Electronic Supplementary Material (ESI) for Journal of Materials Chemistry
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Electronic Supplemental Information (ESI):

Tuning the Miscibility of Gold Nanoparticles Dispersed in Liquid Crystals via the Thiol-for-DMAP Reaction

Jonathan Milette[a], Violeta Toader[a], Linda Reven*[a], and R. Bruce Lennox *[a]

[a] *Department of Chemistry and the FQRNT Centre for Self-Assembled Chemical Structures (CSACS), McGill University, 801 Sherbrooke St. West, Montreal, QC, Canada H3A 2K6 Emails: bruce.lennox@mcgill.ca, linda.reven@mcgill.ca*

I. NMR Characterization of the 4'-(n-mercaptoalkyloxy)biphenyl-4-carbonitrile derivatives

4'-(8-bromooctyloxy)biphenyl-4-carbonitrile (2a) (n=8) (light yellow needle like crystals, η=0.75)

^{1}H-NMR (300MHz, $CDCl_3$) δ(ppm): 7.69 (d, 2H, J=8.4, $H_{aromatic}$ *ortho* to CN), 7.64 (d, 2H, J=9.0, $H_{aromatic}$ *meta* to CN), 7.56 (d, 2H, J=8.7, $H_{aromatic}$ *meta* to OCH_2~), 7.00 (d, 2H, J=8.7, $H_{aromatic}$ *ortho* to OCH_2~), 4.01 (t, 2H, J=6.4, PhO*CH_2*CH_2~), 3.42 (t, 2H, J=6.75, ~CH_2*CH_2*Br), 1.852 (m, 4H, PhOCH_2*CH_2*~ and ~*CH_2*CH_2Br), 1.55-1.3 (m, 8H, ~(*CH_2*)$_4$$CH_2CH_2$Br).

^{13}C-NMR (75 MHz, $CDCl_3$) δ(ppm): 159.99, 145.49, 132.77, 131.51, 128.54, 127.28, 119.31, 115.30, 110.27, 68.30, 34.16, 32.97, 29.37, 28.88, 28.29, 26.15.

4'-(12-bromododecyloxy)biphenyl-4-carbonitrile (2b) (n=12) (white crystals, η=0.83)

^{1}H-NMR (300MHz, $CDCl_3$) δ(ppm): 7.70 (d, 2H, J=9.0, $H_{aromatic}$ *ortho* to CN), 7.64 (d, 2H, J=8.4, $H_{aromatic}$ *meta* to CN), 7.53 (d, 2H, J=8.7, $H_{aromatic}$ *meta* to OCH_2~), 7.00 (d, 2H, J=8.7, $H_{aromatic}$ *ortho* to OCH_2~), 4.01 (t, 2H, J=6.6, PhO*CH_2*CH_2~), 3.41 (t, 2H, J=6.9, ~CH_2*CH_2*Br), 1.82 (m, 4H, PhOCH_2*CH_2*~ and ~*CH_2*CH_2Br), 1.55-1.3 (m, 16H, ~(*CH_2*)$_8$$CH_2CH_2$Br).

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^{13}C-NMR (75 MHz, $CDCl_3$) δ(ppm): 159.98, 145.45, 132.75, 131.40, 128.54, 128.45, 127.24, 119.32, 115.21, 110.19, 68.33, 34.29, 33.00, 29.71, 29.61, 29.56, 29.40, 28.95, 28.35, 26.21.

4'-(16-bromohexadecyloxy)biphenyl-4-carbonitrile (2b) (n=16) (white crystals, η=0.68)

^{1}H-NMR (300MHz, $CDCl_3$) δ(ppm): 7.70 (d, 2H, J=8.1, $H_{aromatic}$ *ortho* to CN), 7.64 (d, 2H, J=8.4, $H_{aromatic}$ *meta* to CN), 7.53 (d, 2H, J=8.7, $H_{aromatic}$ *meta* to OCH_2~), 6.99 (d, 2H, J=8.7, $H_{aromatic}$ *ortho* to OCH_2~), 4.01 (t, 2H, J=6.45, PhO*CH_2*CH_2~), 3.41 (t, 2H, J=6.75, ~CH_2*CH_2*Br), 1.83 (m, 4H, PhOCH_2*CH_2*~ and ~*CH_2*CH_2Br), 1.50-1.2 (m, 24H, ~(*CH_2*)$_{12}$$CH_2CH_2$Br).

