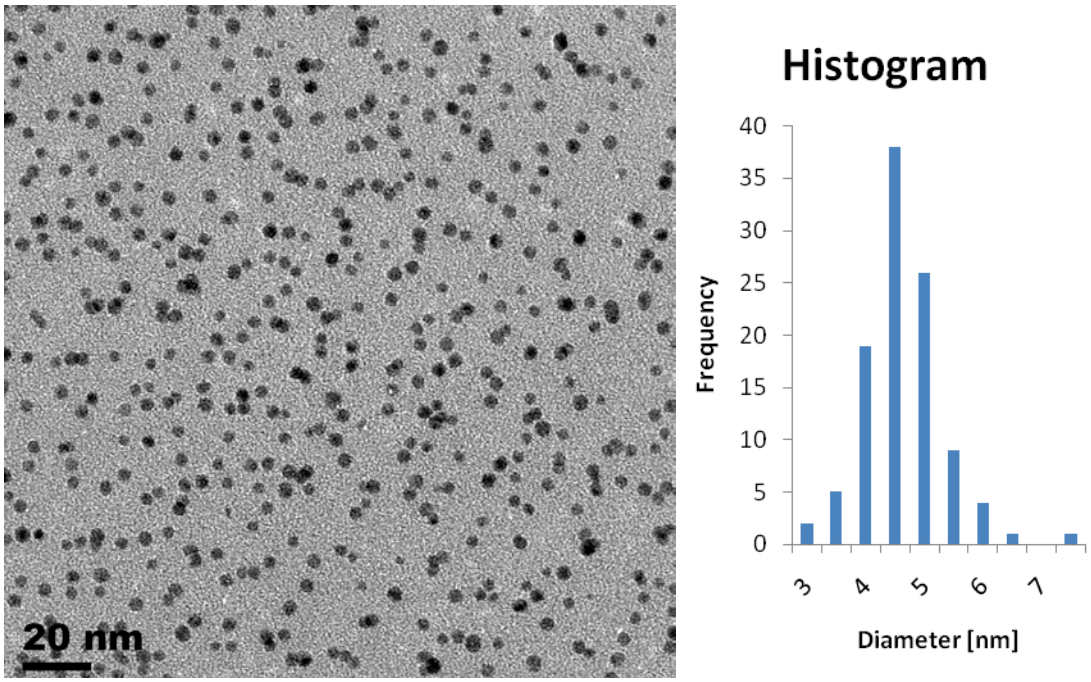


Figure S4b. TEM image of randomly mixed Au-$DPT_{0.35}DMOT_{0.65}$ (D=4.42±0.70)

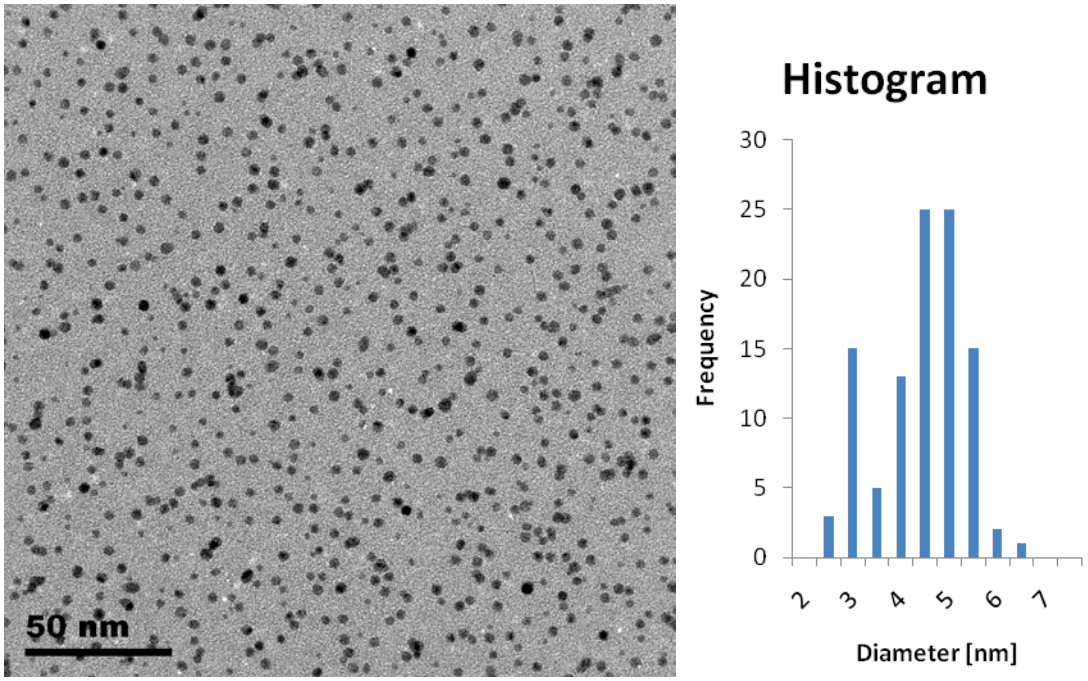


Figure S4c. TEM image of randomly mixed Au-DPT$_{0.46}$DMOT$_{0.54}$ (4.17+/-0.89)

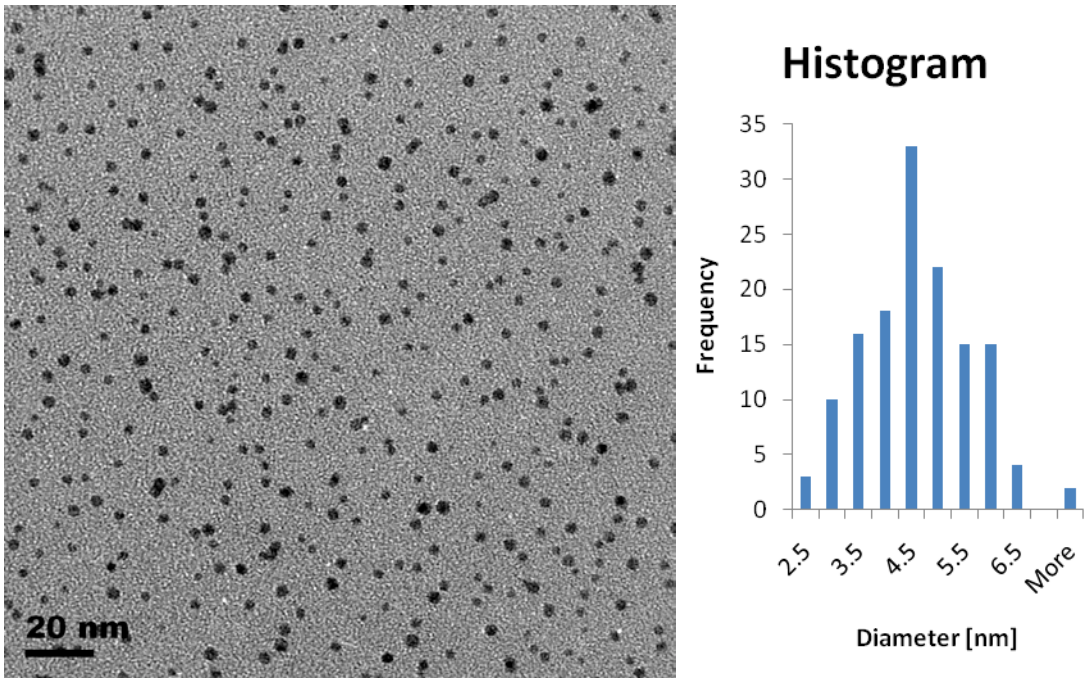


Figure S4d. TEM image of randomly mixed Au-DPT$_{0.60}$DMOT$_{0.40}$ (D=4.41±1.01)

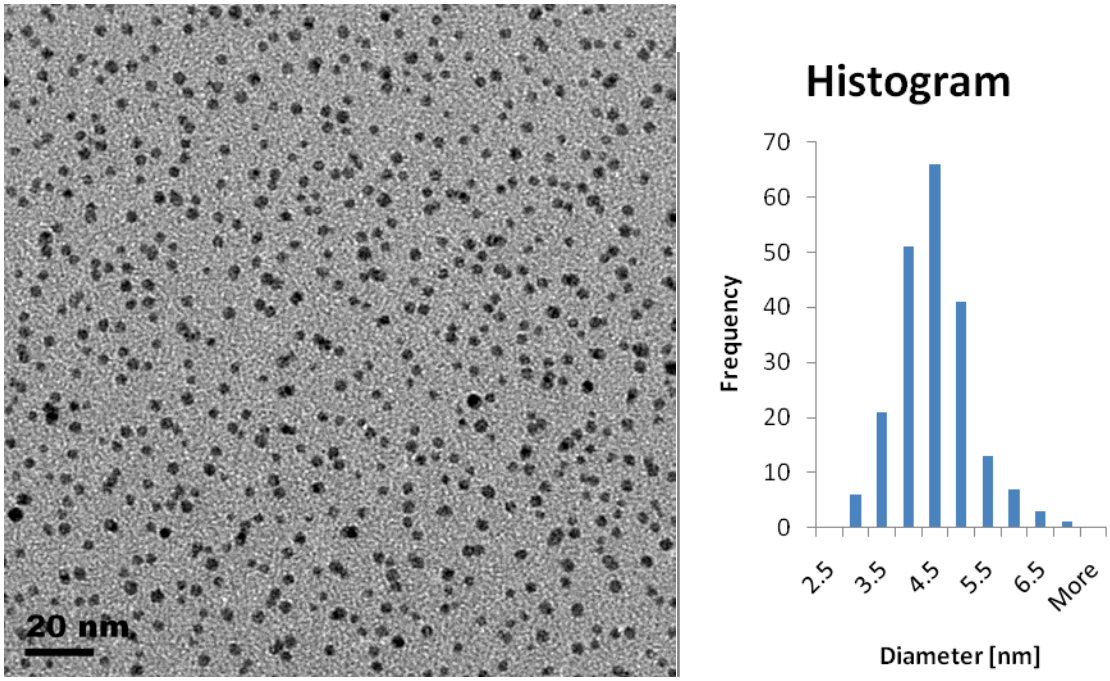


Figure S4e. TEM image of randomly mixed Au-DPT$_{0.71}$DMOT$_{0.29}$ (4.24+/-0.69)

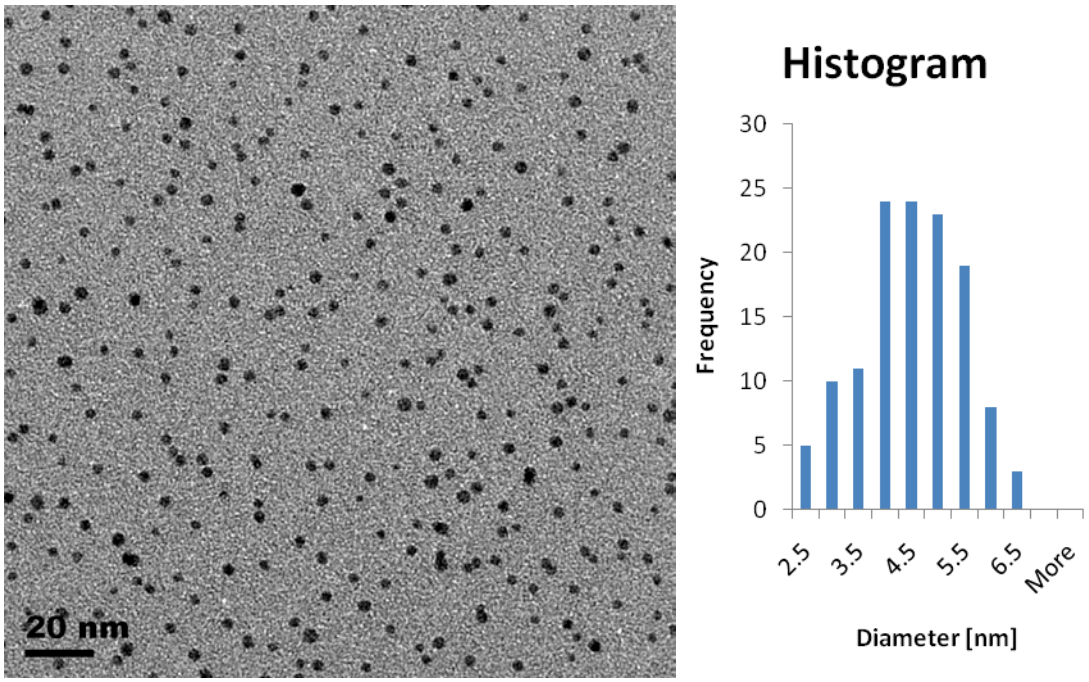


Figure S4f. TEM image of randomly mixed Au-DPT$_{0.82}$DMOT$_{0.18}$ (D=4.14±0.99)

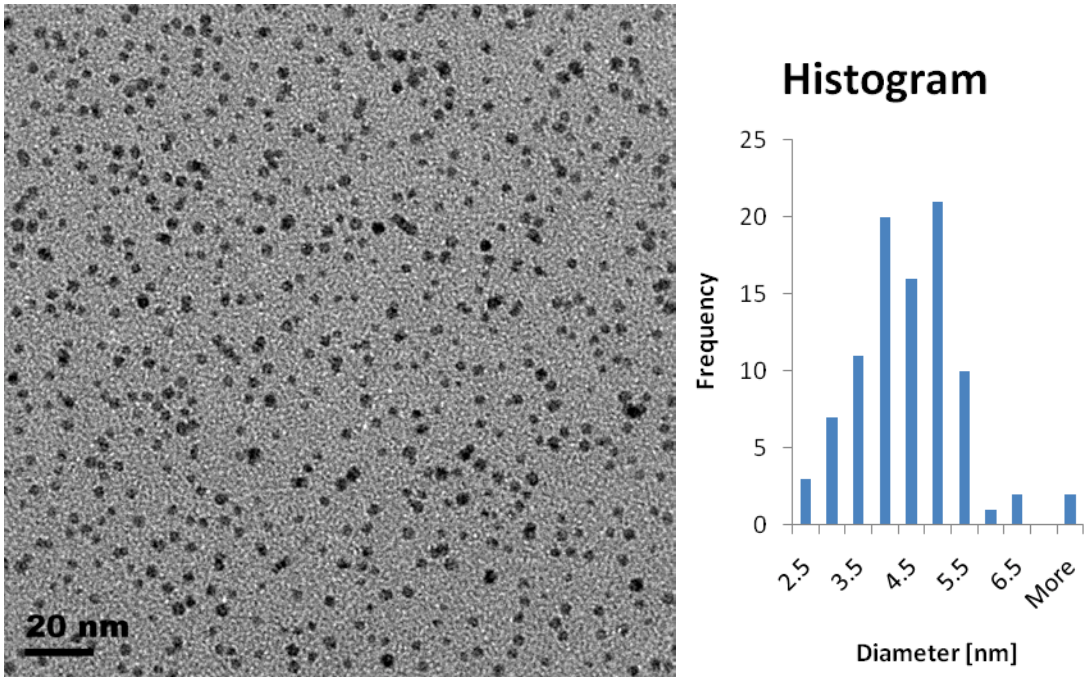


Figure S4g. TEM image of randomly mixed Au-$DPT_{0.93}DMOT_{0.07}$ (D=4.20±0.96)

