## QCM Detection of Molecule-Nanoparticle Interactions for Ligand Shells of Varying Morphology

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## **Supplementary Information**



**Figure S1.** PFOT ligand synthesis route including complete deprotection of the thiol just prior to use (top) as well as <sup>1</sup>H NMR confirmation of product (bottom).



**Figure S2.** Ligand surface density calculations were performed using the (a) absorbance of the NPs at 508 nm and (b) the ratio of the proton integrations of the DT or PFOT ligands and the reference standard at 7.14 ppm. Data are presented from the 0F NP sample.



**Figure S3.** Representative <sup>19</sup>F NMR spectra for the NP series showing data from sample 73F NP. The chemical shift was tracked to determine the morphology.

SAXS measurements were taken immediately after cleaning most NP batches to show size control throughout the exchange reaction. Some were measured after 8 months of storage and exhibited growth that was apparent in both the visual color and the resulting SAXS data, likely due to aggregation. Freshly made samples were prepared to demonstrate relatively constant NP dimensions with ligand exchange (Table S1).

PFOT in Ligand Shell (%)	Mean NP Diameter $(nm)^{\dagger}$
Am. NP	1.8
0	1.7
25	1.8
50	2.0
65	2.0
75	2.0
90	2.1
100	2.0
20 <sup>‡</sup>	3.0
31 <sup>‡</sup>	4.5
39 <sup>‡*</sup>	-
52 <sup>‡</sup>	2.0
59 <sup>‡</sup>	4.8
73 <sup>‡</sup>	2.1
93 <sup>‡</sup>	2.2

**Table S1.** NP Dimensions from SAXS analysis by fitting a polydisperse hard sphere form factor model.

<sup>†</sup> Fitted using a Gaussian distribution of hard spheres with a standard deviation of 25%. <sup>‡</sup>Measured after 8 months of storage as a powder.

<sup>\*</sup>NPs were not dispersible for SAXS measurement after extended storage.

NP	Exchange Solution	Ligand Shell	NP Concentration	Ligand	Ligand Surface
Batch	Composition (mol%	Composition	UV-Vis (Mx10 <sup>-6</sup> )	Concentration NMR	Density, σ
	PFOT)	(mol% PFOT)		(Mx10 <sup>-4</sup> )	(#/nm²)
OF	0	0	2.6	1.2	5.2
20F	25	20	0.92	0.45	1.2
31F	40	31	2.8	3.7	3.7
39F	30	39	1.9	0.92	1.5
52F	45	52	2.3	0.59	1.0
59F	50	59	2.1	0.41	1.2
73F	75	73	1.4	0.19	2.5
93F	80	93	1.5	0.22	4.0
100F	98	100	1.7	3.7	4.1

Table S2. Ligand shell compositions and surface densities for mixed ligand nanoparticles

 Table S3.
 <sup>19</sup>F NMR shift results for the -CF3 and 7th CF2 unit of the PFOT ligand.

	CF₃ Shift (ppm)	7 <sup>th</sup> CF <sub>2</sub> (ppm)
NP Batch		
OF	-	-
20F	-82.00	-126.78
31F	-82.07	-127.05
39F	-82.09	-127.08
52F	-82.32	-127.18
59F	-82.33	-127.20
73F	-82.59	-127.25
93F	-82.52	-127.54
100F	-82.54	-127.54

Table S4. Mass of the NP films and the molecule uptake measured for each benzene derivative.

	Film Mass (g/cm <sup>2</sup> )	Estimated Film	Ben. (g/cm <sup>2</sup> )	Difluoro. (g/cm <sup>2</sup> )	Trifluoro. (g/cm <sup>2</sup> )	Tetrafluoro. (g/cm <sup>2</sup> )	Hexafluoro. (g/cm <sup>2</sup> )
	(8,)	Thickness (nm)*	(8,)	(8, )	(8,)	(8) /	(8) /
0F	2.396E-06	24	3.636E-07	4.380E-07	4.485E-07	4.142E-07	4.399E-07
20F	1.268E-06	13	3.554E-07	4.194E-07	4.338E-07	3.742E-07	4.378E-07
31F	4.486E-06	45	1.216E-06	1.079E-06	1.089E-06	8.552E-07	7.904E-07
39F	5.308E-06	53	5.360E-07	6.497E-07	6.970E-07	6.220E-07	7.192E-07
52F	2.534E-06	25	3.178E-07	3.993E-07	4.422E-07	3.801E-07	4.709E-07
59F	4.566E-06	46	4.994E-07	6.439E-07	6.880E-07	6.282E-07	7.155E-07
73F	3.002E-06	30	7.049E-07	7.887E-07	7.683E-07	8.876E-07	8.446E-07
93F	2.322E-06	23	4.537E-07	5.637E-07	6.075E-07	5.320E-07	5.789E-07
100F	4.387E-06	44	5.057E-07	6.450E-07	8.067E-07	7.587E-07	9.451E-07