^{13}C-NMR (75 MHz, $CDCl_3$) δ(ppm): 159.99, 145.49, 132.78, 131.43, 128.53, 127.27, 119.36, 115.27, 110.20, 68.37, 34.53, 33.04, 29.87, 29.83, 29.76, 29.65, 29.61, 29.43, 28.98, 28.39, 26.24.

4'-(8-mercaptooctyloxy)biphenyl-4-carbonitrile

^{1}H-NMR (300MHz, $CDCl_3$) δ(ppm): 7.70 (d, 2H, J=, $H_{aromatic}$ *ortho* to CN), 7.64 (d, 2H, J=, $H_{aromatic}$ *meta* to CN), 7.53 (d, 2H, J=8.7, $H_{aromatic}$ *meta* to OCH_2~), 7.00 (d, 2H, J=, $H_{aromatic}$ *ortho* to OCH_2~), 4.01 (t, 2H, J=6.45, PhO*CH_2*CH_2~), 2.53(q, 2H, J=7.3, ~CH_2*CH_2*SH), 1.812 (m, 2H, PhOCH_2*CH_2*~), 1.63 (m, 2H, ~*CH_2*CH_2SH), 1.4-1.7 (m, 8H, ~(*CH_2*)$_4$$CH_2CH_2$SH), 1.339 (t, 1H, J=7.5, ~CH_2CH_2S*H*).

^{13}C-NMR (75 MHz, $CDCl_3$) δ(ppm): 159.95, 145.47, 132.77, 131.46, 128.52, 127.27, 119.35, 115.25, 110.21, 68.28, 34.18, 29.44, 29.38, 29.19, 28.48, 26.17, 24.85.

4'-(12-mercaptododecyloxy)biphenyl-4-carbonitrile (5b) (n=12)(CBO$(CH_2)_{12}$SH) (white powder, η=0.52 after purification by column chromatography (SiO_2, 1:1 dichloromethane-hexanes, R_f=0.48)

^{1}H-NMR (300MHz, $CDCl_3$) δ(ppm): 7.71(d, 2H, J=8.4, $H_{aromatic}$ *ortho* to CN), 7.65 (d, 2H, J=8.7, $H_{aromatic}$ *meta* to CN), 7.53 (d, 2H, J=8.7, $H_{aromatic}$ *meta* to OCH_2~), 6.99 (d, 2H, J=9.0, $H_{aromatic}$ *ortho* to OCH_2~), 4.01 (t, 2H, J=6.6, PhO*CH_2*CH_2~), 2.53 (q, 2H, J=7.3, ~CH_2*CH_2*SH), 1.81 (m, 2H,

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PhOCH$_2$*CH$_2$*~), 1.61 (m, 2H, ~*CH$_2$*CH$_2$SH), 1.34 (t, 1H, J=7.8 ~CH$_2$CH$_2$S*H*), 1.55-1.25 (m, 16H, ~(*CH$_2$)$_8$*CH$_2$CH$_2$SH).

^{13}C-NMR (75 MHz, $CDCl_3$) δ(ppm): 159.96, 145.45, 132.75, 131.39, 128.47, 127.24, 119.33, 115.23, 110.17, 68.33, 34.23, 29.74, 29.69, 29.57, 29.39, 29.25, 28.56, 26.21, 24.85.