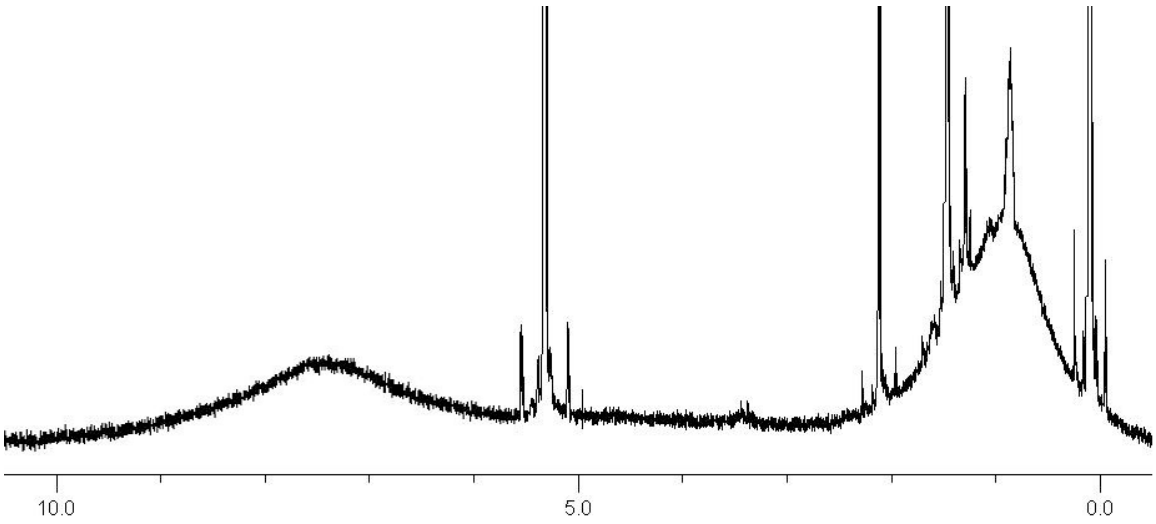


Figure S5a. ^{1}H NMR of randomly mixed Au-$DPT_{0.22}DMOT_{0.78}$

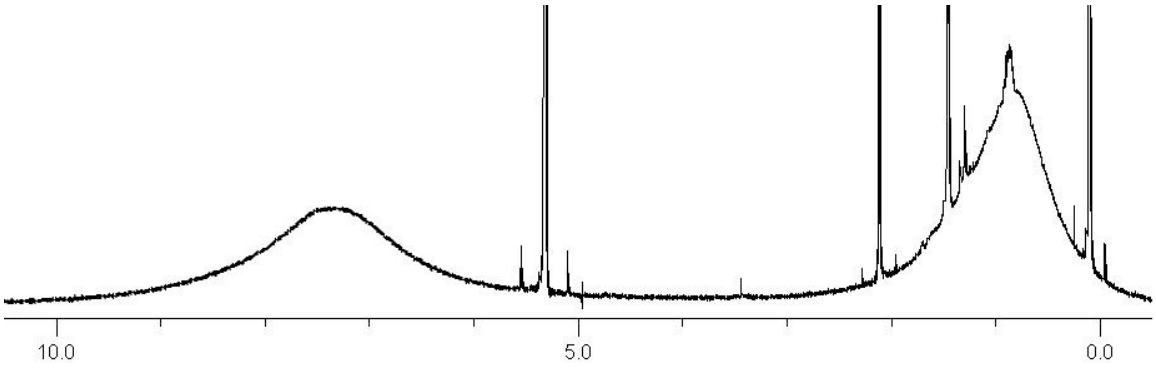


Figure S5b. ^{1}H NMR of randomly mixed Au-DPT$_{0.35}$DMOT$_{0.65}$

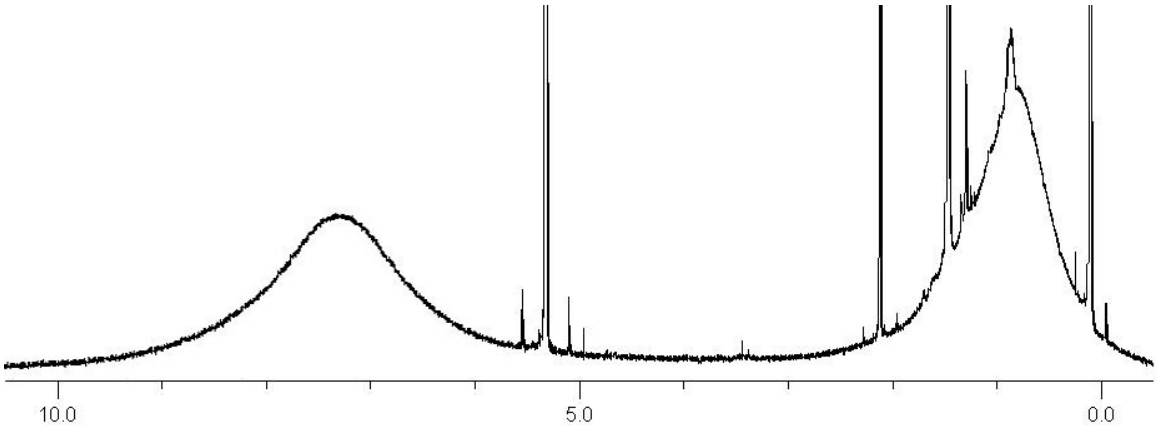


Figure S5c. ^{1}H NMR of randomly mixed Au-DPT$_{0.46}$DMOT$_{0.54}$

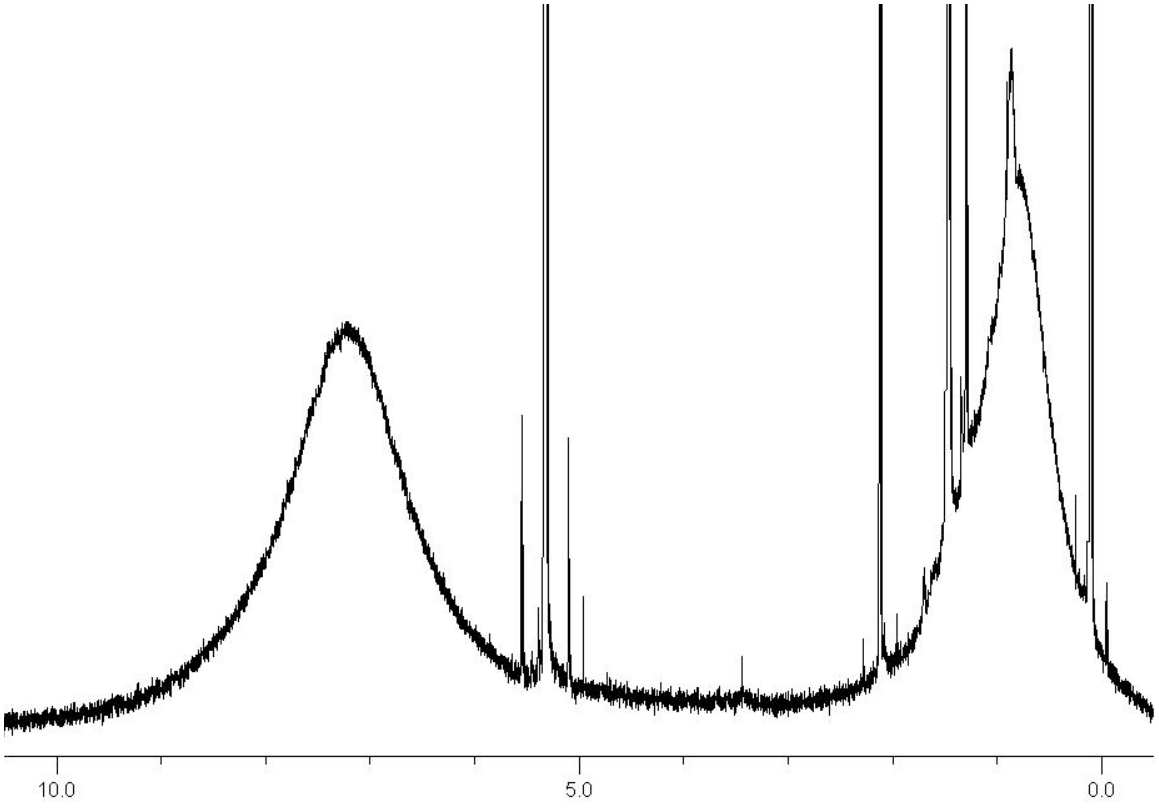


Figure S5d. ^{1}H NMR of randomly mixed Au-DPT$_{0.60}$DMOT$_{0.40}$

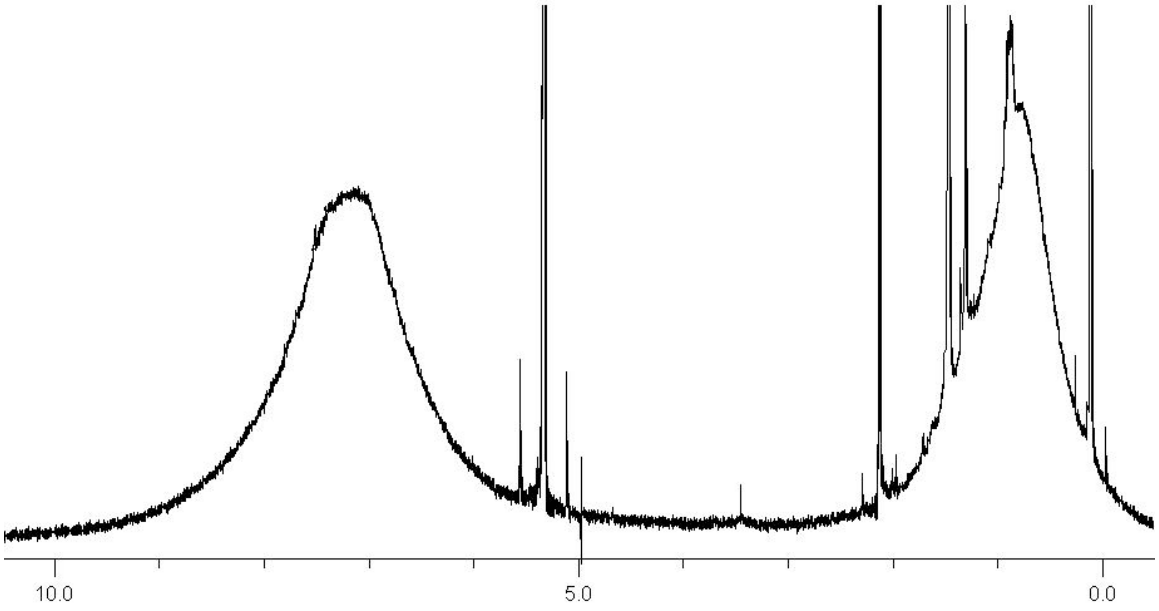


Figure S5e. ^{1}H NMR of randomly mixed Au-DPT$_{0.71}$DMOT$_{0.29}$

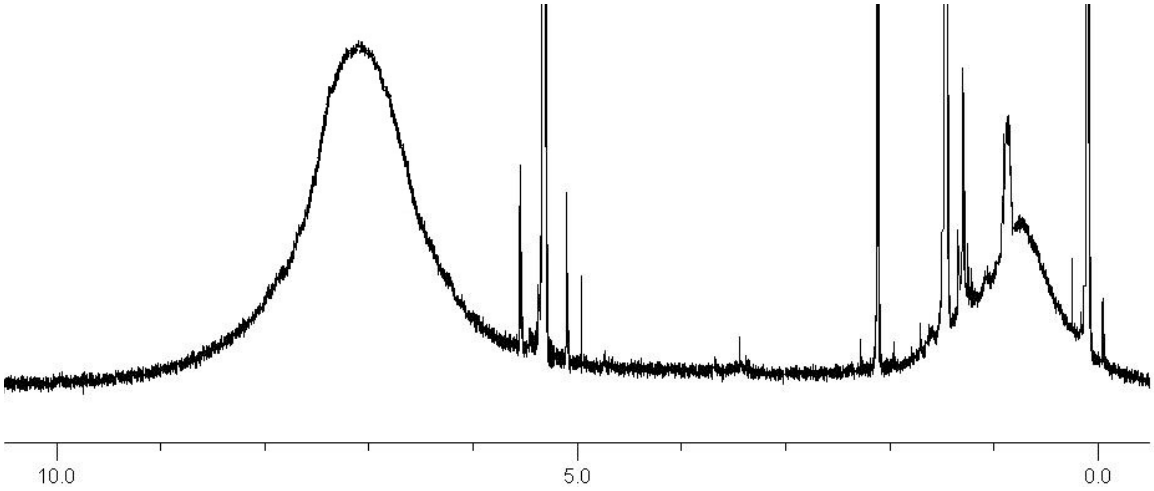


Figure S5f. ^{1}H NMR of randomly mixed Au-DPT$_{0.82}$DMOT$_{0.18}$

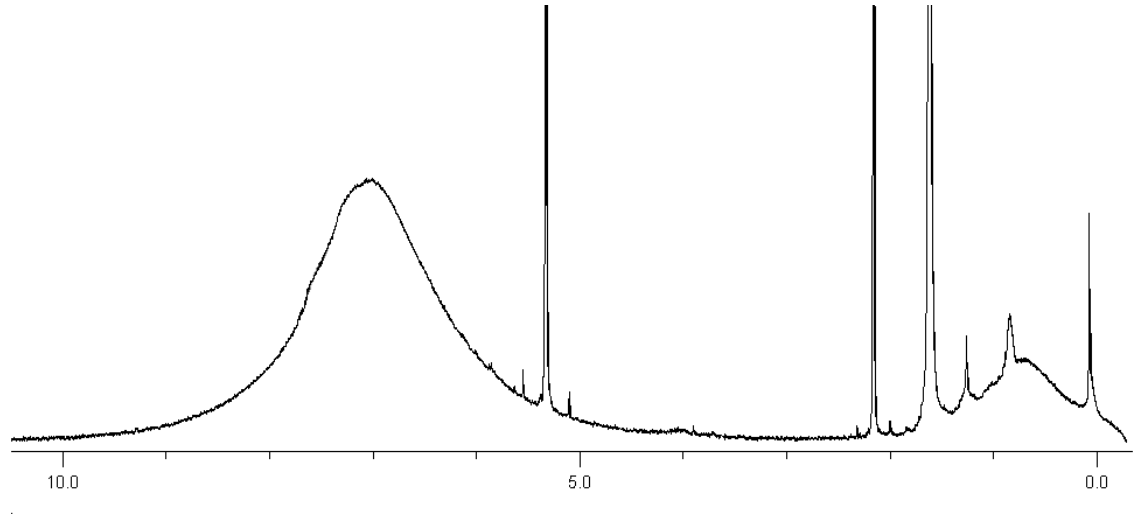


Figure S5g. ^{1}H NMR of randomly mixed Au-DPT$_{0.93}$DMOT$_{0.07}$

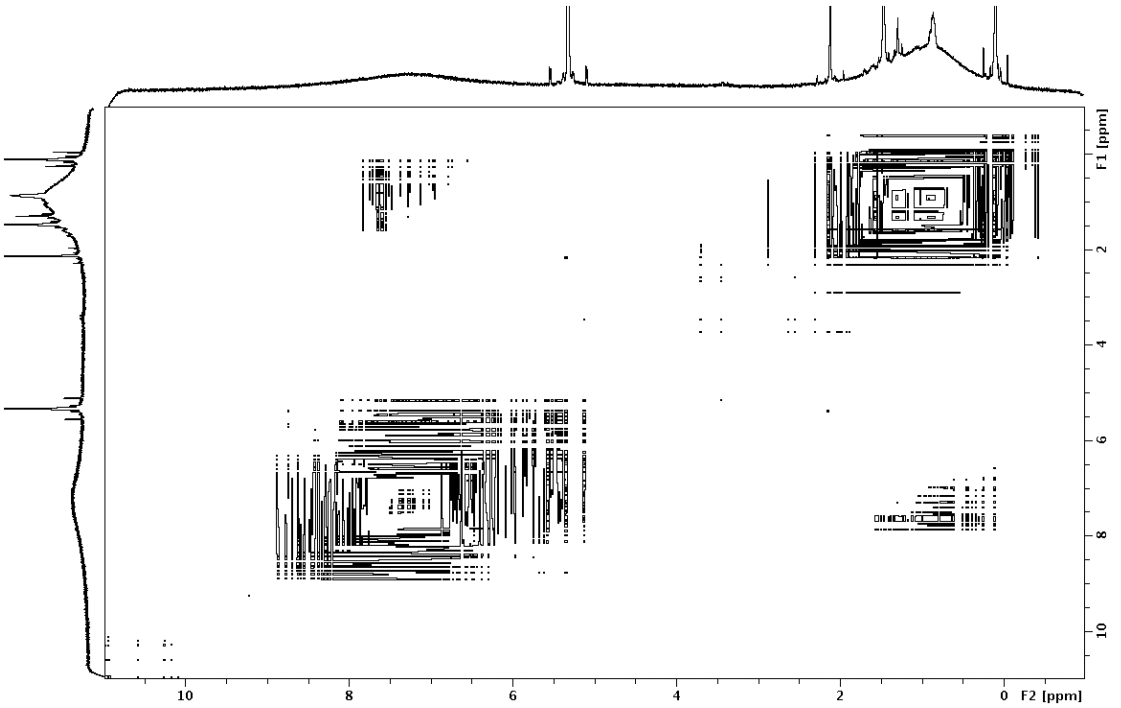


Figure S6a. NOESY of randomly mixed Au-DPT$_{0.22}$DMOT$_{0.78}$

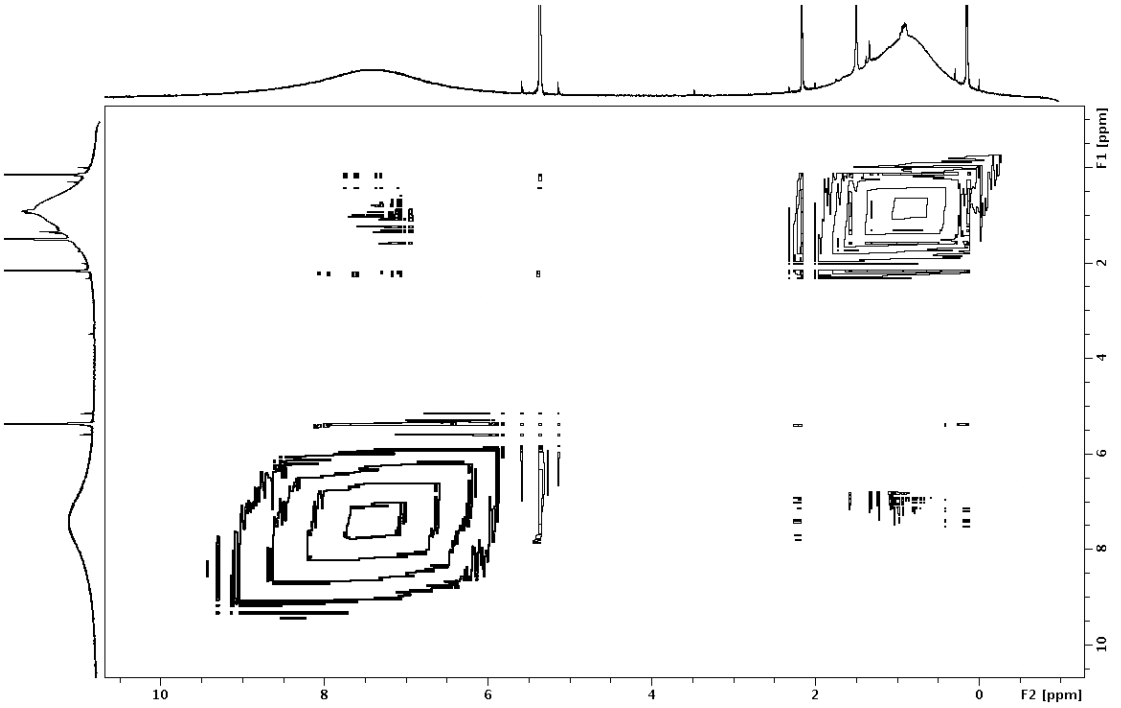


Figure S6b. NOESY of randomly mixed Au-DPT$_{0.32}$DMOT$_{0.68}$

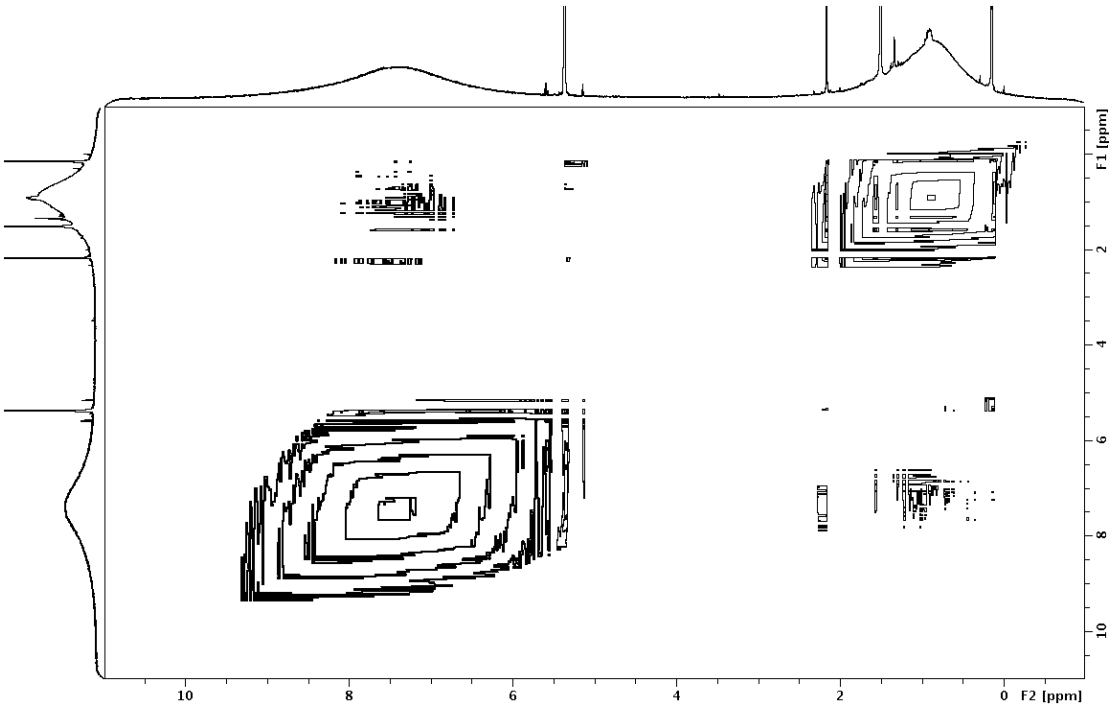


Figure S6c. NOESY of randomly mixed Au-DPT$_{0.40}$DMOT$_{0.60}$

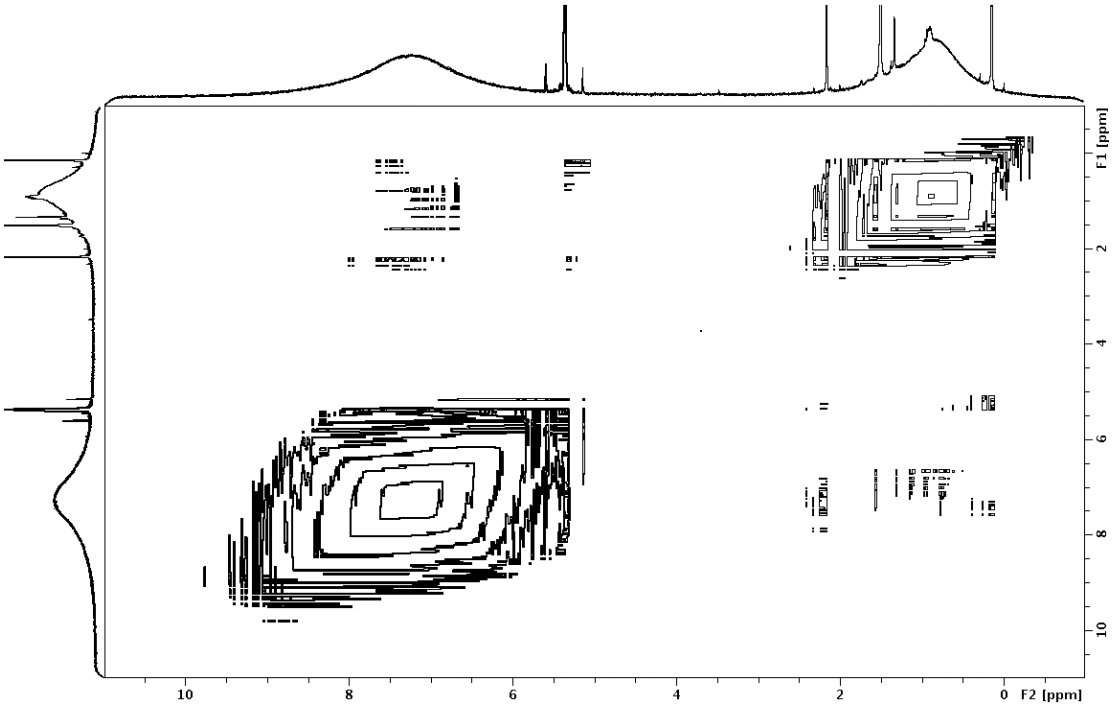


Figure S6d. NOESY of randomly mixed Au-DPT$_{0.60}$DMOT$_{0.40}$