\*Film thickness was crudely estimated using a nominal density of 1 g/cm<sup>3</sup>, typical for organic components

Number           1         0.1145           2         0.1023           Mean and         0.1084±0.0087 (8.01%)           Stdev         0.1084±0.0087 (8.01%)           43F NP: Hexafluorobenzene         Run         Relative Uptake Value (gsolvent/gnim)           Number         1         0.00460096           2         0.004770584         3           3         0.004562336         3           Mean and         0.0046±.0001 (2.39%)         5           Stdev         8         8           43F NP: Trifluorobenzene         Run         Relative Uptake Value (gsolvent/gnim)           Number         1         0.001988694           1         0.0019880374         3           3         0.001713936         3           62F NP: Trifluorobenzene         Run         Relative Uptake Value (gsolvent/gnim)           Number         1         0.003707888           62F NP: Hexafluorobenzene         Run         Nean and           Number         3         0.004466173           1         0.003707888         3           G2F NP: Trifluorobenzene         Mean and         .0042±.0005 (10.59%)           Stdev         1         0.005474842		Run	Relative Optake Value (Bsolvent/Bfilm)
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Mean and Stdev        0019±0002 (7.47%)           62F NP: Hexafluorobenzene         Run Number         Relative Uptake Value (g <sub>solvent</sub> /g <sub>film</sub> )           Number         1         0.003707888           2         0.004466173         0.004498251           Mean and         .0042±.0005 (10.59%)         Stdev           62F NP: Trifluorobenzene         Run Number         Relative Uptake Value (g <sub>solvent</sub> /g <sub>film</sub> )           62F NP: Trifluorobenzene         Run Number         0.005478482           1         0.005274893         3           3         0.005126597         Mean and           3         0.0053±.0002 (3.34%)         Stdev		3	0.001713936
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1         0.003707888           2         0.004466173           3         0.004498251           Mean and Stdev         .0042±.0005 (10.59%)           62F NP: Trifluorobenzene         Run Number           1         0.005478482           2         0.005274893           3         0.005126597           Mean and Stdev         .0053±.0002 (3.34%)		Number	
2         0.004466173           3         0.004498251           Mean and         .0042±.0005 (10.59%)           Stdev		1	0.003707888
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Mean and Stdev         .0042±.0005 (10.59%)           62F NP: Trifluorobenzene         Run Number         Relative Uptake Value (g <sub>solvent</sub> /g <sub>film</sub> )           1         0.005478482           2         0.005274893           3         0.005126597           Mean and Stdev         .0053±.0002 (3.34%)           Stdev         .0053±.0002 (3.4%)		3	0.004498251
Stdev           62F NP: Trifluorobenzene         Run Number         Relative Uptake Value (g <sub>solvent</sub> /g <sub>film</sub> )           1         0.005478482           2         0.005274893           3         0.005126597           Mean and Stdev         .0053±.0002 (3.34%)		Mean and	.0042±.0005 (10.59%)
62F NP: Trifluorobenzene         Run Number         Relative Uptake Value (g <sub>solvent</sub> /g <sub>film</sub> )           1         0.005478482           2         0.005274893           3         0.005126597           Mean and         .0053±.0002 (3.34%)           Stdev		Stdev	
Number           1         0.005478482           2         0.005274893           3         0.005126597           Mean and         .0053±.0002 (3.34%)           Stdev	62F NP: Trifluorobenzene	Run	Relative Uptake Value (g <sub>solvent</sub> /g <sub>film</sub> )
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2         0.005274893           3         0.005126597           Mean and Stdev         .0053±.0002 (3.34%)		1	0.005478482
3         0.005126597           Mean and         .0053±.0002 (3.34%)           Stdev		2	0.005274893
Mean and .0053±.0002 (3.34%) Stdev		3	0.005126597
Stdev		Mean and	.0053±.0002 (3.34%)
		Stdev	

Table S5. Data from repeated measurements of molecule vapor uptake into NP films, including statistical variation.OF NP: HexafluorobenzeneRunRelative Uptake Value (g<sub>solvent</sub>/g<sub>film</sub>)



**Figure S4.** QCM measurement of a series of molecule vapors using 20F NPs, the asterisk corresponds to a gas line disruption during the experiment.



Figure S5. QCM measurement of a series of molecule vapors using 31F NPs.



Figure S6. QCM measurement of a series of molecule vapors using 39F NPs.



Figure S7. QCM measurement of a series of molecule vapors using 52F NPs.



Figure S8. QCM measurement of a series of molecule vapors using 59F NPs.



Figure S9. QCM measurement of a series of molecule vapors using 73F NPs.



Figure S10. QCM measurement of a series of molecule vapors using 93F NPs.



**Figure S11.** QCM measurement of a series of molecule vapors using 100F NPs. The asterisk corresponds to a gas line disruption during the experiment.



**Figure S12.** SAXS data from different NP batches measured immediately after synthesis. Data fits (solid lines) were calculated using a Gaussian distribution of hard spheres.