4'-(16-mercaptohexadecyloxy)biphenyl-4-carbonitrile (5c) (n=16) (CBO(CH$_2$)$_{16}$SH) (waxy white solid, η=0.99)

^{1}H-NMR (300MHz, $CDCl_3$) δ(ppm): 7.70 (d, 2H, J=8.1, H$_{aromatic}$ *ortho* to CN), 7.64 (d, 2H, J=8.7, H$_{aromatic}$ *meta* to CN), 7.53 (d, 2H, J=9.0, H$_{aromatic}$ *meta* to OCH$_2$~), 6.99 (d, 2H, J=8.7, H$_{aromatic}$ *ortho* to OCH$_2$~), 4.01 (t, 2H, J=6.6, PhO*CH$_2$*CH$_2$~), 2.53 (q, 2H, J=7.4, ~CH$_2$*CH$_2$*SH), 1.81 (m, 2H, PhOCH$_2$*CH$_2$*~), 1.61 (m, 2H, ~*CH$_2$*CH$_2$SH), 1.34 (t, 1H, J=7.8 ~CH$_2$CH$_2$S*H*), 1.55-1.25 (m, 24H, ~(*CH$_2$)$_{12}$*CH$_2$CH$_2$SH).

^{13}C-NMR (75 MHz, $CDCl_3$) δ(ppm): 160.0, 145.47, 132.75, 131.41, 128.50, 127.25, 119.32, 115.27, 110.20, 68.37, 34.24, 29.85, 29.79, 29.71, 29.59, 29.41, 29.27, 28.57, 26.23, 24.86.

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III. Reaction conditions and Resulting AuNP Ligand Compositions

TABLE S1. Reaction conditions used for the preparation of Au nanoparticles.

#	$CH_3(CH_2)_mSH$			$CBO(CH_2)_nSH$			Total	Mixing
	m	**%**	**mM**	**n**	**%**	**mM**	**mM**	
I	-	0	0	8	100	0.60	0.60	Dropwise
II	-	0	0	12	100	0.60	0.60	Dropwise
III	-	0	0	16	100	0.60	0.60	Dropwise
IV	5	80	2.46	12	20	0.54	3.00	Dropwise
V	5	50	0.30	12	50	0.30	0.60	Direct
VI	5	67	0.40	12	33	0.20	0.60	Direct
VII	5	83	0.50	12	17	0.10	0.60	Direct
VIII	5	100	0.60	-	0	0	0.60	Direct
IX	11	100	0.60	-	0	0	0.60	Direct

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TABLE S2. Gold nanoparticle characterization.

#	$CBO(CH_2)_nSH$			λ_{max} [b] (nm)	Size [c] (nm)	TGA (%)		Footprint ($Å^2$) [d]	
	n	Reaction mixture (%)	LC thiol coverage (%) [a]			Org.	Gold	Sphere	Truncated octahedron
I	8	100	100	543	4.5±0.8	17.2	82.8	18.6	23.3
II	12	100	100	540	4.7±0.9	17.4	82.6	20.6	25.7
III	16	100	100	534	4.7±0.8	20.5	79.5	19.2	23.9
IV	12	20	87 [e]	535	4.5±0.9	16.5	83.5	20.8	26.0
V	12	50	70 [e]	528	4.6±0.8	15.5	84.5	19.0	23.8
VI	12	33	49 [e]	519	4.7±0.9	11.9	88.1	20.6	25.7

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VII	12	17	28 [e]	523	4.7±0.8	9.8	90.2	19.7	24.6
VIII	**$CH_3(CH_2)_5SH$**			509	4.5±0.7	7.0	93.0	17.9	22.3
IX	**$CH_3(CH_2)_{11}SH$**			515	4.5±0.8	12.1	87.9	16.8	20.9

[a] Calculated from ^{1}H-NMR data; % of total thiol.
[b] Solvents: acetonitrile (I-III), acetonitrile:tetrahydrofurane 1:1 (IV) and chloroform (V-IX).
[c] Mean diameter metal core size obtained by TEM analysis.
[d] Calculation of the surface area at the Au core for the case of a spherical geometry or the more realistic truncated octahedron are assumed.
[e] Outcome represents the average of 2 or more experiments. The range is < 4% in each case.