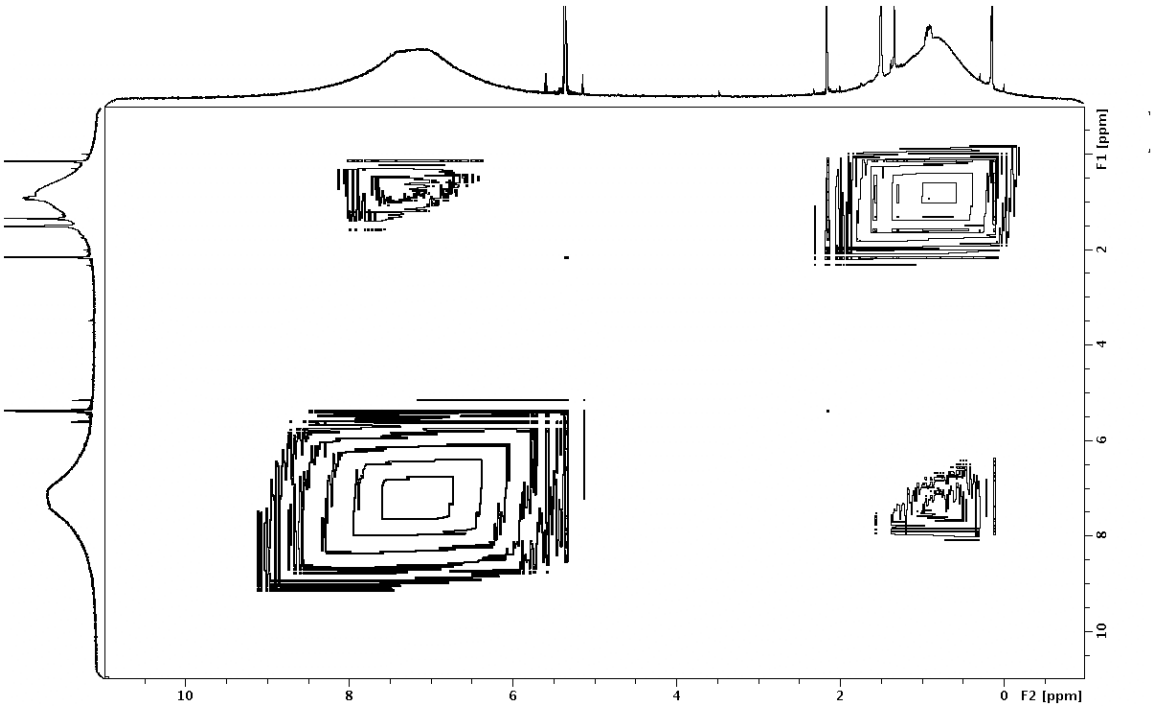


Figure S6e. NOESY of randomly mixed Au-DPT$_{0.71}$DMOT$_{0.29}$

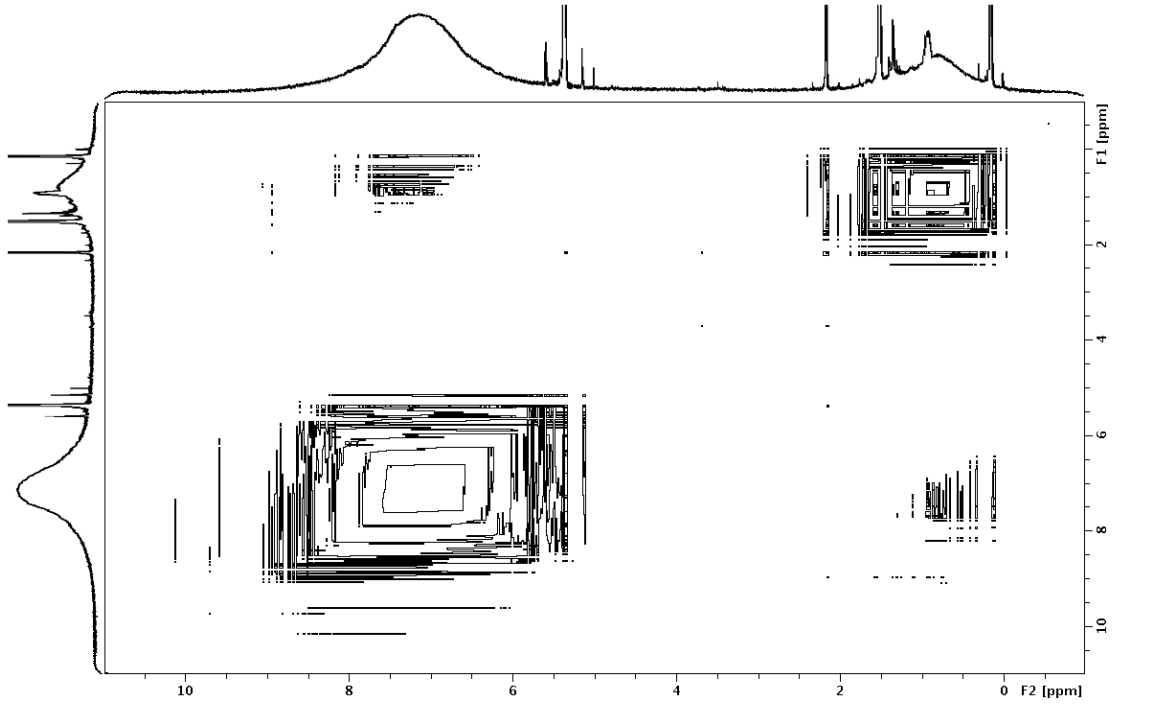


Figure S6f. NOESY of randomly mixed Au-DPT$_{0.82}$DMOT$_{0.18}$

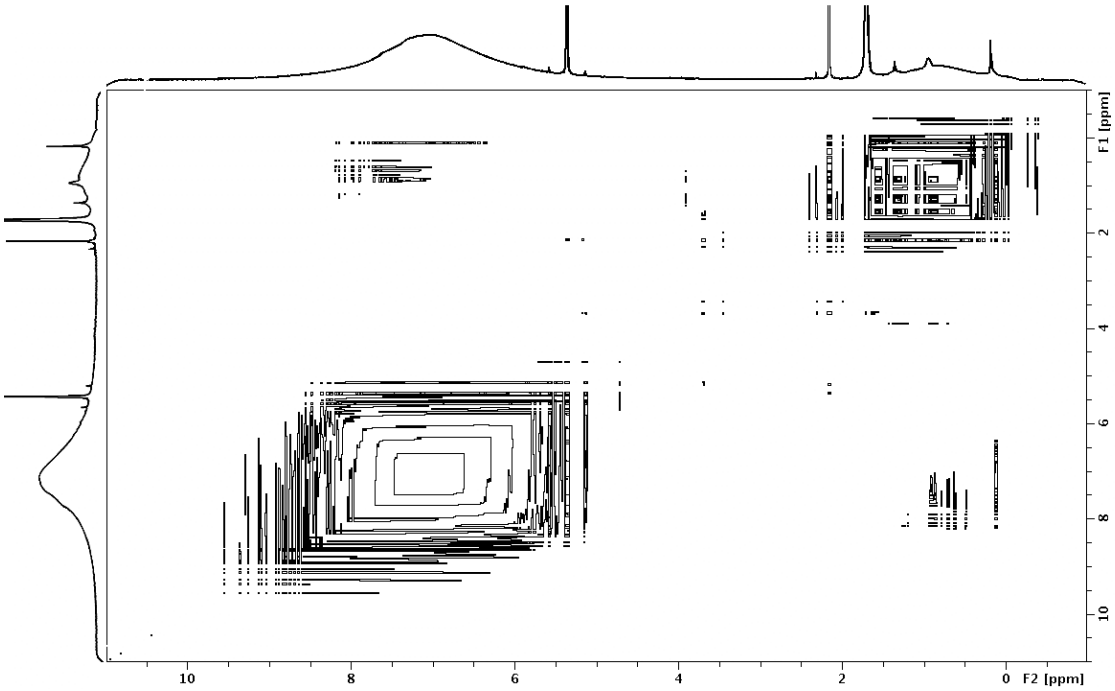


Figure S6g. NOESY of randomly mixed Au-DPT$_{0.93}$DMOT$_{0.07}$

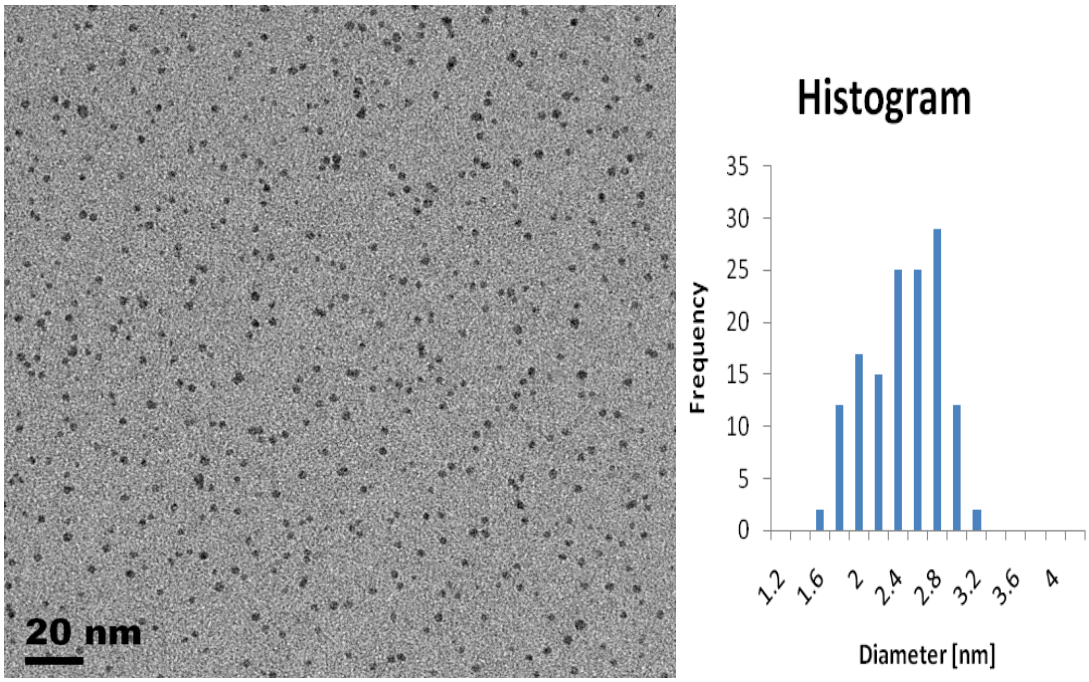


Figure S7a. TEM image of Janus Au-DPT$_{0.10}$DDT$_{0.90}$ (2.36 +/- 0.38 nm)

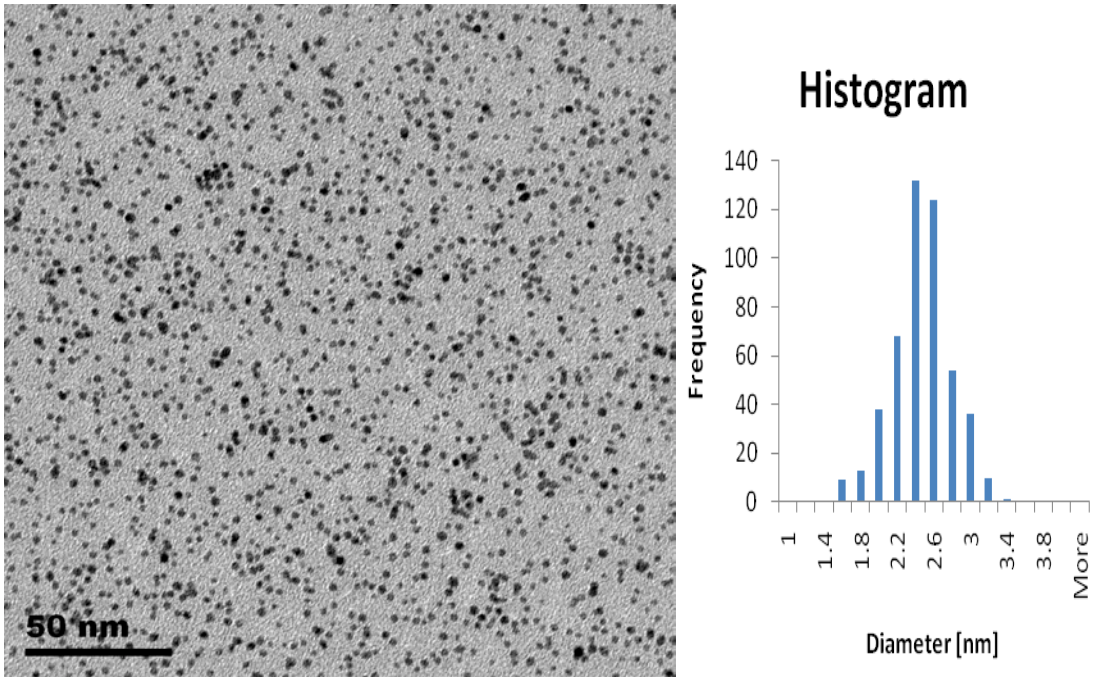


Figure S7b. TEM image of Janus Au-$DPT_{0.19}DDT_{0.81}$ (2.39 +/- 0.32 nm)

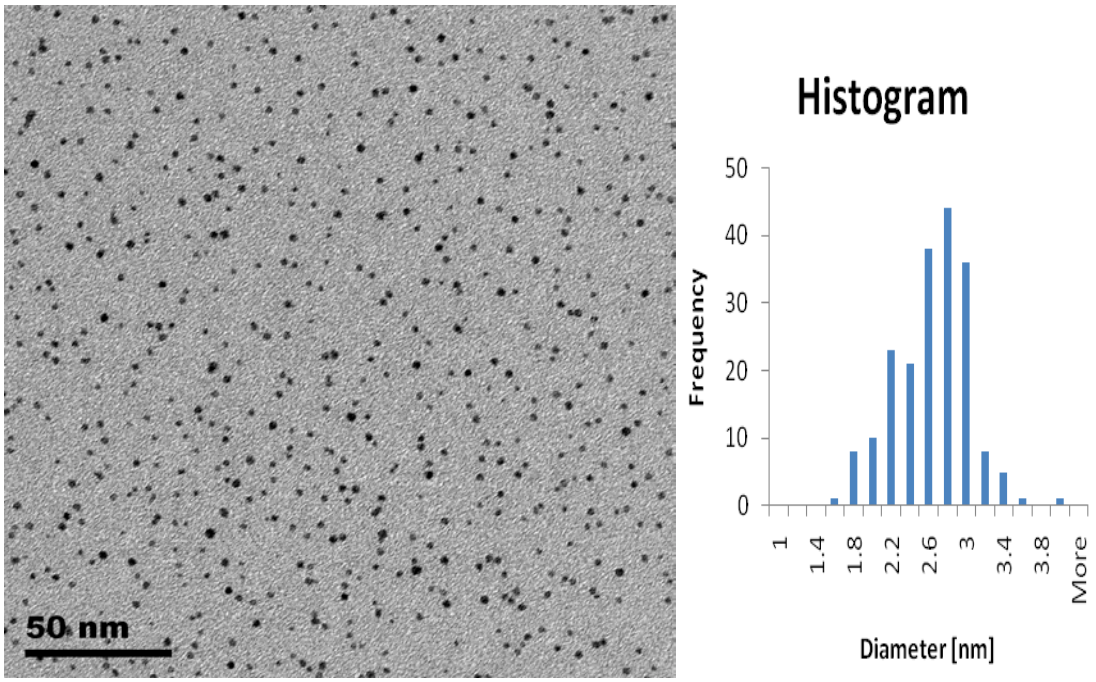


Figure S7c. TEM image of Janus Au-$DPT_{0.28}DDT_{0.72}$ (2.55 +/- 0.39)

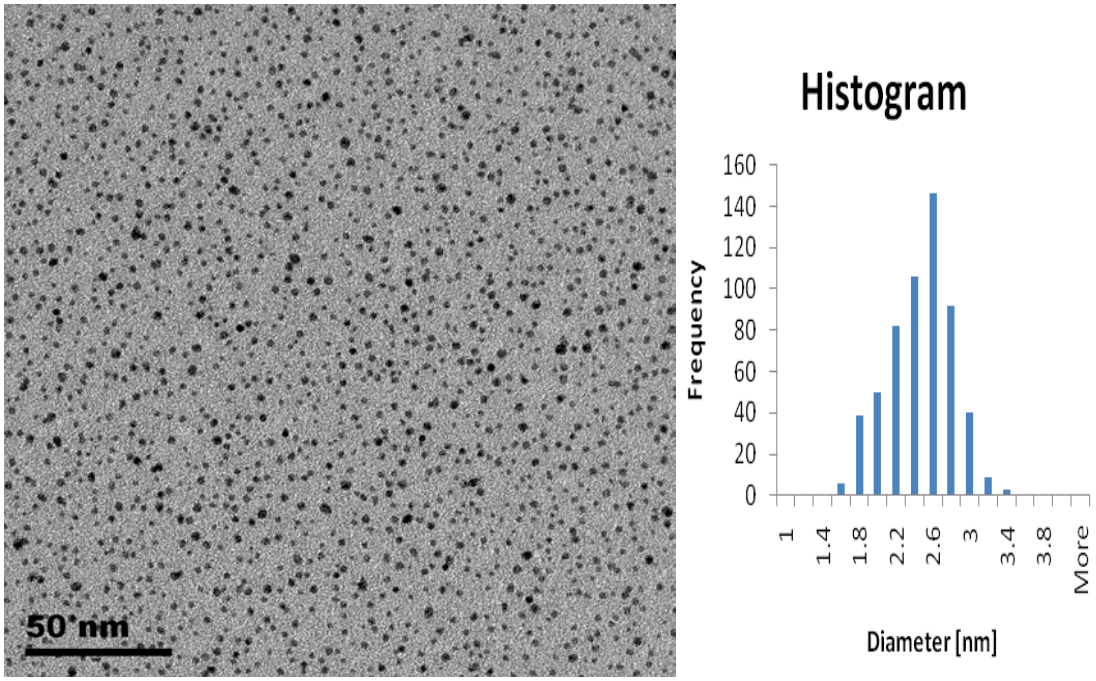


Figure S7d. TEM image of Janus Au-$DPT_{0.41}DDT_{0.59}$ (2.38+/- 0.35)

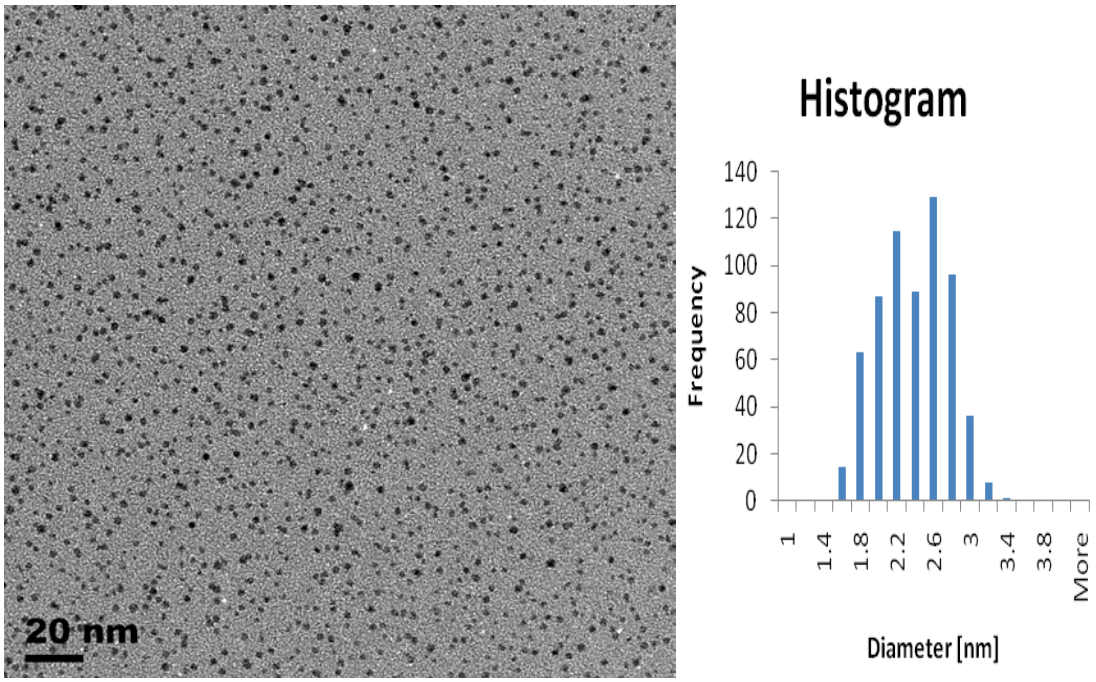


Figure S7e. TEM image of Janus Au-$DPT_{0.56}DDT_{0.44}$ (2.28 +/- 0.36 nm)

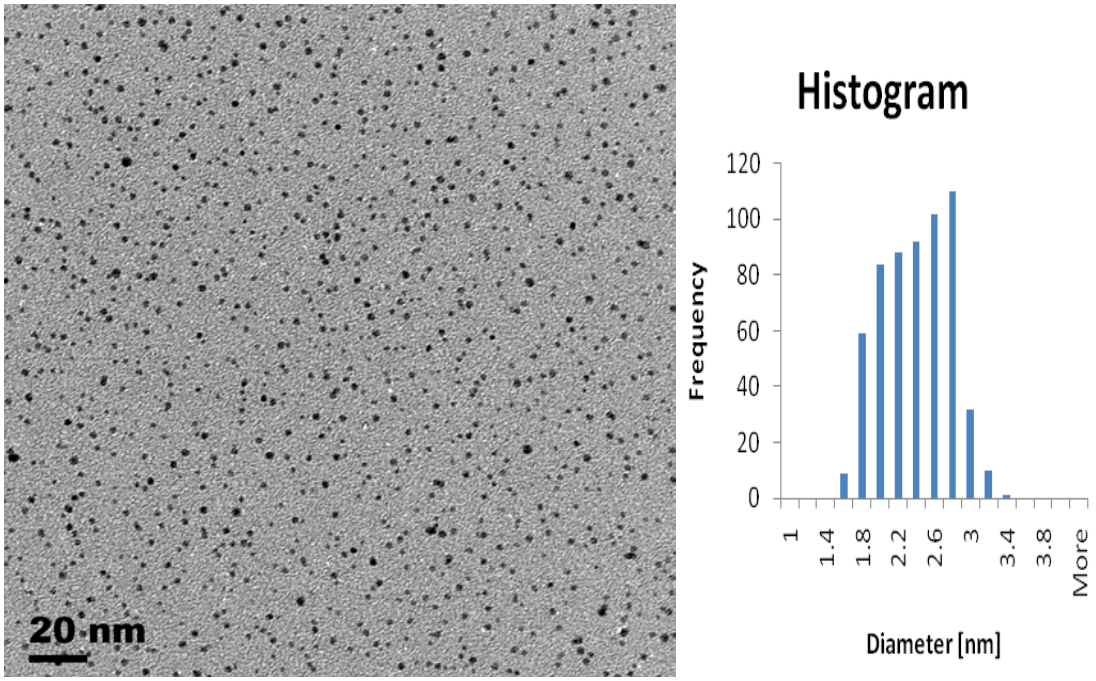


Figure S7f. TEM image of Janus Au-$DPT_{0.70}DDT_{0.30}$ (2.30+/-0.37)

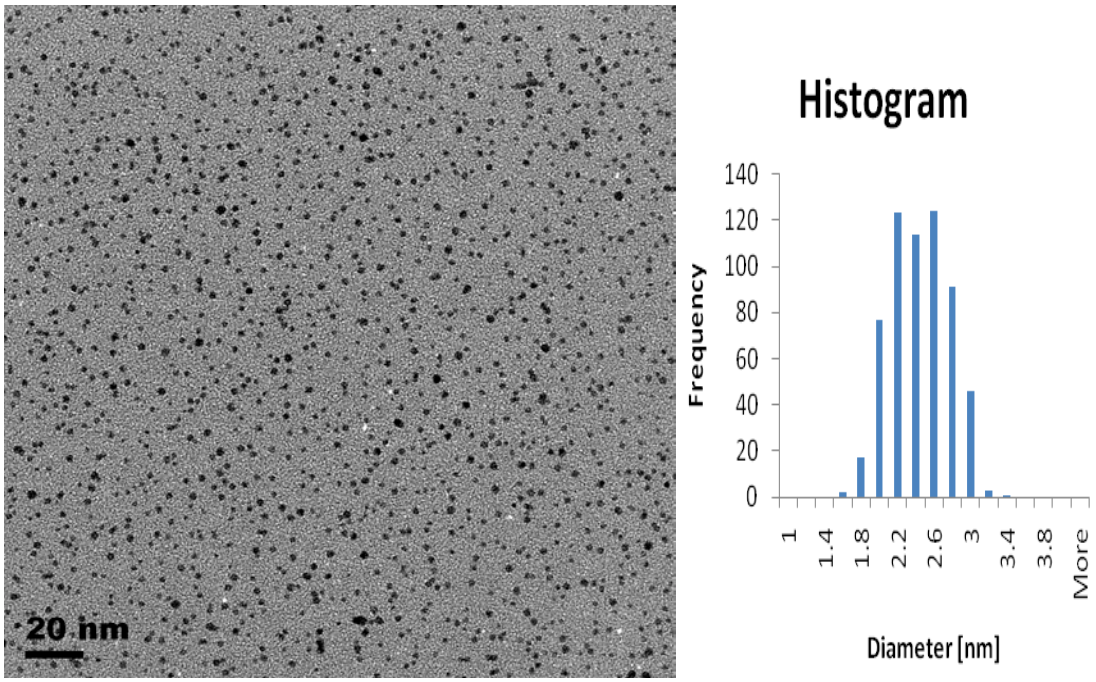


Figure S7g. TEM image of Janus Au-$DPT_{0.82}DDT_{0.18}$ (2.33+/-0.33 nm)

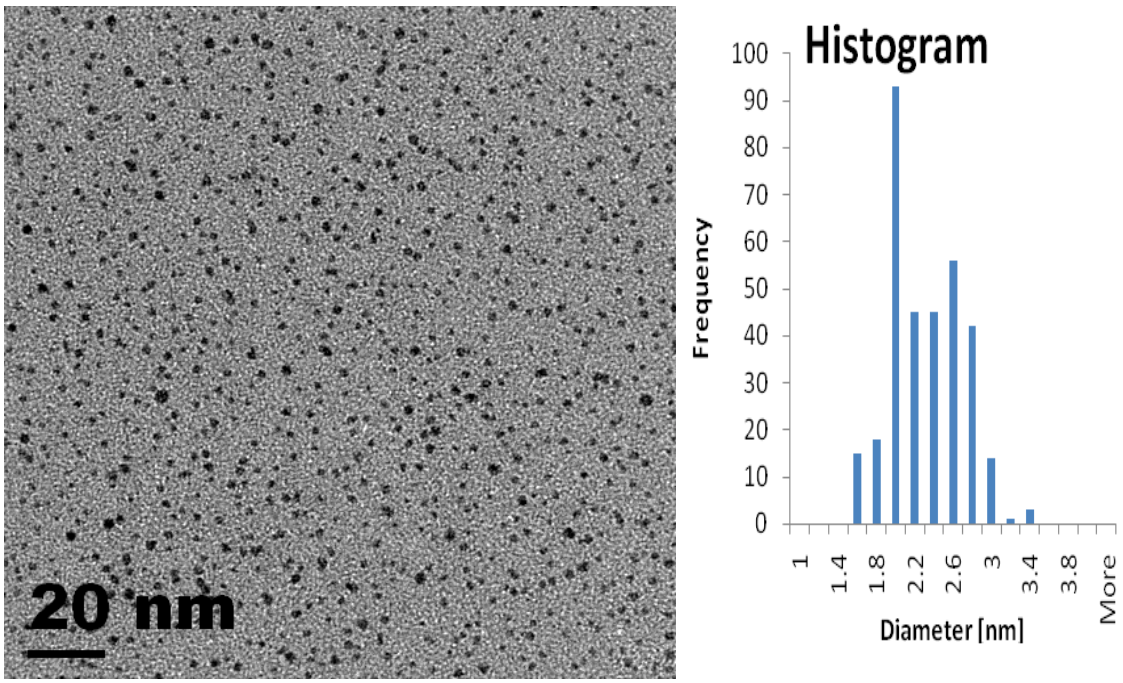


Figure S7h. TEM image of ~2 nm Au-DPT (2.20+/-0.37)

