Electronic Supplementary Material (ESI) for Journal of Materials Chemistry C

SUPPORTING INFORMATION

Network assembly of gold nanoparticles linked through fluorenyl dithiol bridge

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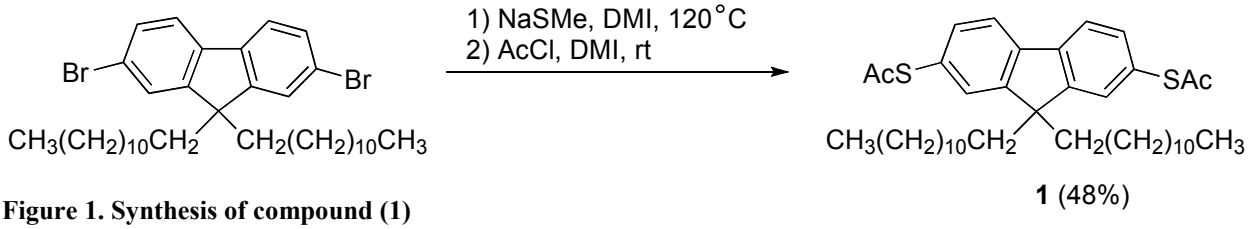
Fluorenyl bis-thiolacetate **(1)** has been prepared starting from commercially available 9,9-didodecyl-2,7-dibromo-fluorene using a three-step one-pot protocol reported in the literature for the functionalization of 2,7-dibromofluorene (Figure 1).**Error! Bookmark not defined.**



1 (48%)

Figure 1. Synthesis of compound (1)

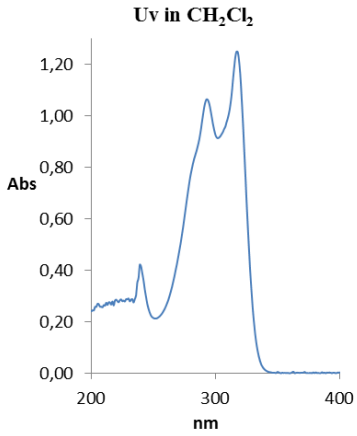


Figure 2: UV-vis for compound (1)

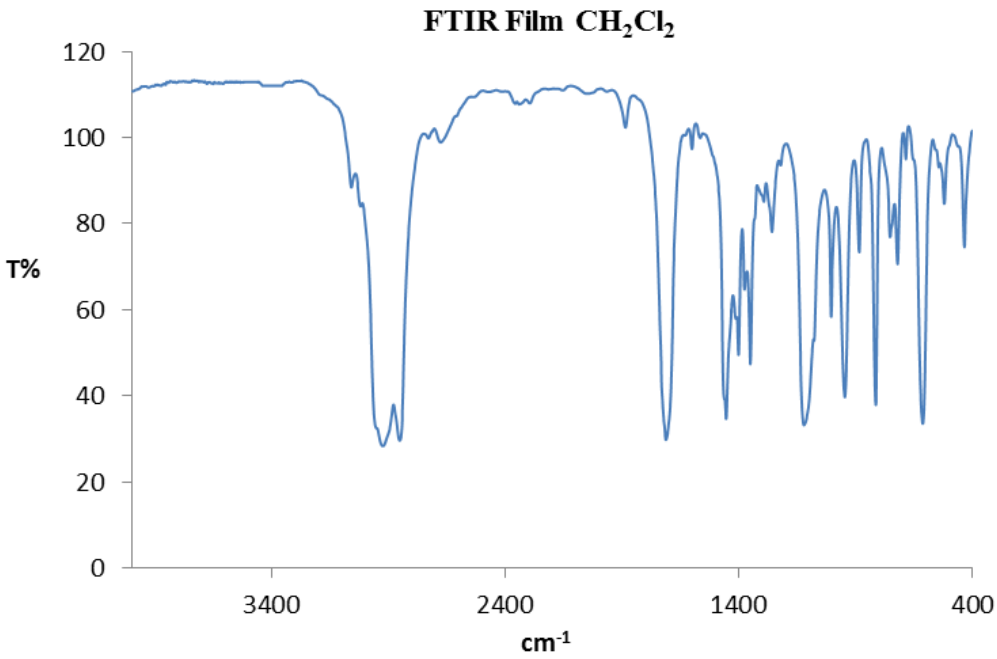


Figure 3: FTIR of compound (1)