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III. Characterization of sample VI

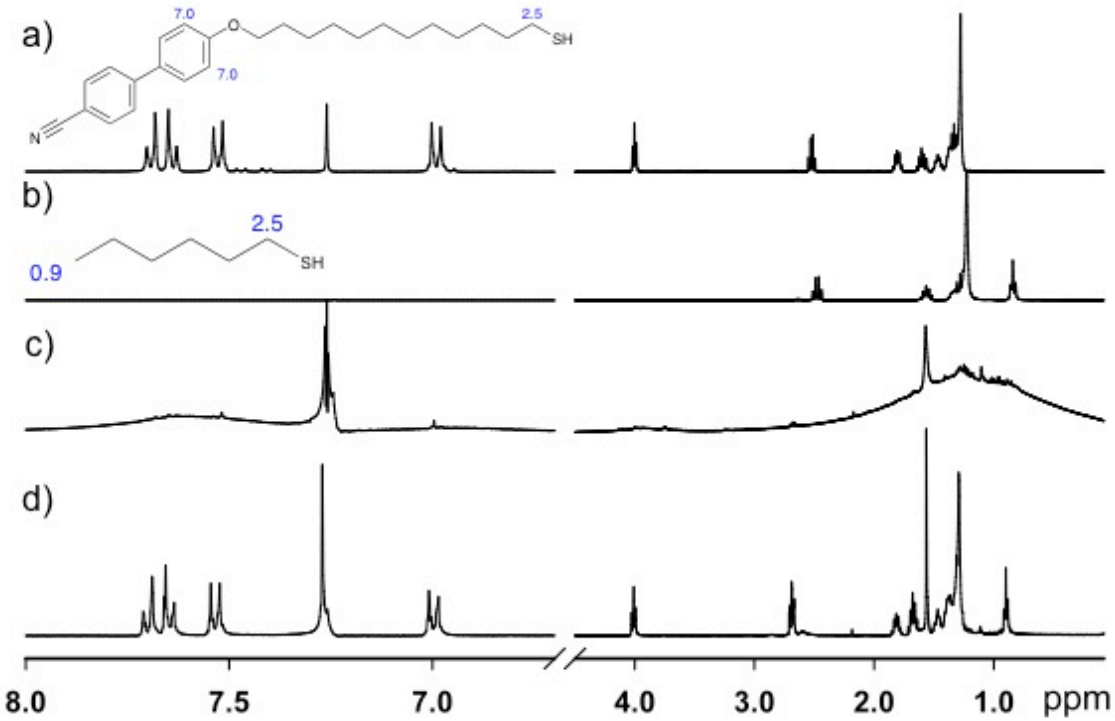

Fig. S1 Liquid state NMR spectra of (a) $CBO(CH_2)_{12}SH$, (b) $\mathbf{CH_3(CH_2)_5SH}$ and sample VI (c) before and (d) after the iodine reaction.

5

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Thermogravimetric Analysis (TGA)

Experiments were performed on a TA Instruments Q500 model with two mass flow controllers. 5-10 mg of accurately weighed samples were studied at 20°C/min under nitrogen (60mL/min) from room temperature to 100°C (standby for 5min) and 550°C, then switched to air (60mL/min), and studied up to 700°C.