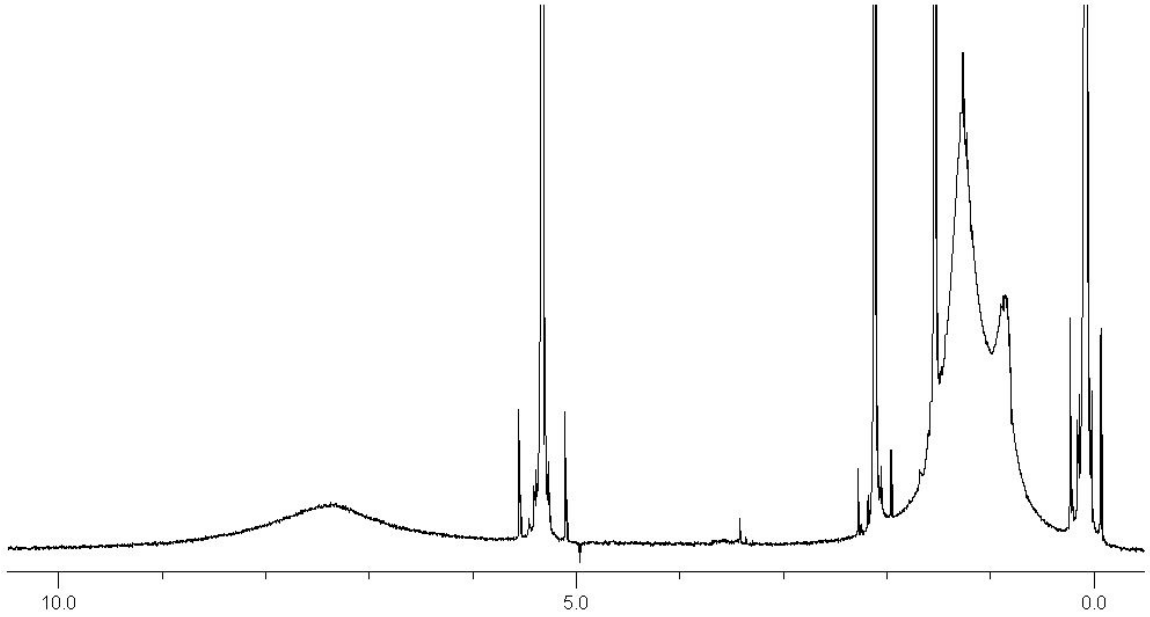


Figure S8a. ^{1}H NMR of Janus Au-DPT$_{0.10}$DDT$_{0.90}$

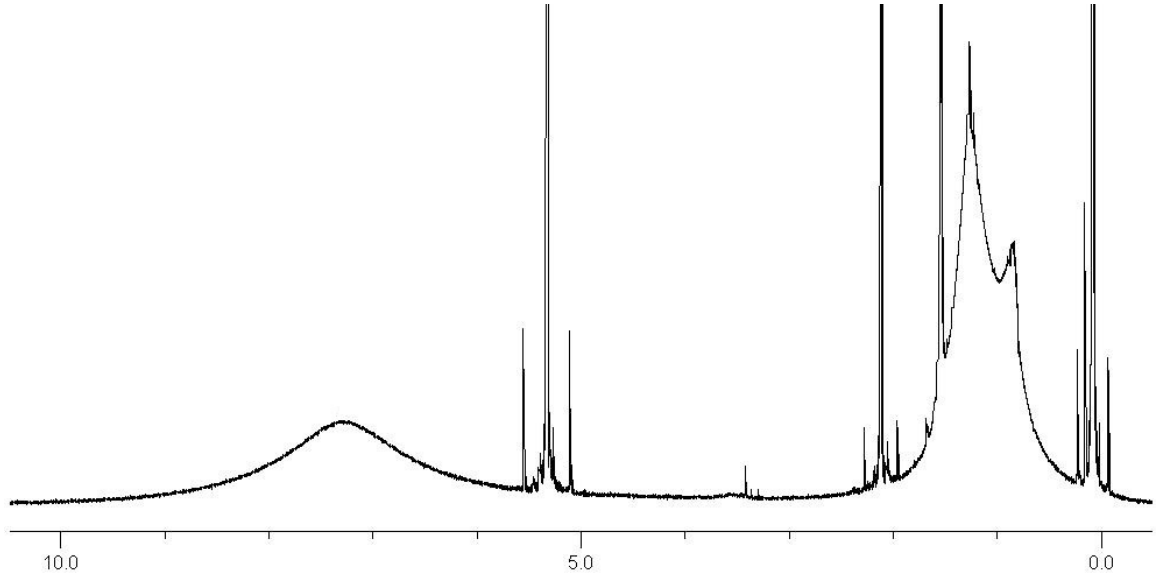


Figure S8b. ^{1}H NMR of Janus Au-DPT$_{0.19}$DDT$_{0.81}$

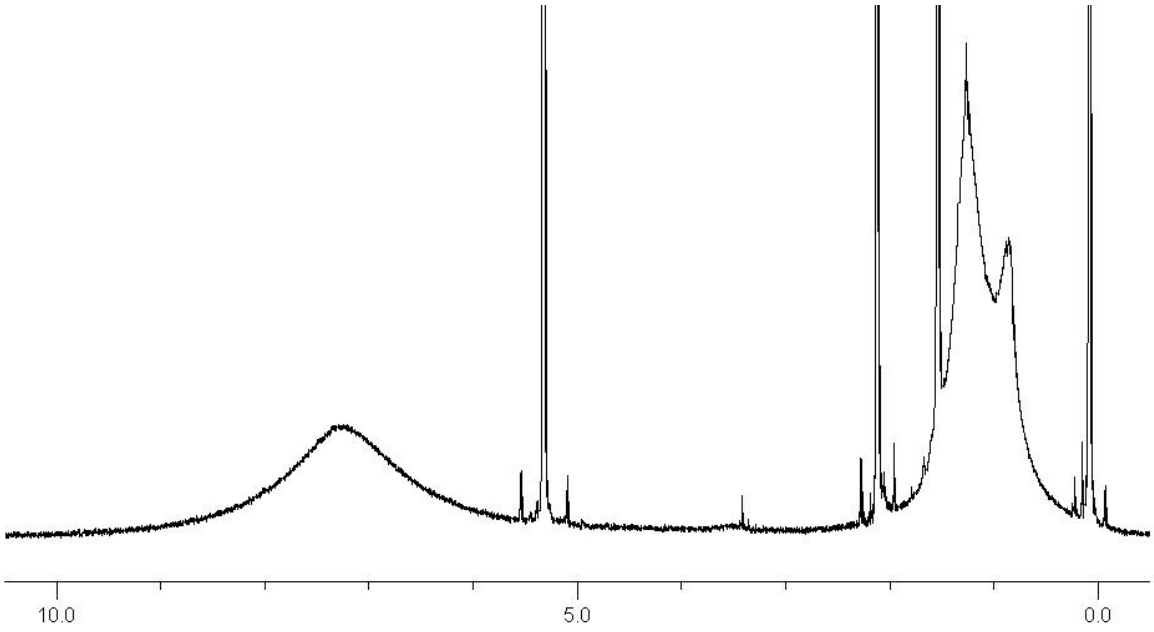


Figure S8c. ^{1}H NMR of Janus Au-DPT$_{0.28}$DDT$_{0.72}$

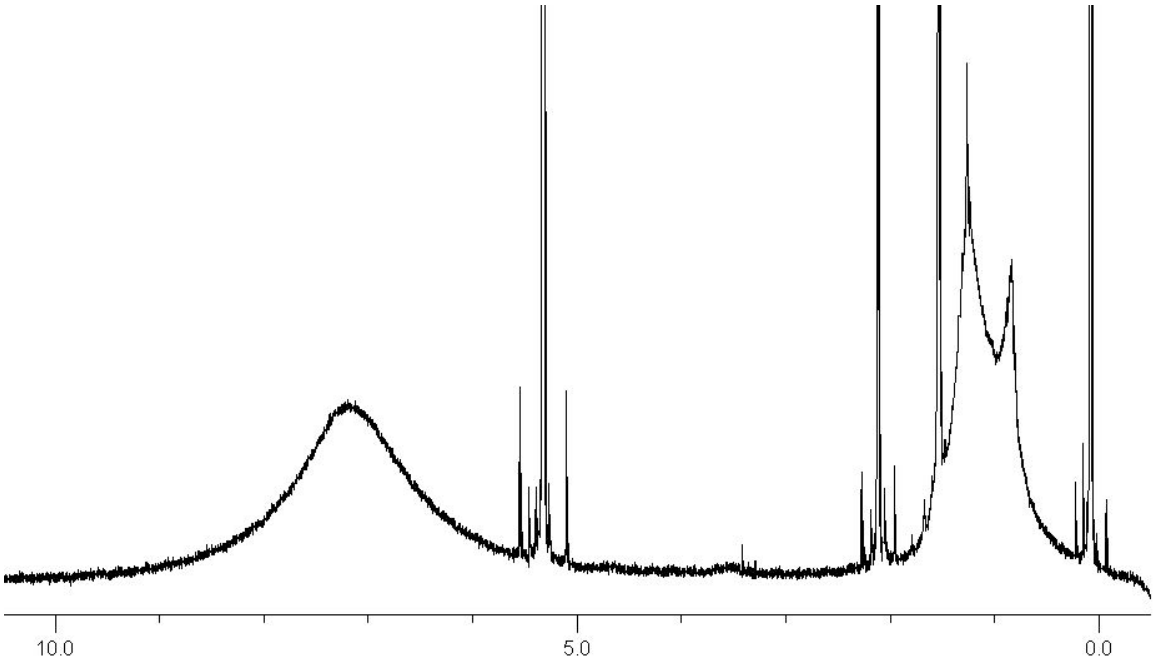


Figure S8d. ^{1}H NMR of Janus Au-DPT$_{0.41}$DDT$_{0.59}$

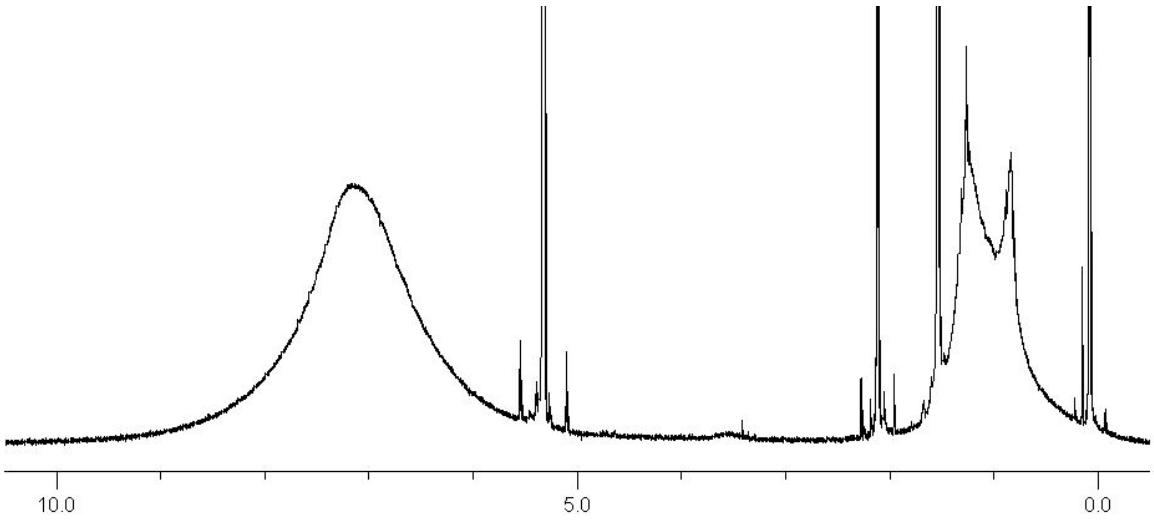


Figure S8e. ^{1}H NMR of Janus Au-DPT$_{0.56}$DDT$_{0.44}$

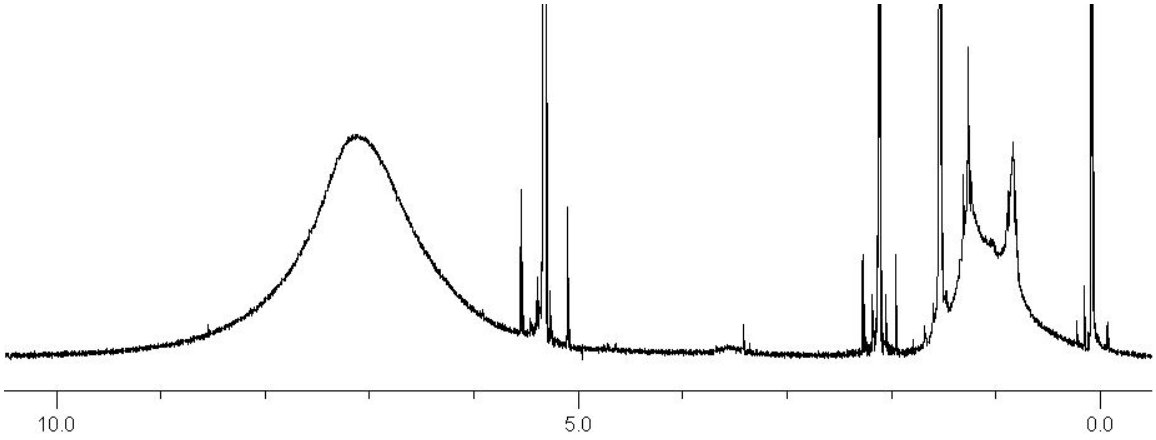


Figure S8f. ^{1}H NMR of Janus Au-DPT$_{0.70}$DDT$_{0.30}$

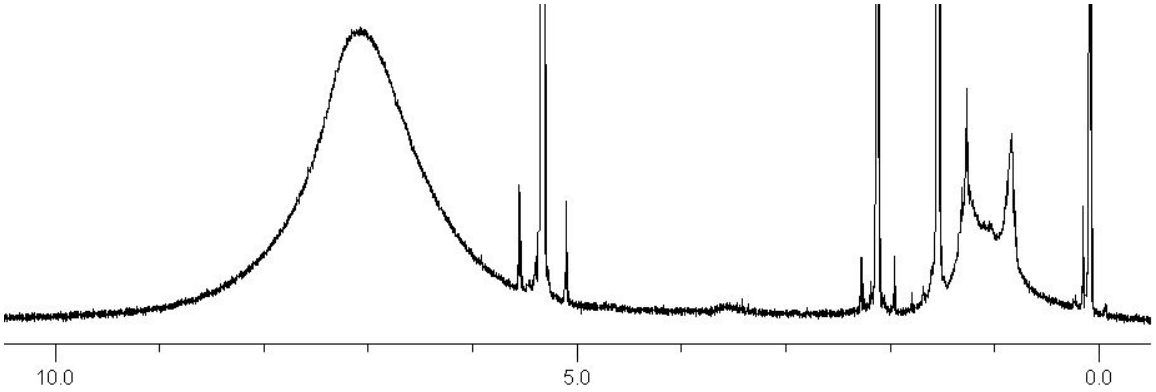


Figure S8g. ^{1}H NMR of Janus Au-DPT$_{0.82}$DDT$_{0.18}$

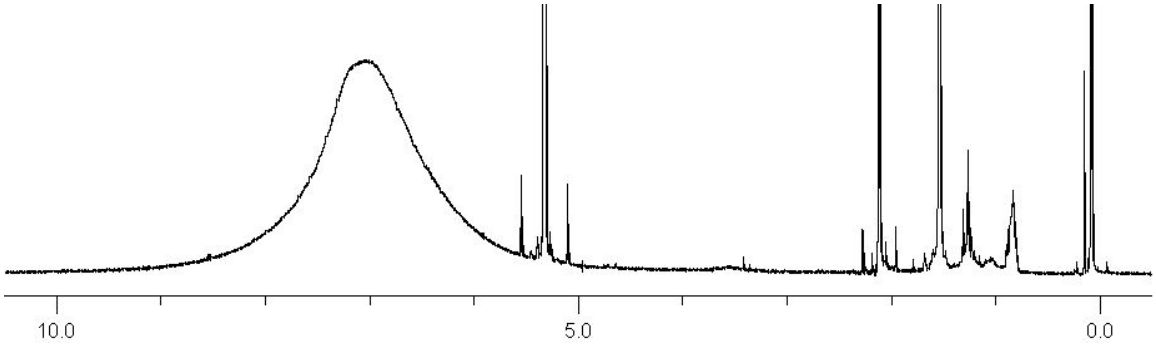


Figure S8h. ^{1}H NMR of ~2 nm Au-DPT this specific particles could contain some impurities, whose presence is irrelevant for the scope of this paper.

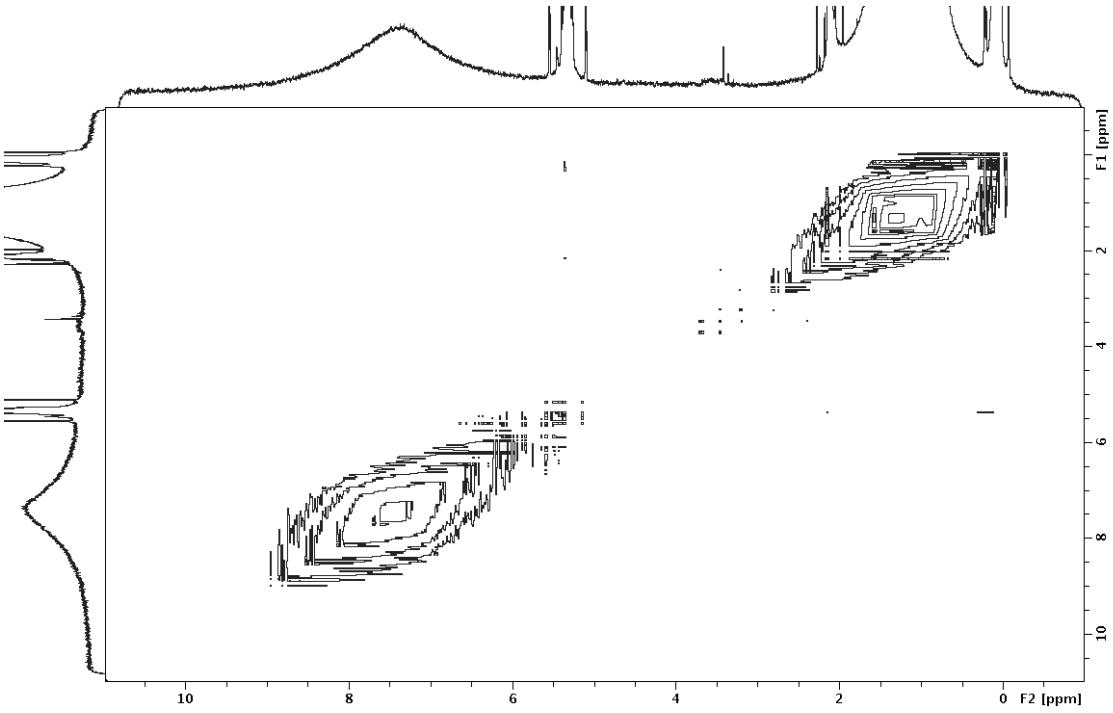


Figure S9a. NOESY of Janus Au-$DPT_{0.10}DDT_{0.90}$

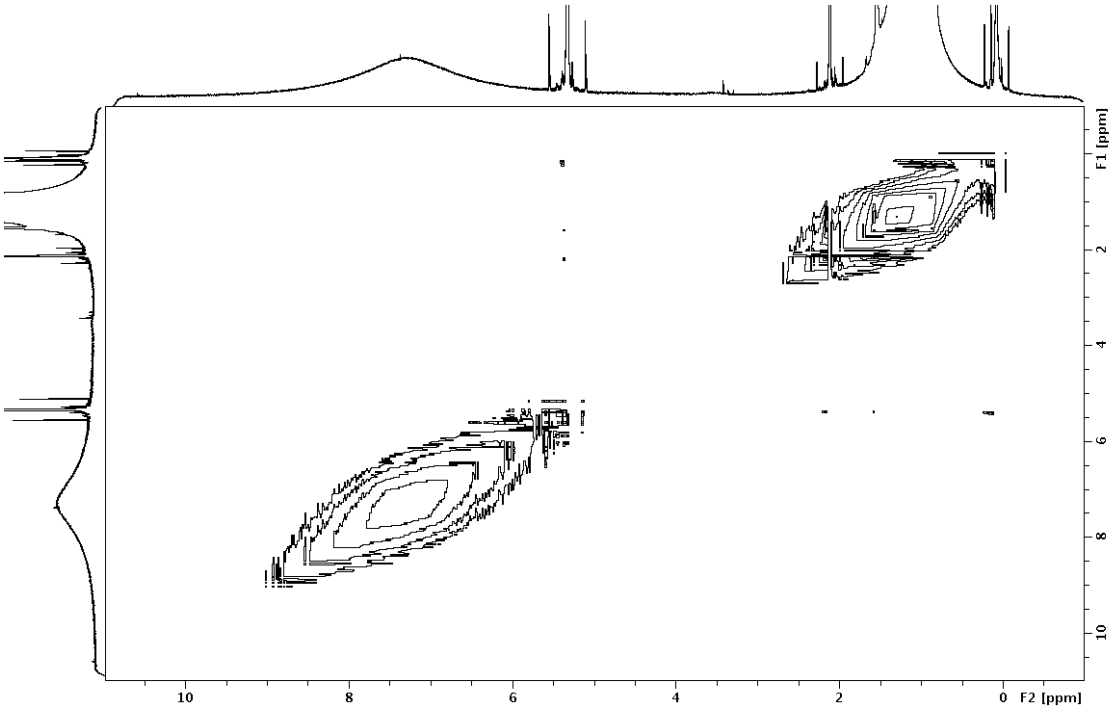


Figure S9b. NOESY of Janus Au-$DPT_{0.19}DDT_{0.81}$

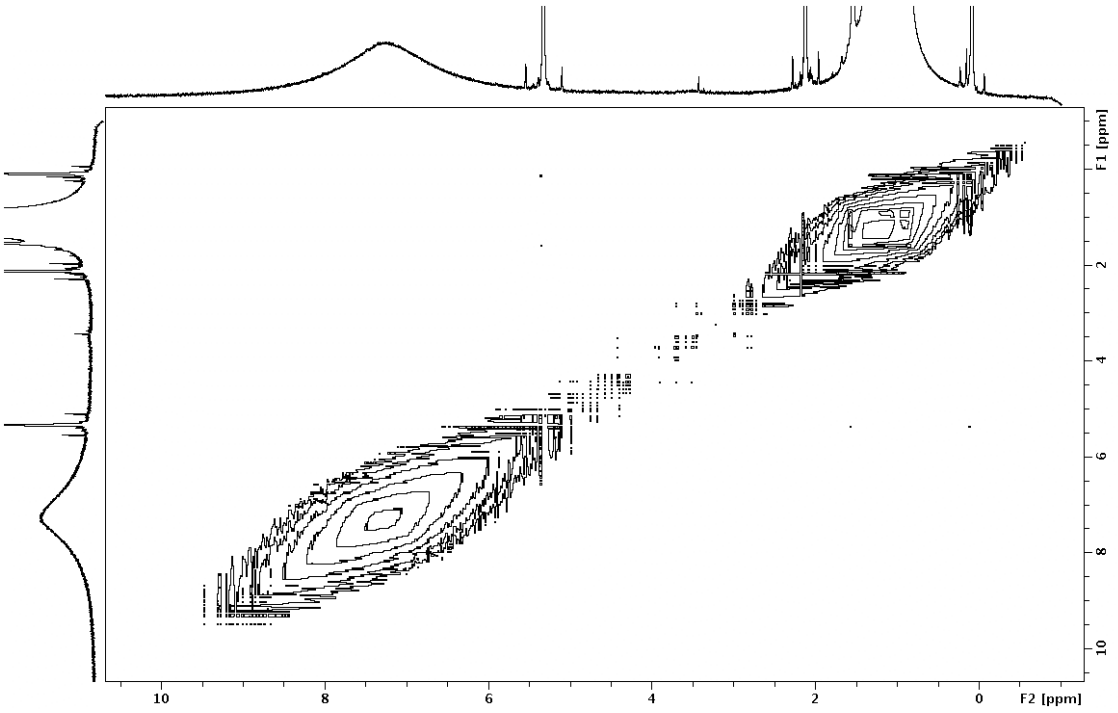


Figure S9c. NOESY of Janus Au-$DPT_{0.28}DDT_{0.72}$

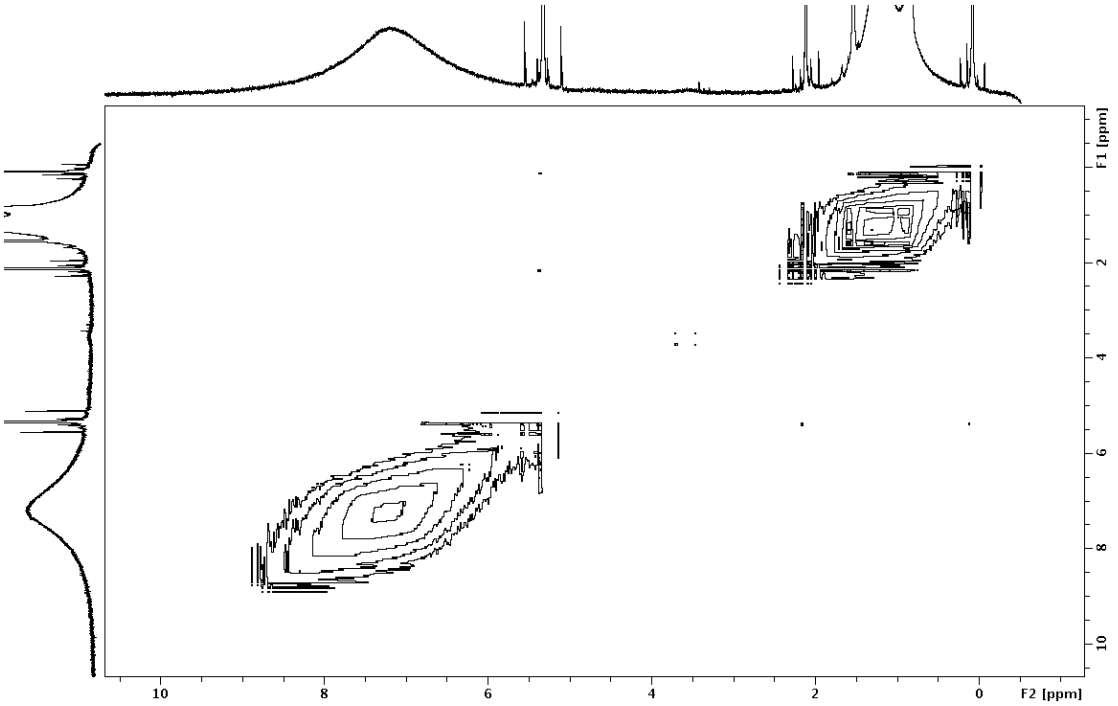


Figure S9d. NOESY of Janus Au-$DPT_{0.41}DDT_{0.59}$

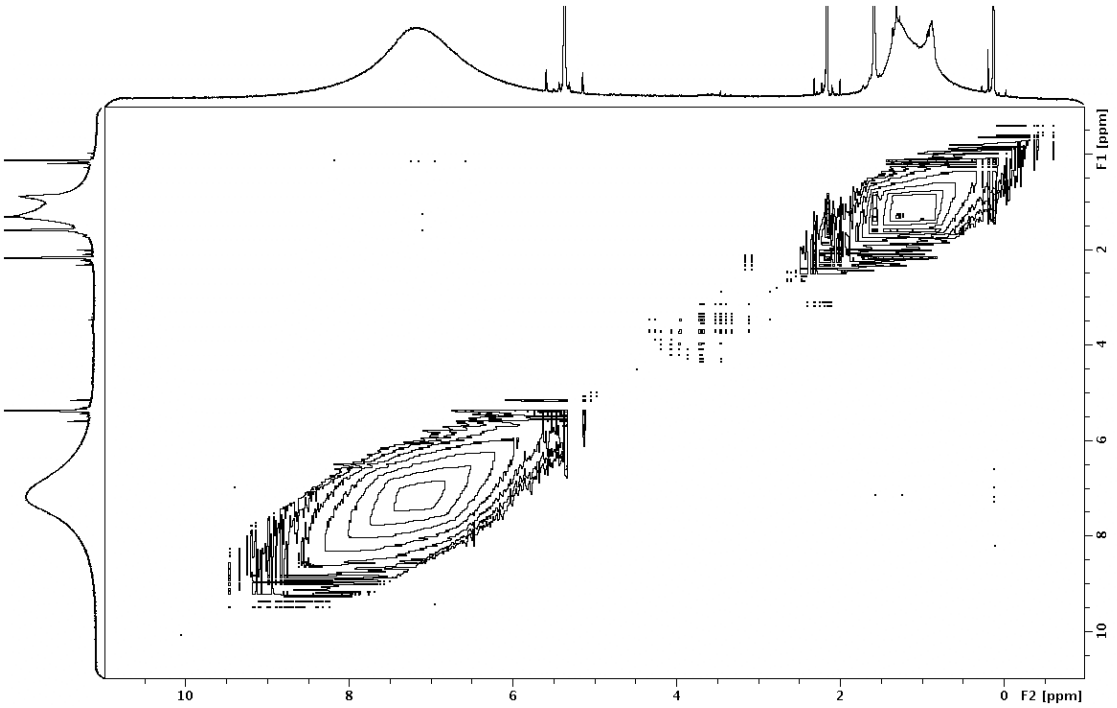


Figure S9e. NOESY of Janus Au-$DPT_{0.56}DDT_{0.44}$

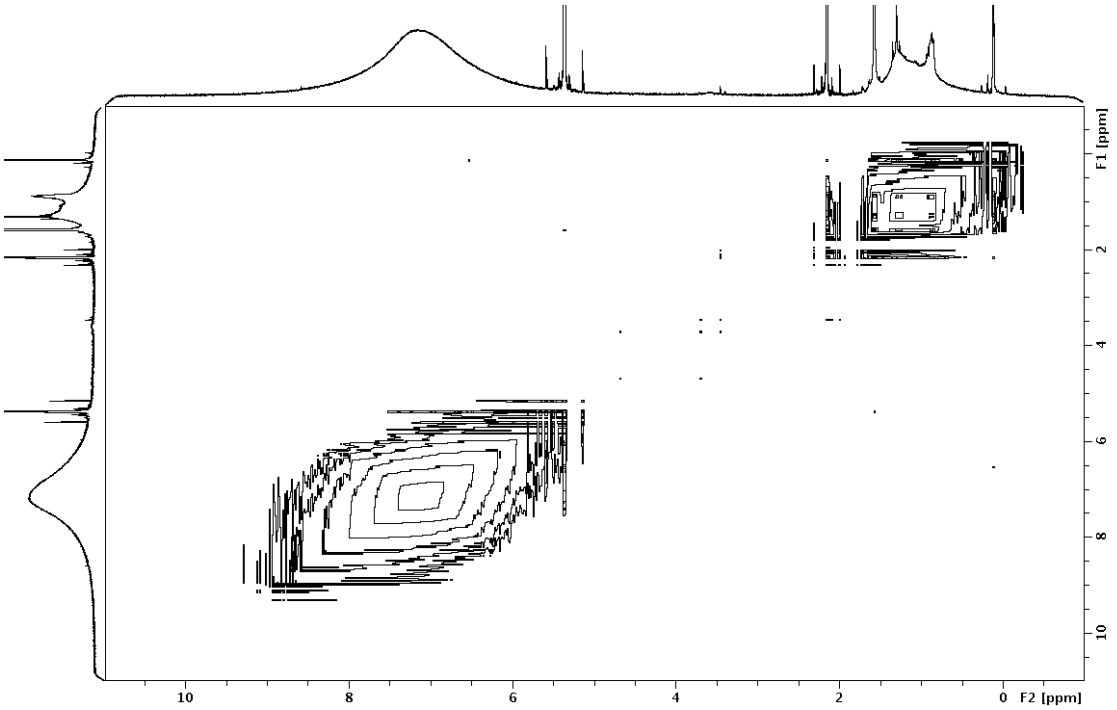


Figure S9f. NOESY of Janus Au-$DPT_{0.70}DDT_{0.30}$

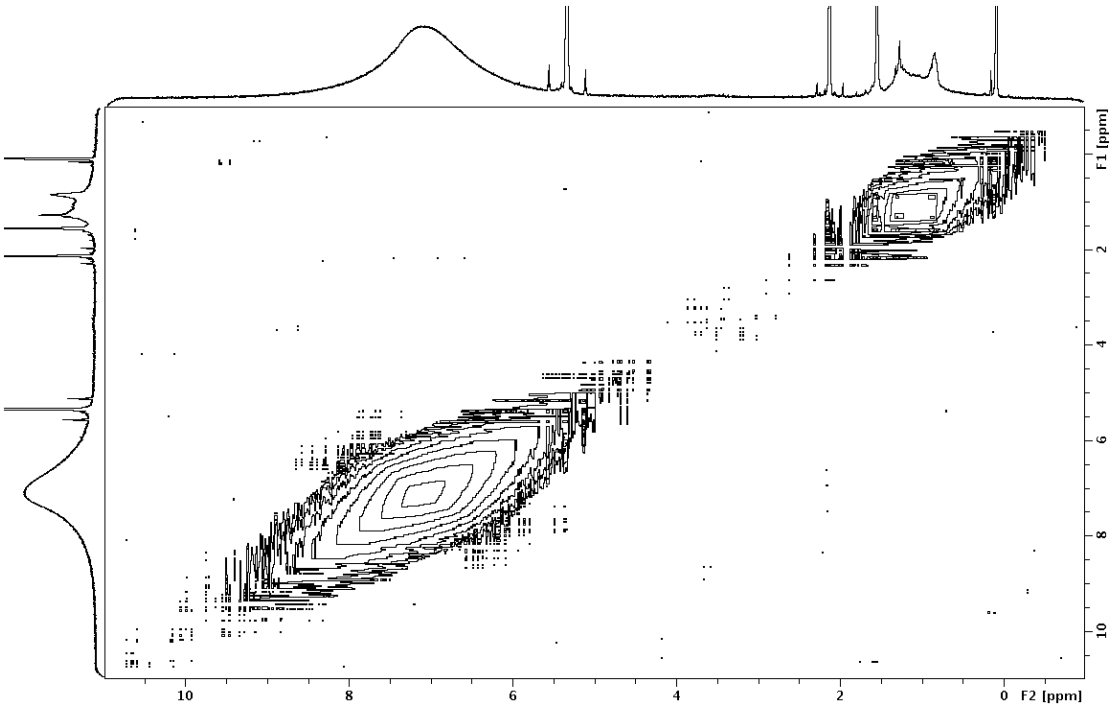


Figure S9g. NOESY of Janus Au-$DPT_{0.82}DDT_{0.18}$

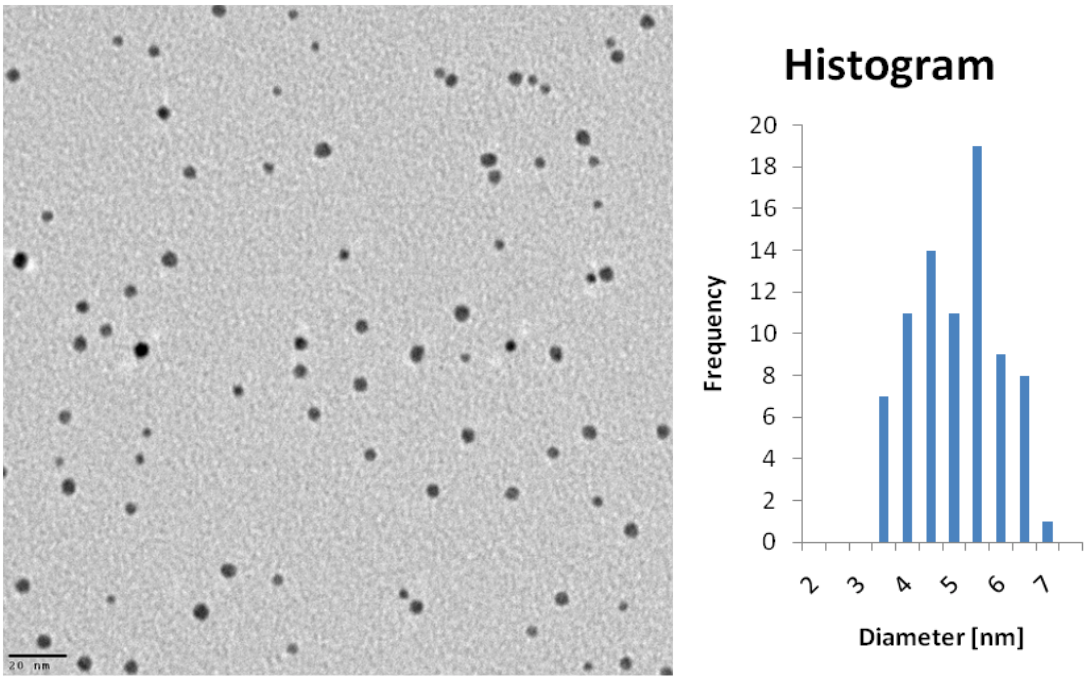


Figure S10a. TEM image of striped Au-$DPT_{0.13}DDT_{0.87}$ (D=4.93±0.91 nm)

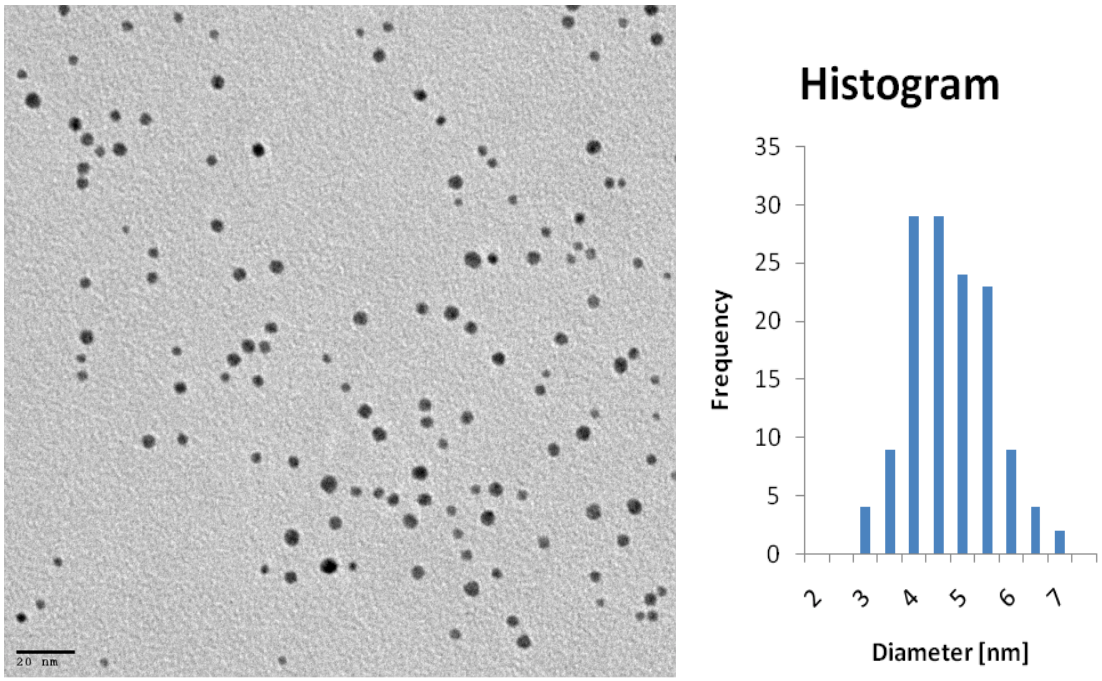


Figure S10b. TEM image of striped Au-$DPT_{0.21}DDT_{0.79}$ (D=4.43±0.86 nm)

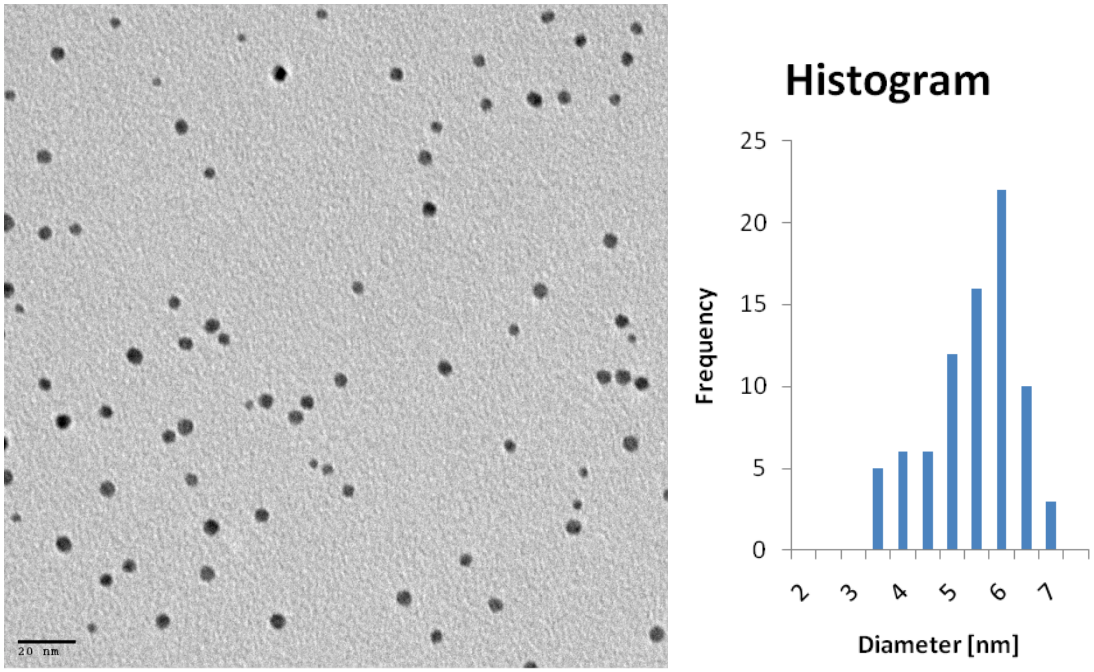
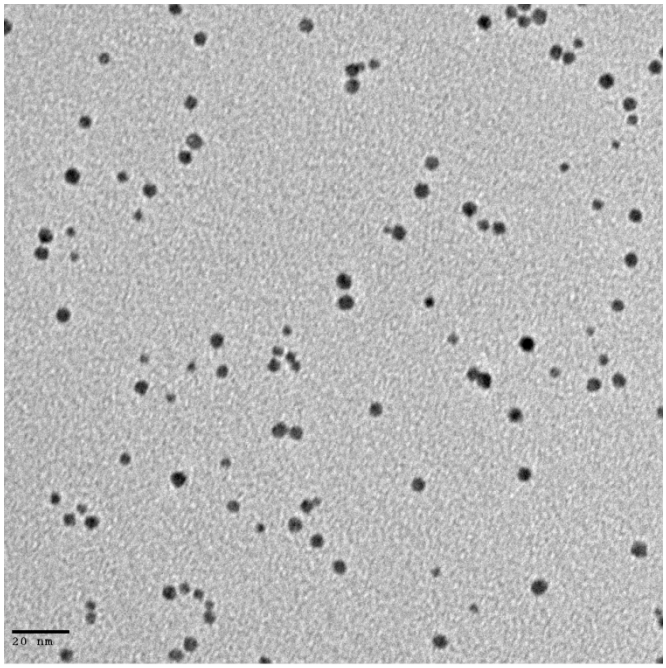


Figure S10c. TEM image of striped Au-$DPT_{0.27}DDT_{0.73}$ (D=5.30±0.89 nm)