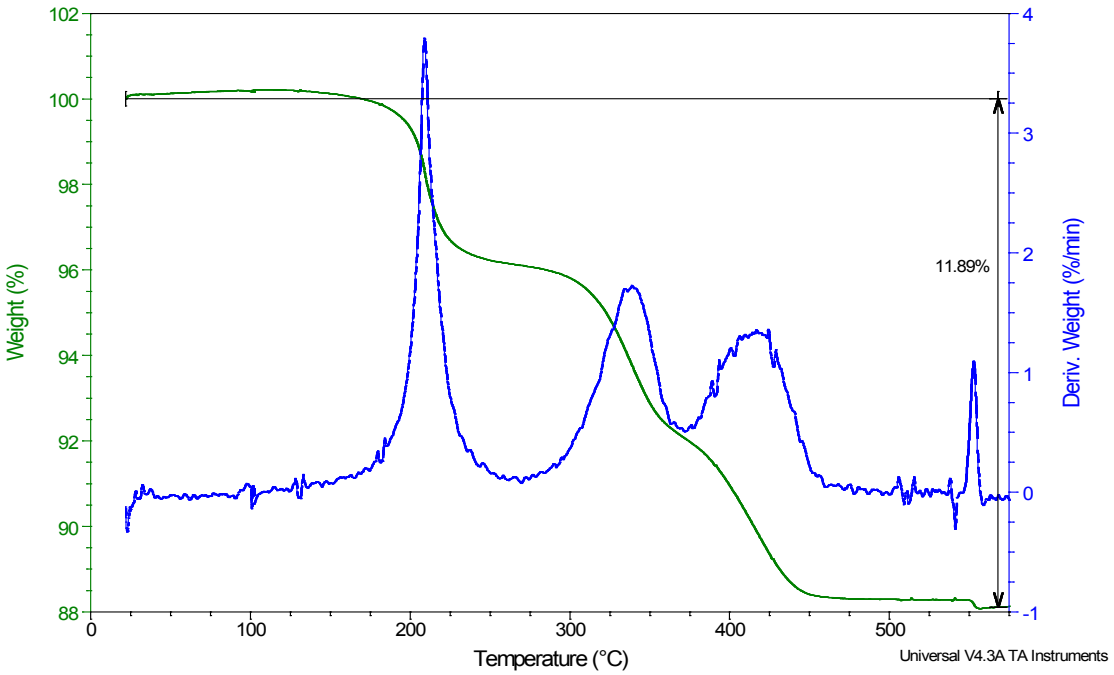

Fig. S2 TGA spectrum of sample VI.

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Differential Scanning Calorimetry (DSC)

Experiments were performed on a DSC Q1000 machine from TA Instruments. Samples (5-10 mg) in sealed aluminum- or aluminium hermetic- pans were studied under a purging nitrogen atmosphere. Heating and cooling rates were set at 10°C/min between room temperature and 150°C. Neither the single nor binary ligand AuNPs exhibit DSC-detectable LC properties. The smaller surface curvature of the 4 to 5nm NPs and the relatively short length of the $CBO(CH_2)_nSH$ likely leads to less interparticle ligand intercalation, compared to the LC-capped 2nm AuNPs [18, 19]. The observation of LC properties in the DSC measurements was used to detect unbound LC thiol ligands that maybe present with the functionalized particles because of incomplete purification.

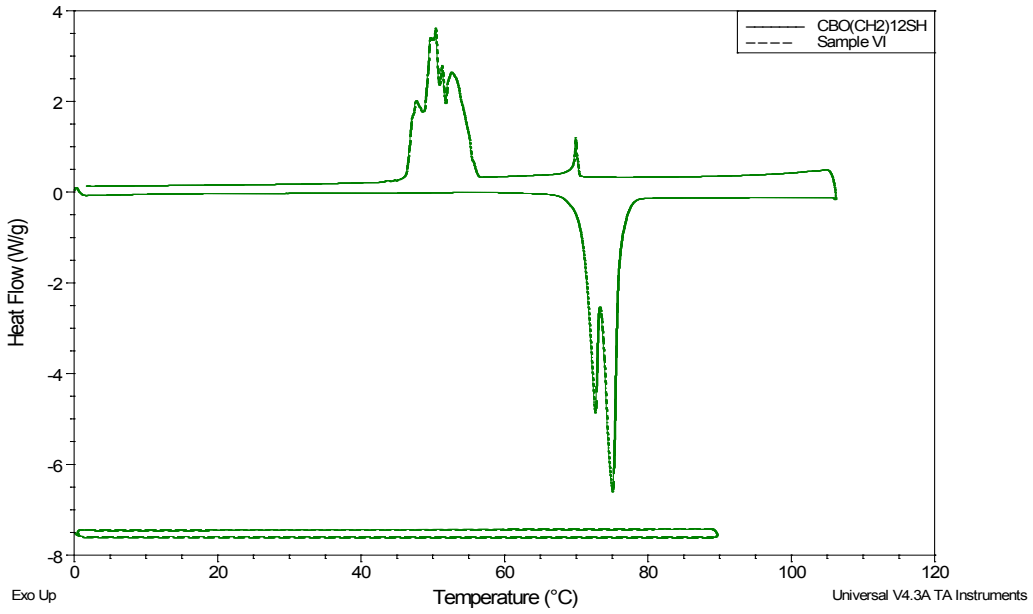

Fig. S3 DSC spectrum of $CBO(CH_2)_{12}SH$ (top plain lines) and sample VI (bottom dash lines).