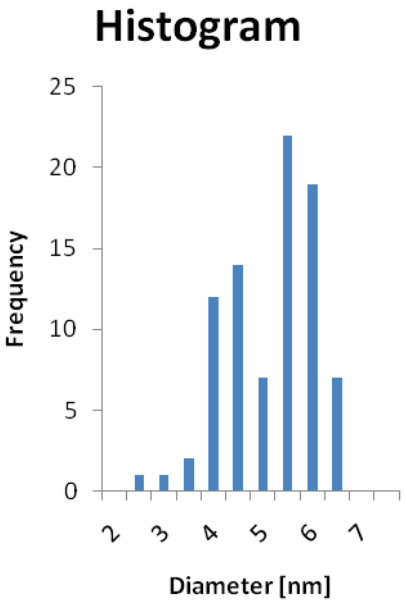
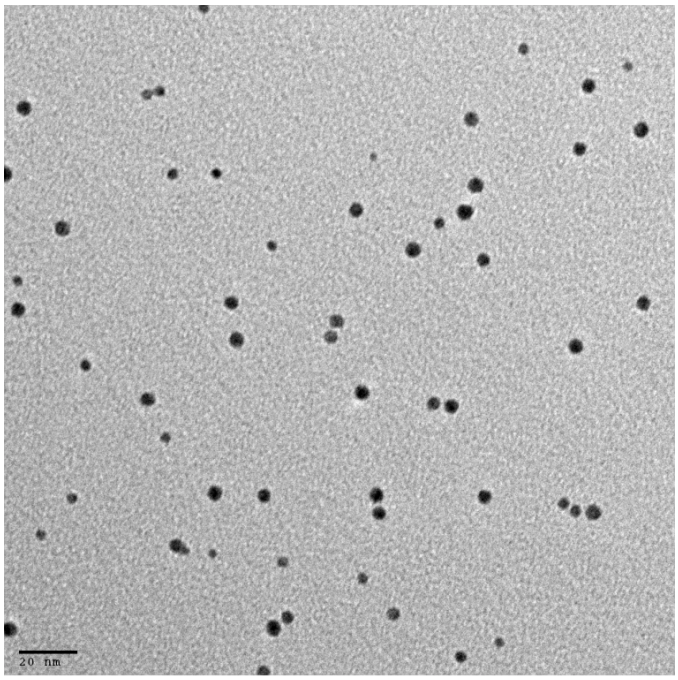


Figure S10d. TEM image of striped Au-$DPT_{0.40}DDT_{0.60}$ (D=5.19±0.91 nm)



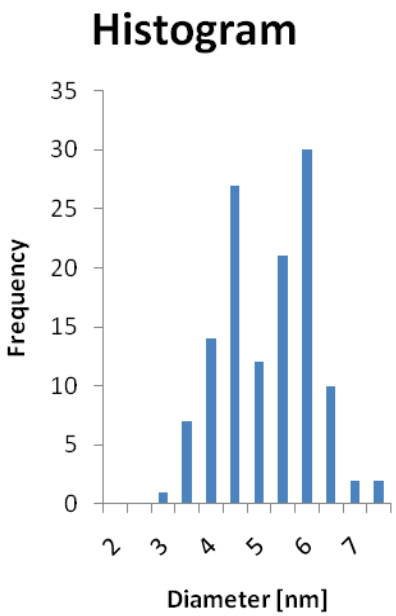


Figure S10e. TEM image of striped Au-$DPT_{0.58}DDT_{0.42}$ (D=5.05±0.97 nm)

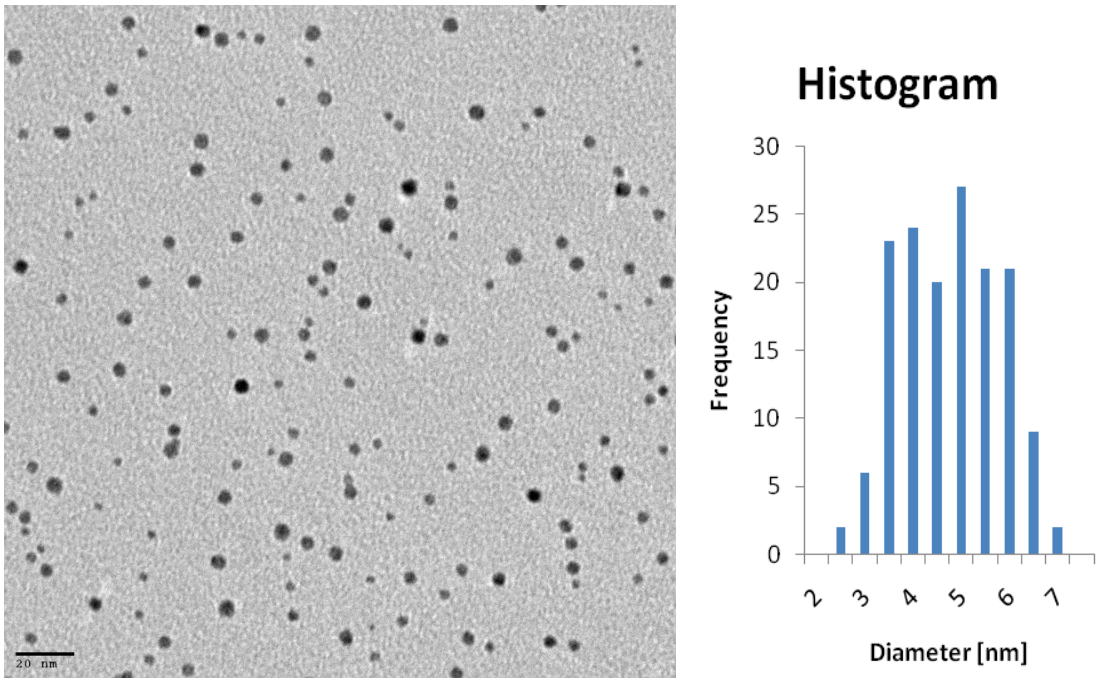


Figure S10f. TEM image of striped Au-$DPT_{0.68}DDT_{0.32}$ (D=4.54±1.00 nm)

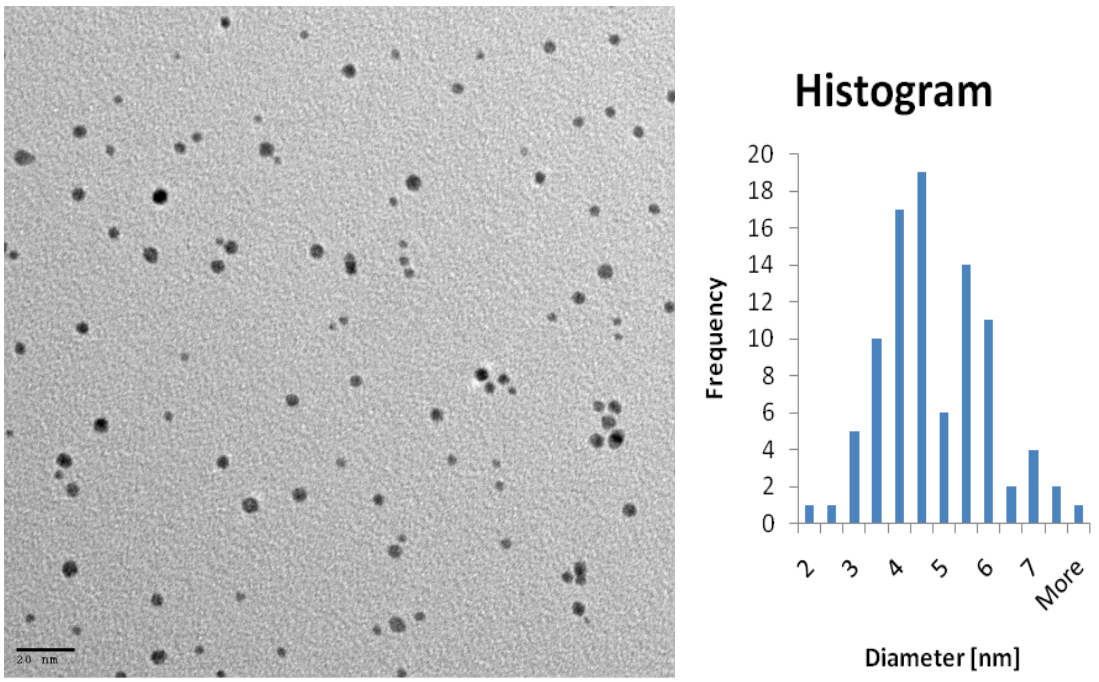


Figure S10g. TEM image of striped Au-$DPT_{0.78}DDT_{0.22}$ (D=4.32±1.21 nm)

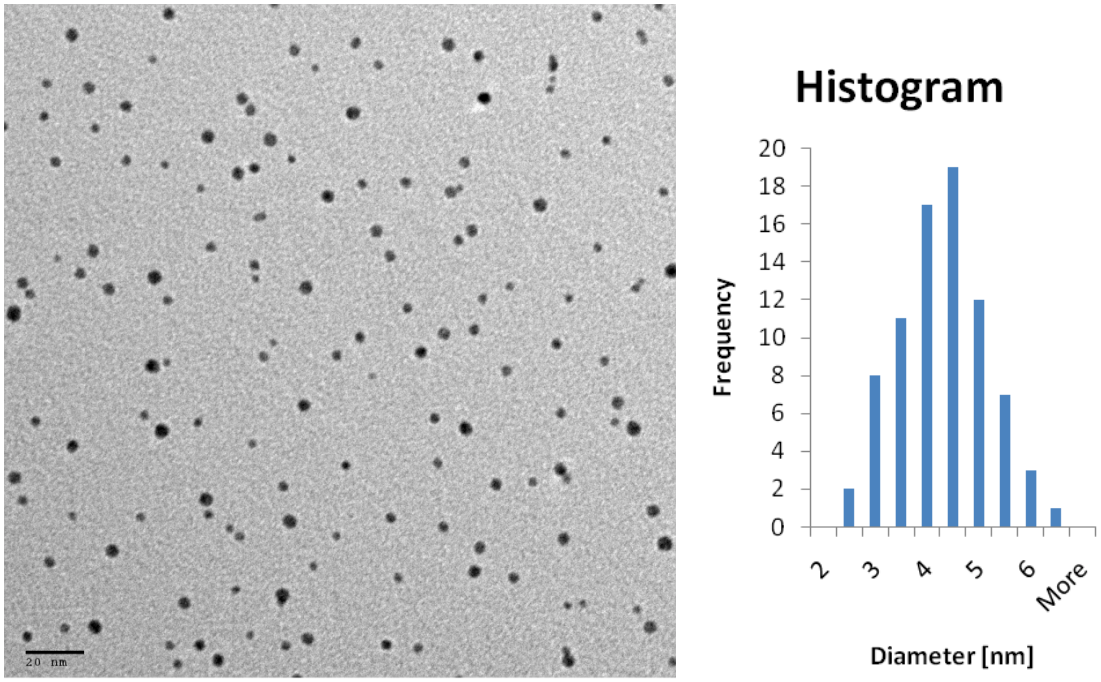


Figure S10h. TEM image of ~4 nm Au-DPT (D=4.02±0.85 nm)

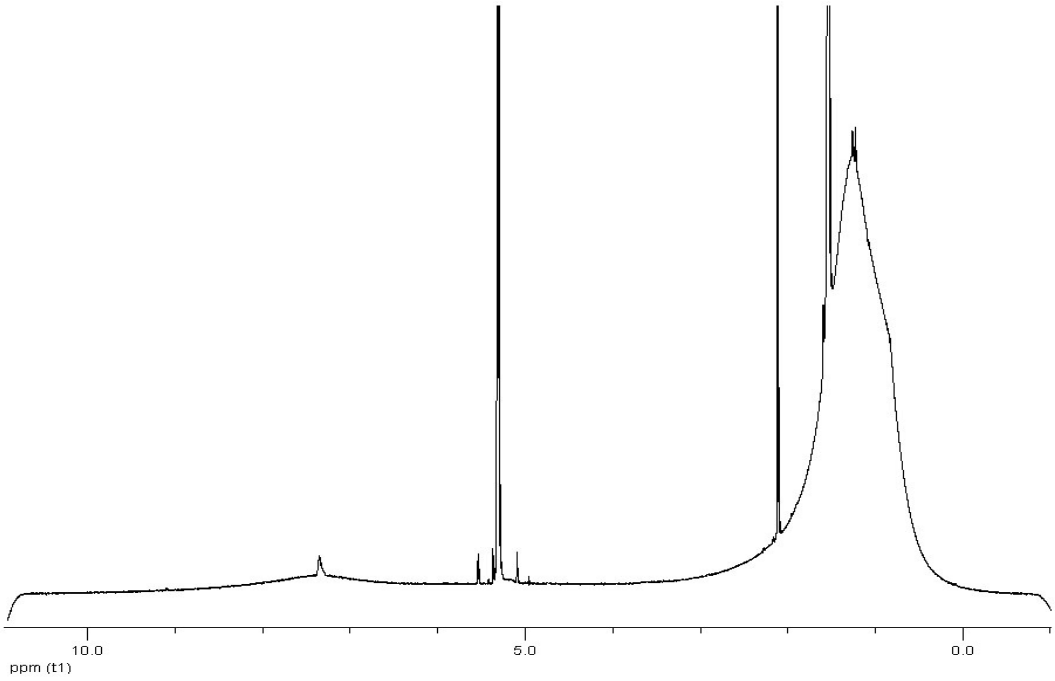


Figure S11a. ^{1}H NMR of striped Au-DPT$_{0.13}$DDT$_{0.87}$ (D=4.93±0.91 nm)

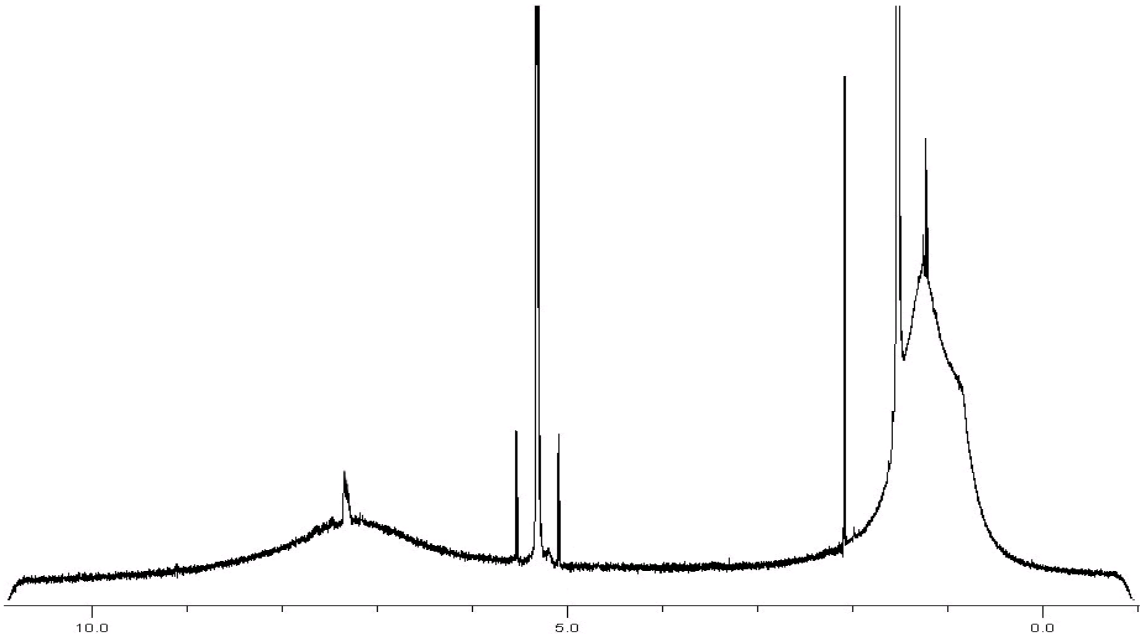


Figure S11b. ^{1}H NMR of striped Au-DPT$_{0.21}$DDT$_{0.79}$

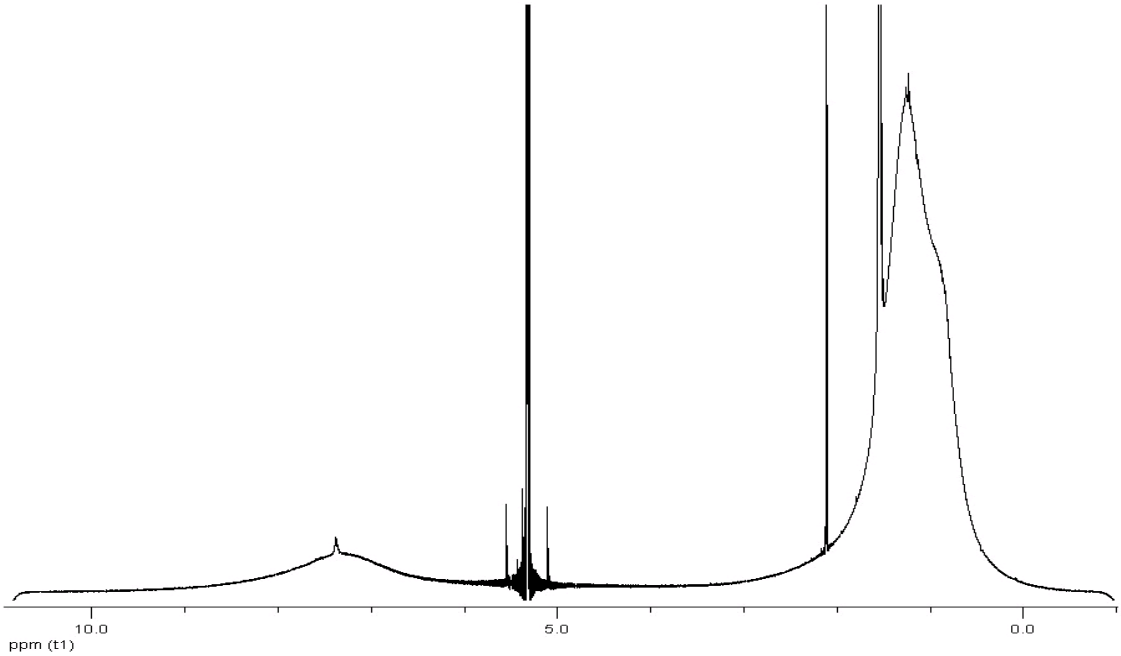


Figure S11c.^{1}H NMR of striped Au-DPT$_{0.27}$DDT$_{0.73}$

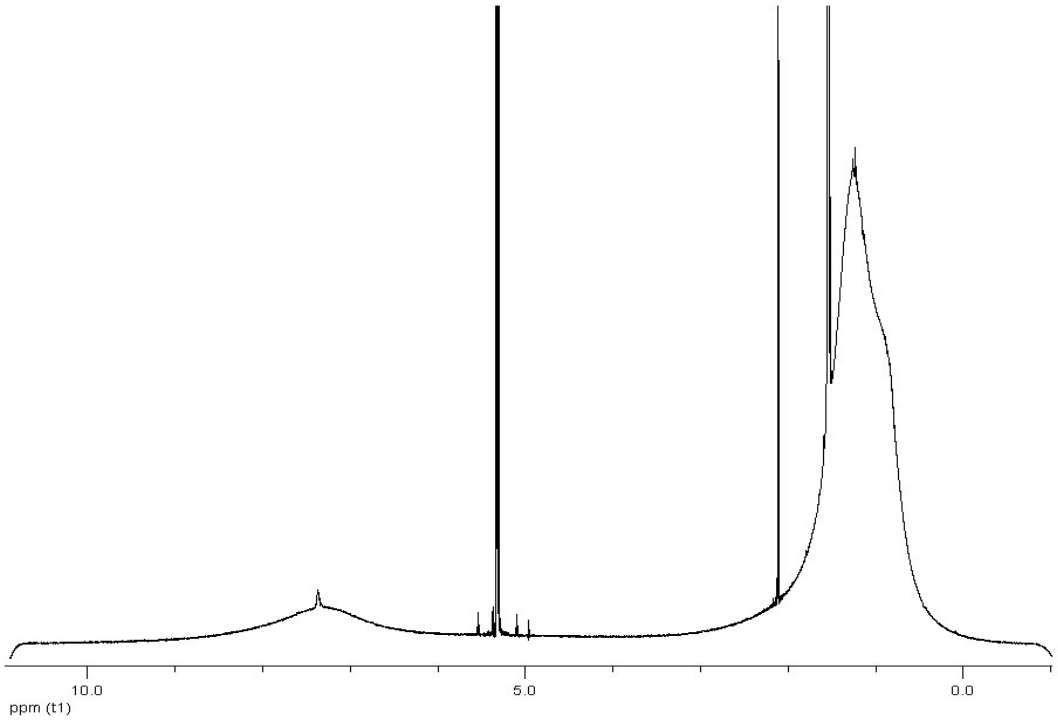


Figure S11d. ^{1}H NMR of striped Au-DPT$_{0.40}$DDT$_{0.60}$

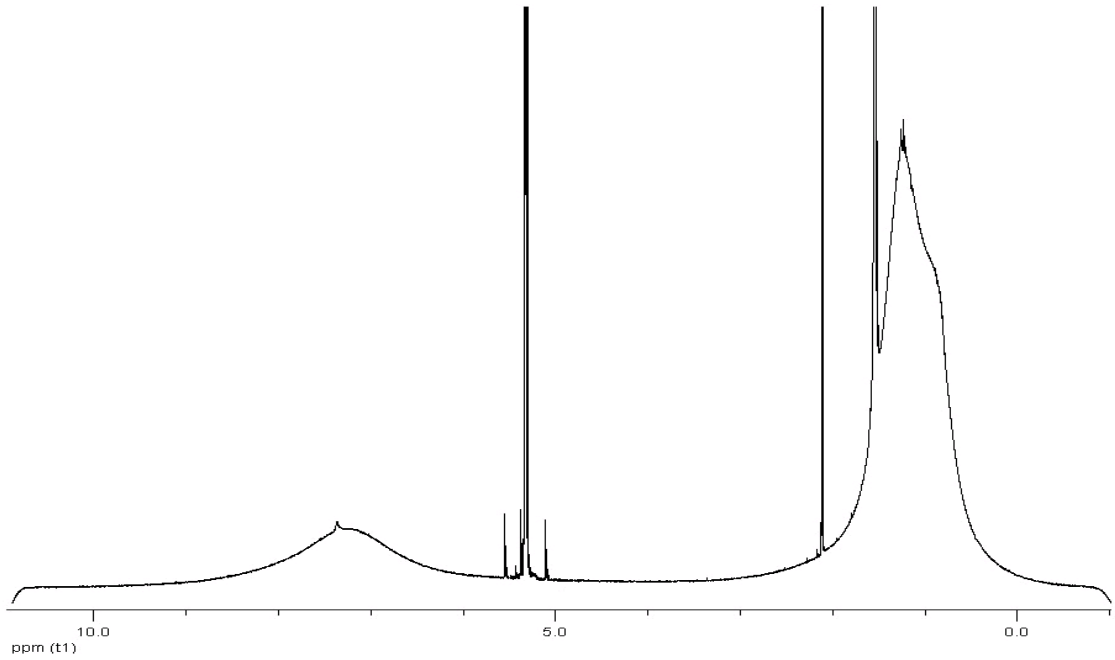


Figure S11e. ^{1}H NMR of striped Au-DPT$_{0.58}$DDT$_{0.42}$

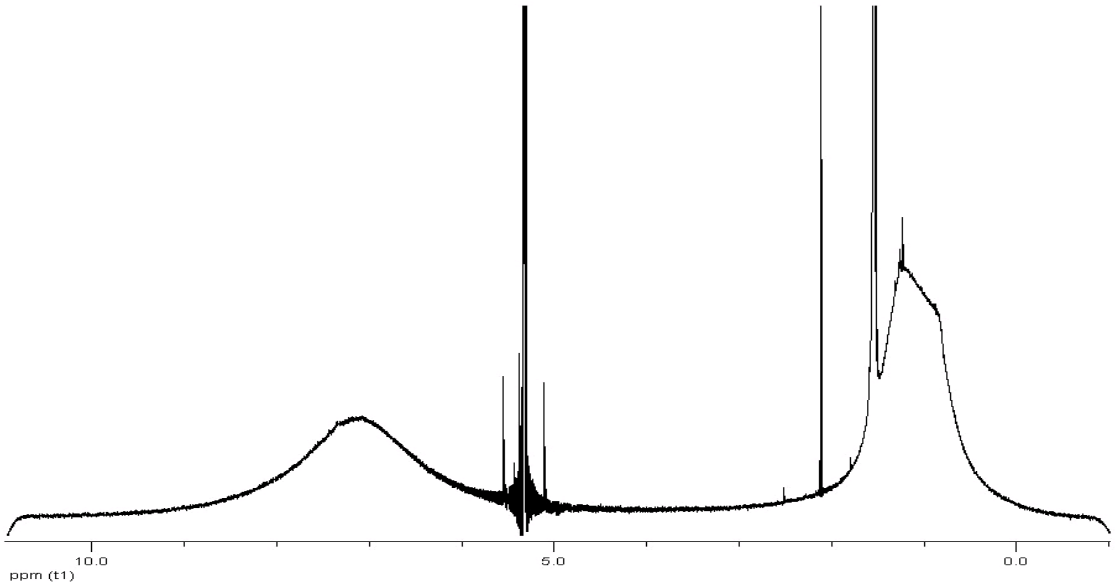


Figure S11f. ^{1}H NMR of striped Au-DPT$_{0.68}$DDT$_{0.32}$

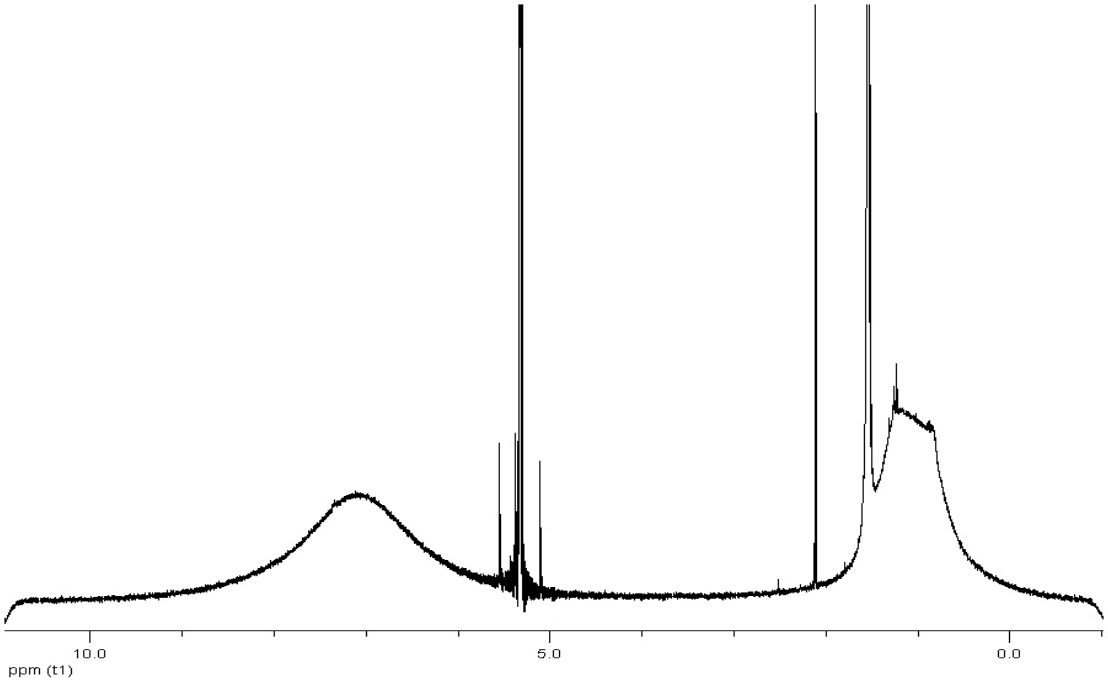


Figure S11g.^{1}H NMR of striped Au-DPT$_{0.78}$DDT$_{0.22}$

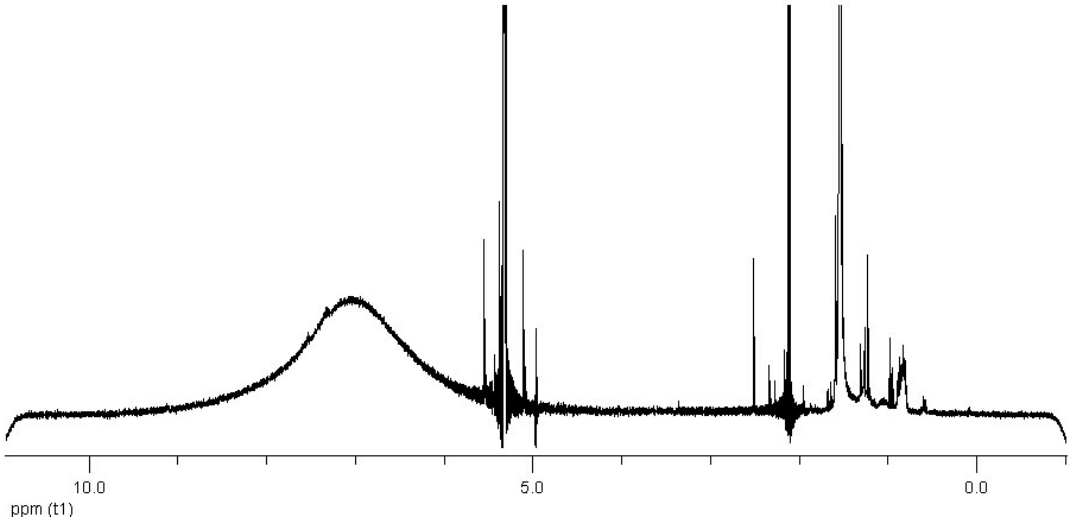


Figure S11h. ^{1}H NMR of ~4 nm Au-DPT

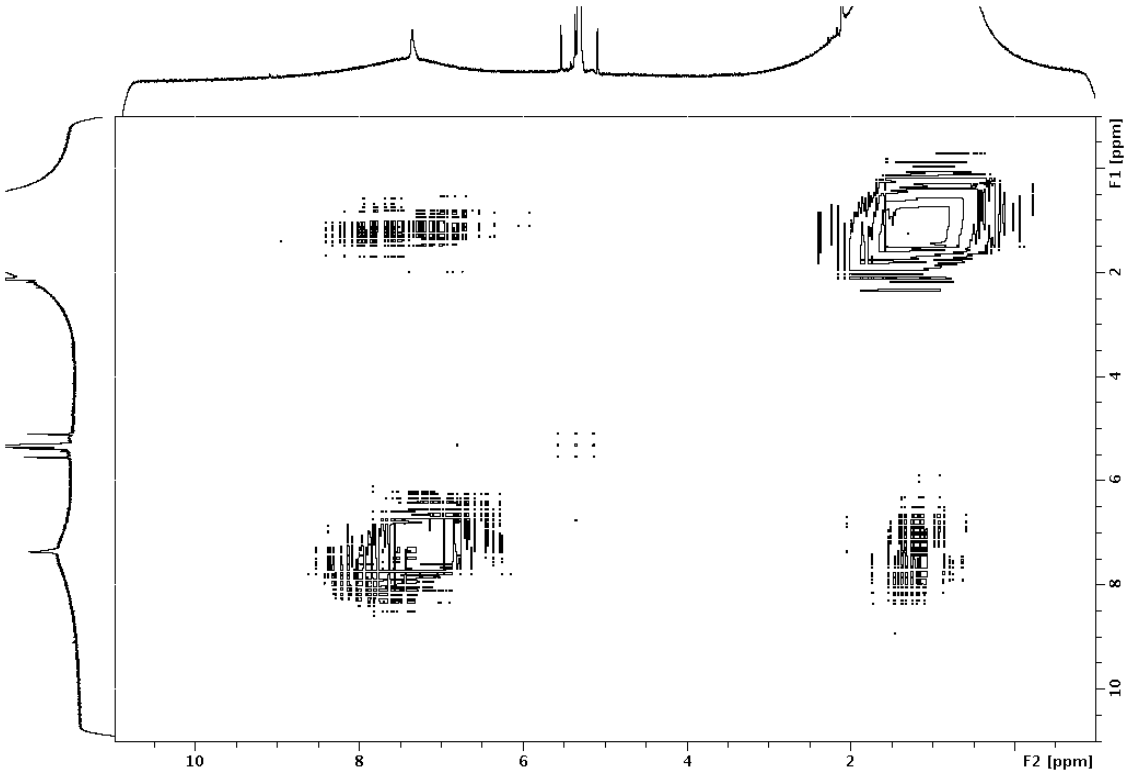


Figure S12a. NOESY of striped Au-DPT$_{0.13}$DDT$_{0.87}$

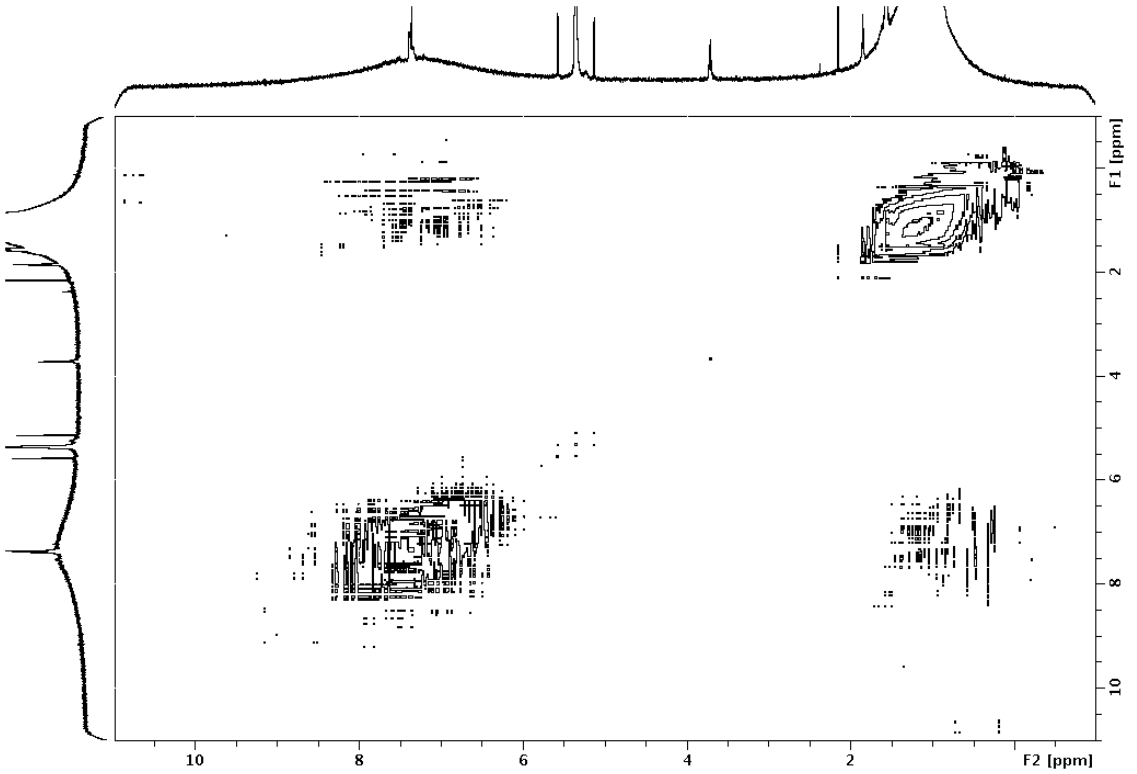


Figure S12b. NOESY of striped Au-$DPT_{0.21}DDT_{0.79}$

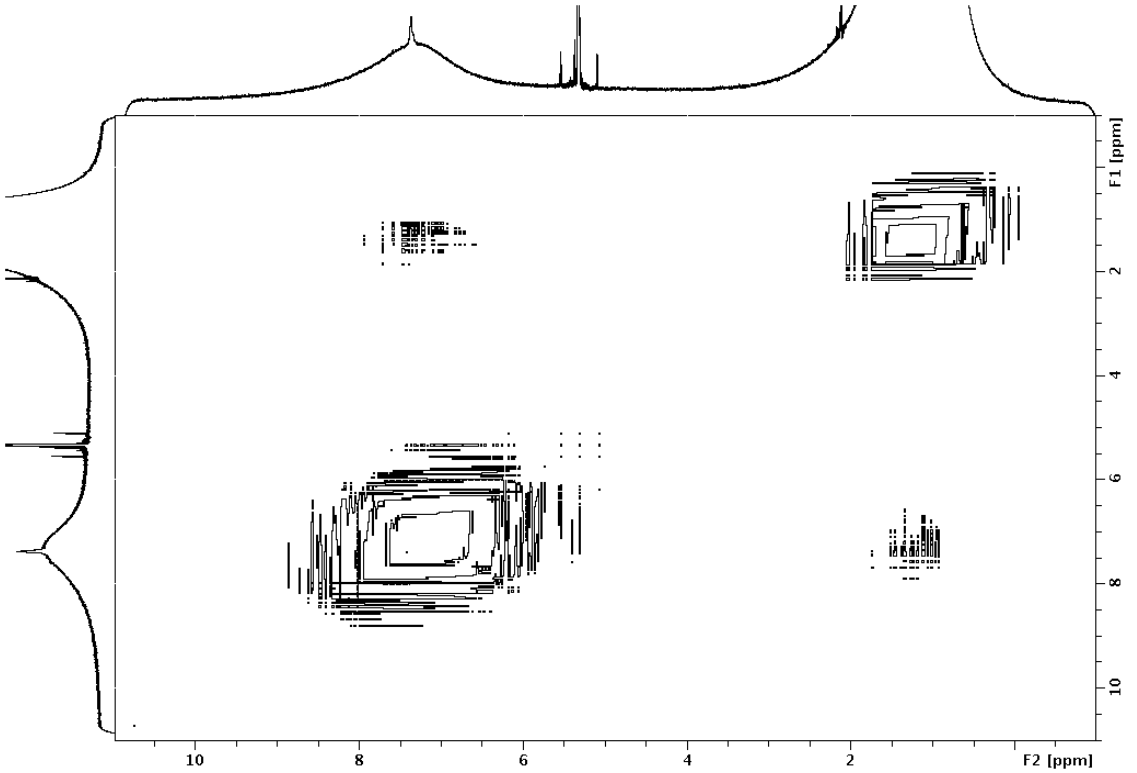


Figure S12c. NOESY of striped Au-$DPT_{0.27}DDT_{0.73}$

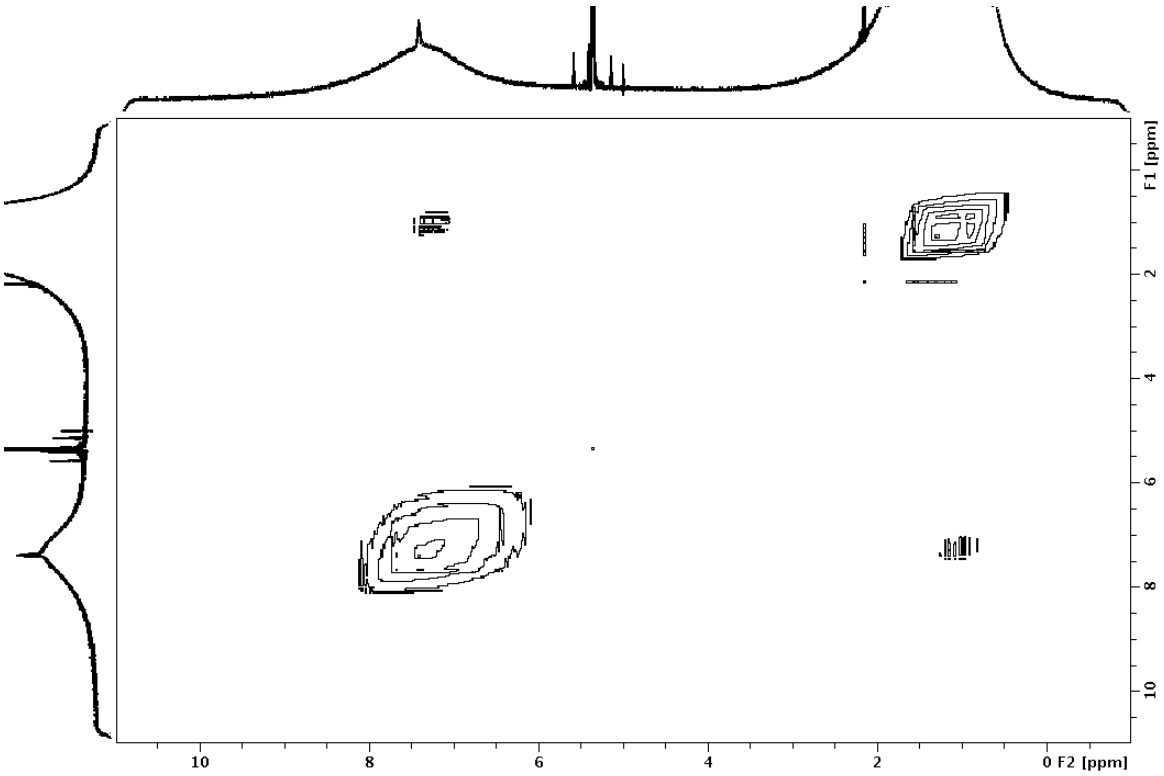


Figure S12d. NOESY of striped Au-$DPT_{0.40}DDT_{0.60}$

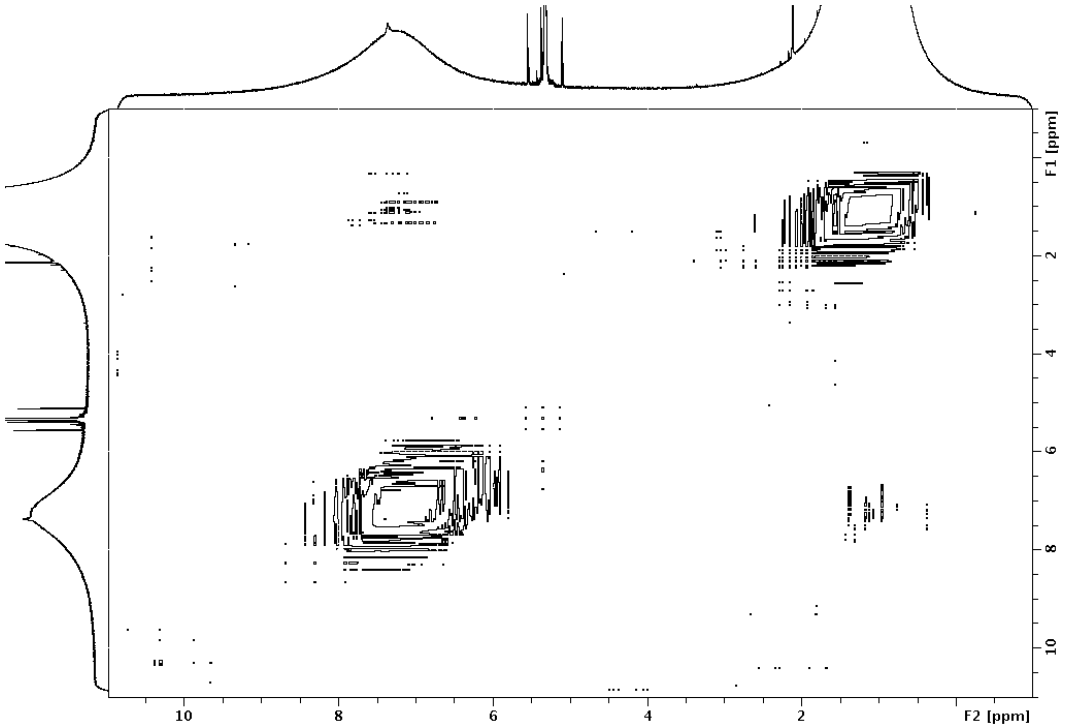


Figure S12e.NOESY of striped Au-$DPT_{0.58}DDT_{0.42}$

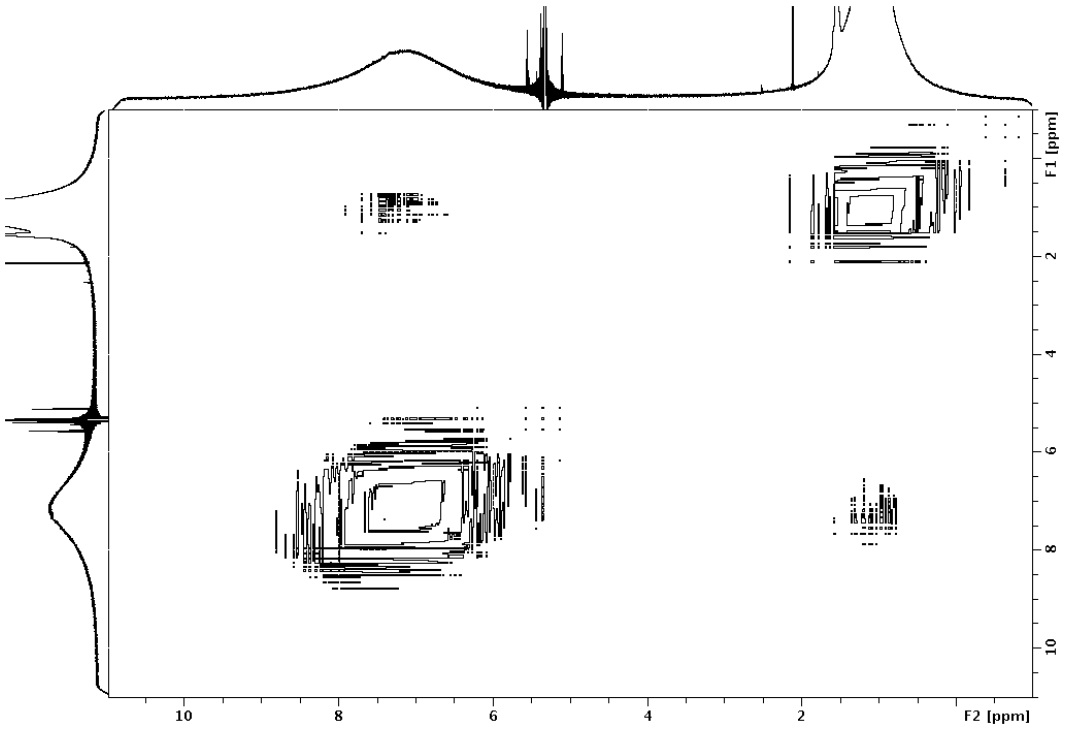


Figure S12f. NOESY of striped Au-$DPT_{0.68}DDT_{0.32}$

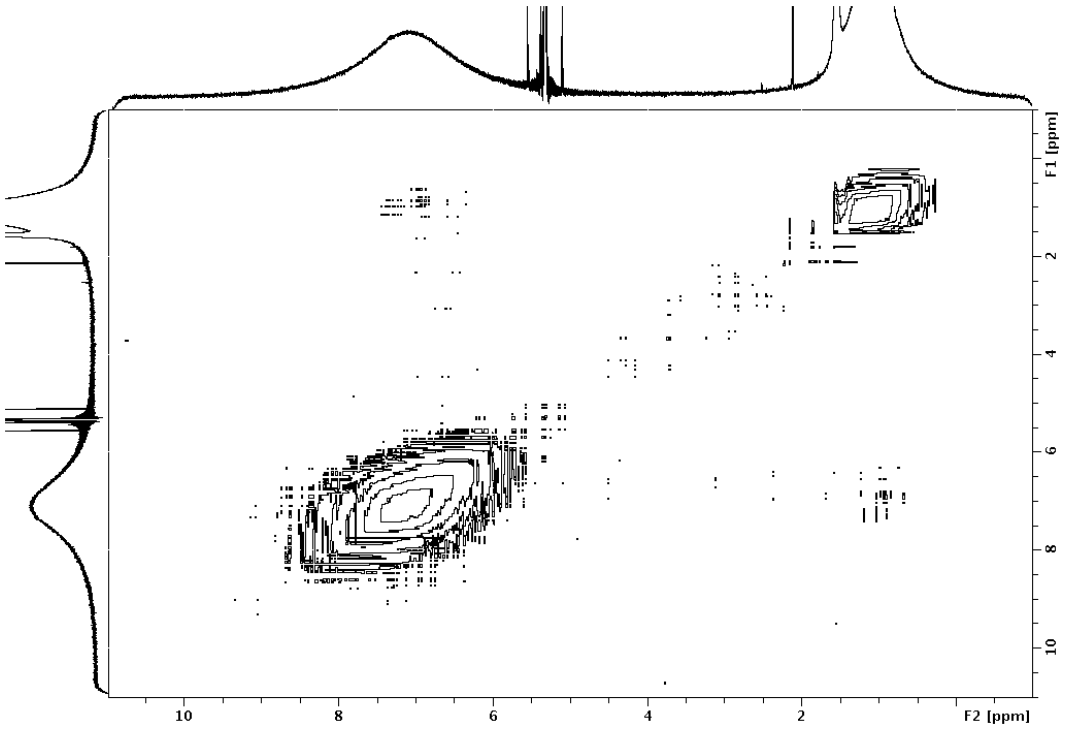


Figure S12g. NOESY of striped Au-$DPT_{0.78}DDT_{0.22}$

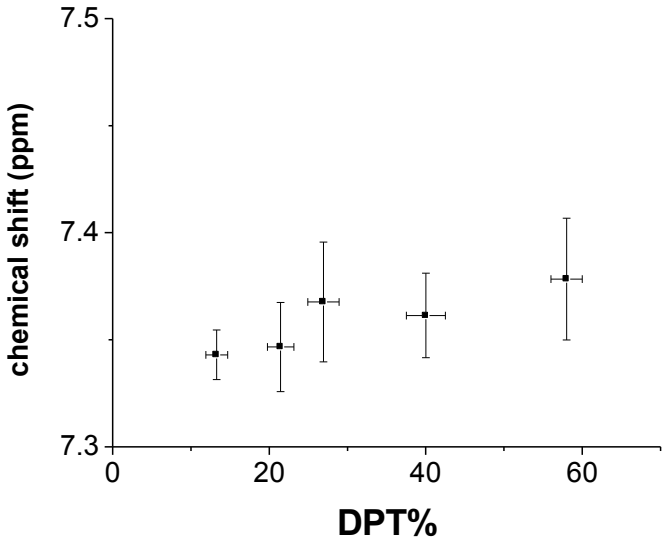
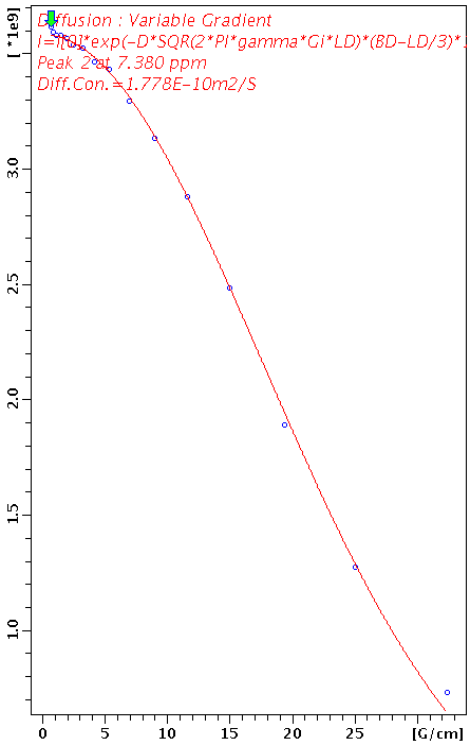
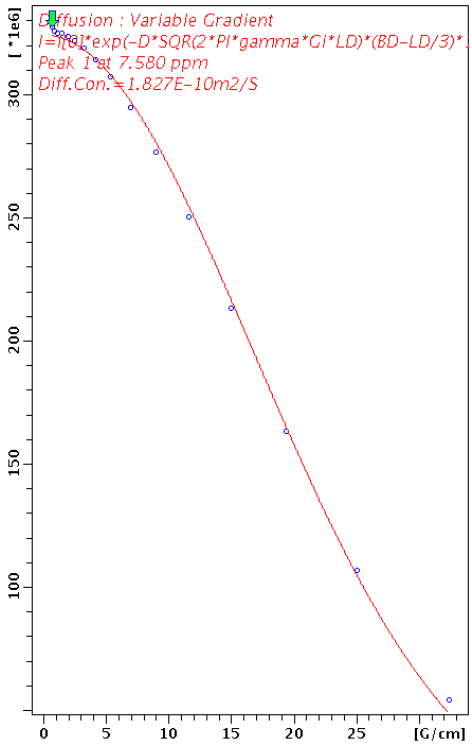


Figure S13. Chemical shift of the sharp peak on striped nanoparticles as a function of DPT%

a.



b.



c.

d.

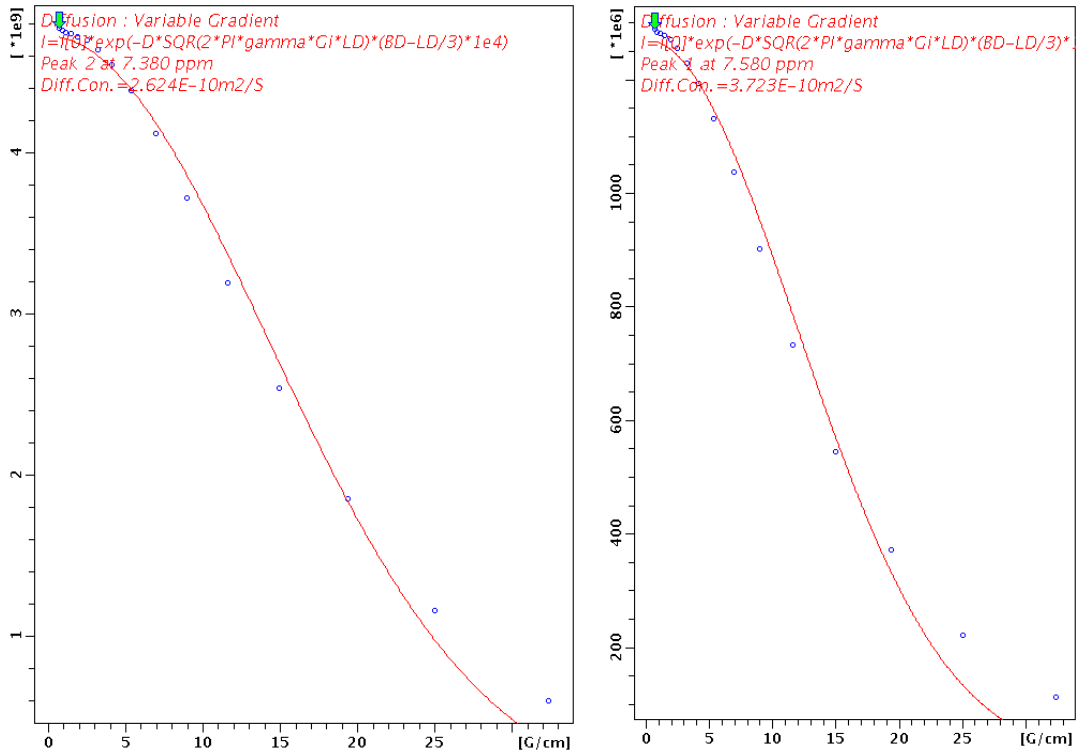


Figure S14. Diffusion coefficient of nanoparticles by DOSY NMR. a: pure nanoparticles at 7.38 ppm. b: pure nanoparticles at 7.58 ppm. c: mixture of nanoparticles and free DPT at 7.38 ppm. d: mixture of nanoparticles and DPT at 7.58 ppm. The ^{1}H NMR spectrum of nanoparticles and DPT mixture is shown in Figure S12d.

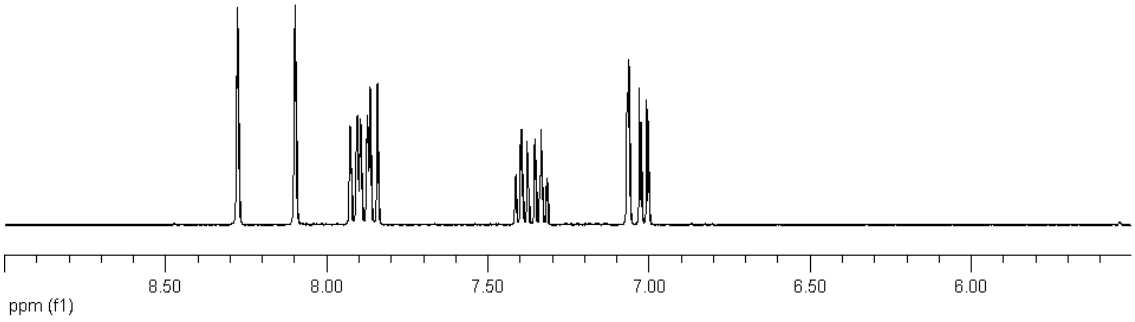


Figure S15. ^{1}H NMR of aminoanthracene (5.5-9 ppm) in CD_2Cl_2

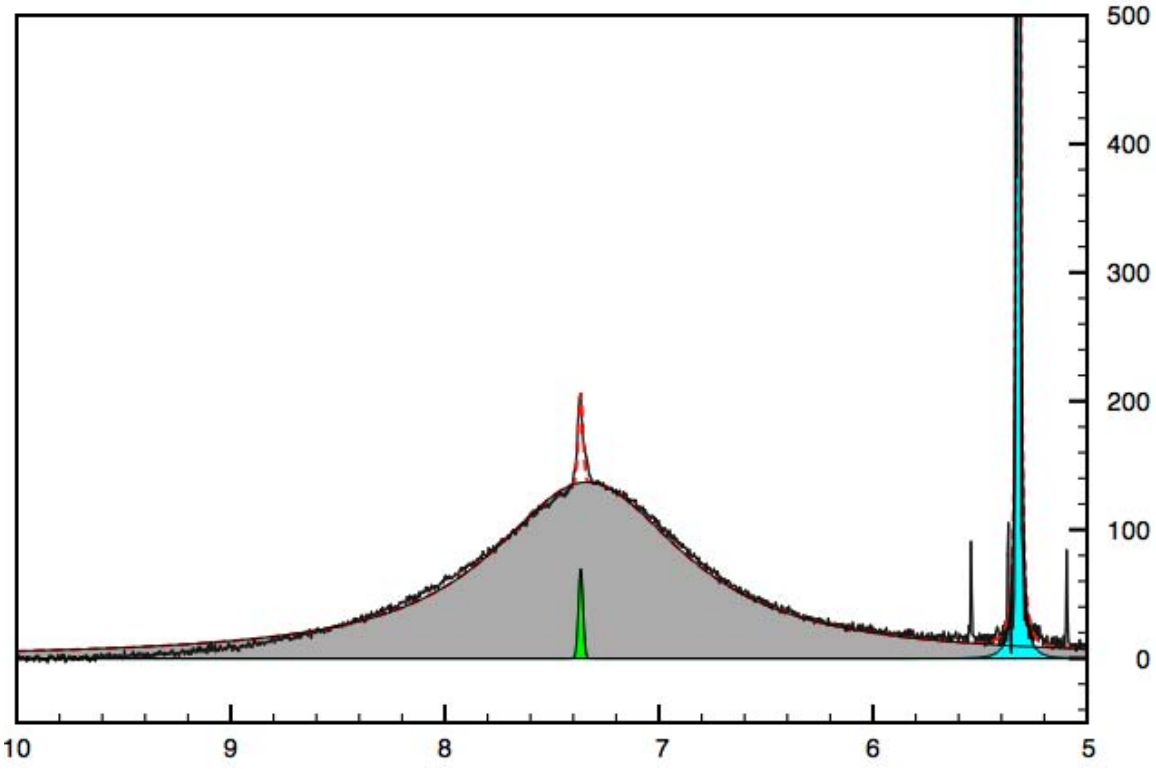


Figure S16. Representative peak deconvolution by Gaussian-Lorentzian fit

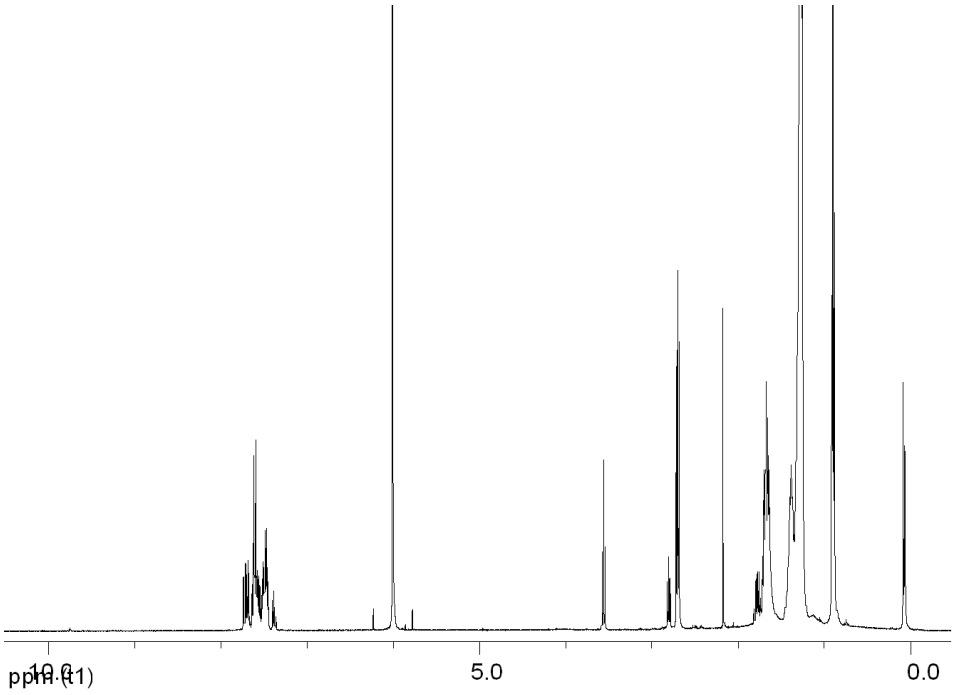


Figure S17. Representative ^{1}H NMR of ligand cleaved from nanoparticle surface by heating in $CDCl_2$-$CDCl_2$ at 75 ^{o}C for a week.

Table S1. Size, ligand composition and chemical shift of the broad aryl peak of random NP

Entry	Diameter (nm)	DPT%	Peak center (ppm)
1a	4.54±0.82	22.2	7.38
1b	4.27±0.88	25.8	7.34
1c	4.32±0.97	20.1	7.355
$1_{average}$		**22.7±2.88**	**7.358±0.020**
2a	4.42±0.70	34.6	7.32
2b	4.56±0.89	35.9	7.3
2c	4.15±0.76	38.5	7.275
$2_{average}$		**36.3±1.99**	**7.298±0.023**
3a	4.17±0.89	45.7	7.275
3b	4.38±0.94	48.6	7.255
3c	4.16±1.02	50.4	7.23
$3_{average}$		**48.2±2.37**	**7.253±0.023**
4a	4.41±1.01	60.3	7.225
4b	4.23±0.79	62.4	7.195
4c	4.20±0.87	58.6	7.25
$4_{average}$		**60.4±1.90**	**7.223±0.027**
5a	4.24±0.69	70.9	7.15
5b	4.25±0.99	74.2	7.135
5c	4.31±0.84	67.2	7.18
$5_{average}$		**70.8±3.50**	**7.155±0.023**
6a	4.14±0.99	82.2	7.15
6b	4.16±0.93	76.3	7.17

6c	4.25±1.01	86	7.10
$6_{average}$		**81.5±4.89**	**7.140±0.036**
7a	4.20±0.96	93.9	7.045
7b	4.09±0.76	91.4	7.055
7c	4.11±0.88	94.9	7.025
$7_{average}$		**93.4±1.80**	**7.042±0.015**
8a	4.02±0.85	100	7.025
8b	4.12±0.93	100	7.00
8c	4.03±0.94	100	6.955
$8_{average}$		**100**	**6.993±0.035**

Table S2. Size, ligand composition and chemical shift of the broad aryl peak of Janus NP

Entry	Diameter (nm)	DPT%	Peak center (ppm)
1a	2.36±0.38	9.8	7.41
1b	2.28±0.37	11.4	7.405
1c	2.44±0.45	13.7	7.375
$1_{average}$		**11.6±1.96**	**7.397±0.019**
2a	2.39±0.32	18.7	7.31
2b	2.42±0.40	21.2	7.305
2c	2.36±0.39	23.5	7.27
$2_{average}$		**21.1±2.40**	**7.295±0.022**
3a	2.55±0.39	27.5	7.21
3b	2.44±0.34	33.1	7.21
3c	2.35±0.36	30.0	7.22
$3_{average}$		**30.2±2.81**	**7.213±0.006**

4a	2.38±0.35	40.7	7.185
4b	2.42±0.41	43.3	7.165
4c	2.29±0.34	45.8	7.14
$4_{average}$		**43.3±2.55**	**7.163±0.023**
5a	2.28±0.36	56.4	7.11
5b	2.52±0.40	56.2	7.135
5c	2.40±0.37	60.8	7.04
$5_{average}$		**57.8±2.60**	**7.095±0.049**
6a	2.30±0.37	70.3	7.085
6b	2.26±0.33	72.9	7.06
6c	2.58±0.54	68.9	7.1
$6_{average}$		**70.7±2.03**	**7.082±0.020**
7a	2.33±0.33	81.9	7.09
7b	2.31±0.35	84.4	7.075
7c	2.29±0.34	85.2	7.055
$7_{average}$		**83.8±1.72**	**7.073±0.176**
8a	2.20±0.37	100	7.06
8b	2.28±0.34	100	7.035
8c	2.33±0.35	100	7.015
$8_{average}$		**100**	**7.034±0.023**

Table S3. Size, ligand composition and chemical shift of the broad aryl peak of Stripe NP

Entry	Diameter (nm)	DPT%	Peak center (ppm)
1a	4.93±0.91	16.6	7.39
1b	5.24±1.02	12.6	7.365

1c	5.32±1.10	11.2	7.35
$1_{average}$		**13.47±2.80**	**7.368±0.020**
2a	4.43±0.86	21.4	7.3
2b	4.87±0.95	22.9	7.31
2c	5.13±1.07	19.8	7.325
$2_{average}$		**21.37±1.55**	**7.312±0.013**
3a	5.30±0.89	27.1	7.33
3b	5.21±0.94	29	7.31
3c	4.95±1.06	24.8	7.325
$3_{average}$		**26.97±2.10**	**7.323±0.010**
4a	5.19±0.91	40.2	7.33
4b	5.06±0.88	43.1	7.30
4c	4.84±0.93	37.7	7.305
$4_{average}$		**40.33±2.70**	**7.311±0.016**
5a	5.05±0.97	57.9	7.33
5b	4.80±0.92	59.6	7.31
5c	4.75±0.87	56.1	7.25
$5_{average}$		**57.87±1.75**	**7.293±0.047**
6a	4.54±1.00	67.6	7.13
6b	4.47±0.84	71.3	7.125
6c	4.39±1.17	66.3	7.21
$6_{average}$		**67.40±2.59**	**7.155±0.048**
7a	4.32±1.21	77.7	7.10
7b	4.26±0.96	80.4	7.085
7c	4.18±0.86	76.2	7.155

$7_{average}$		**78.10±2.12**	**7.113±0.037**
8a	4.02±0.85	100	7.025
8b	4.12±0.93	100	7.00
8c	4.03±0.94	100	6.955
$8_{average}$		**100**	**6.993±0.035**

Table S4. Ligand composition and FWHM of broad peak (b.p) and sharp peak (s.p.) of Stripe NP

Entry	DPT%	FWHM (b.p.)	FWHM (s.p.)
$1_{average}$	13.47±2.80	1.14±0.23	0.054±0.002
$2_{average}$	21.37±1.55	1.21±0.12	0.052±0.005
$3_{average}$	26.97±2.10	1.13±0.19	0.047±0.009
$4_{average}$	40.33±2.70	1.19±0.18	0.045±0.014
$5_{average}$	57.87±1.75	1.19±0.13	No peak
$6_{average}$	67.40±2.59	1.23±0.11	No peak
$7_{average}$	78.10±2.12	1.22±0.07	No peak
$8_{average}$	100	1.15±0.12	No peak