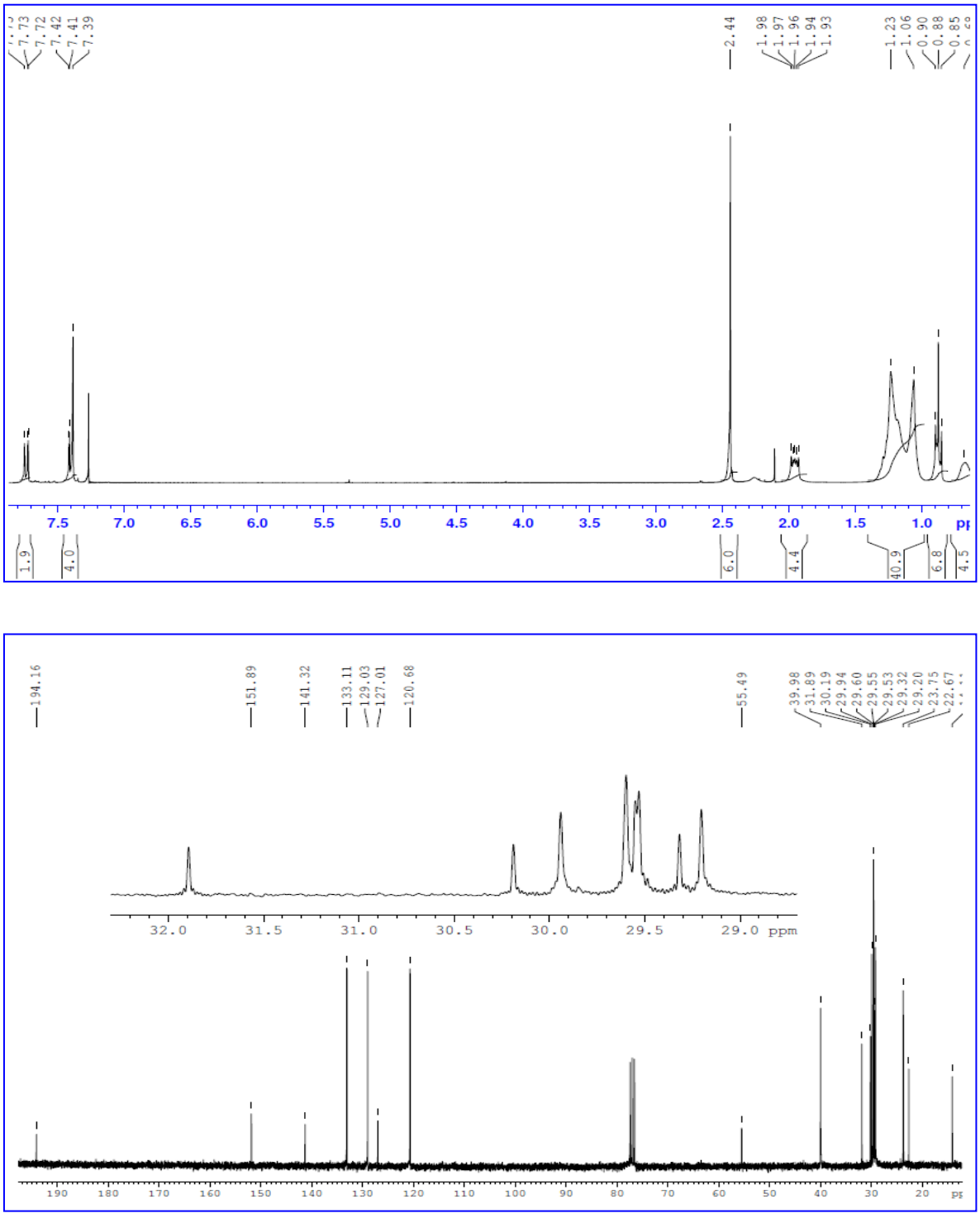


Figure 4: ^{1}H and ^{31}C NMR of compound (1)

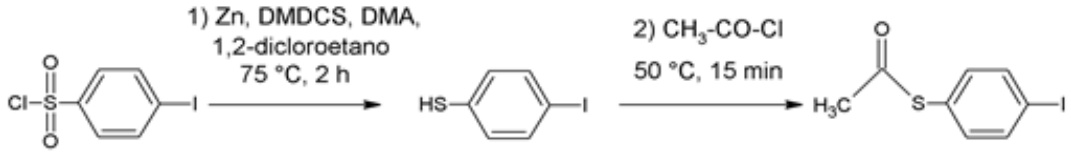


Figure 5: Scheme for the preparation of 1-(S-acetylthio)-4-iodobenzene

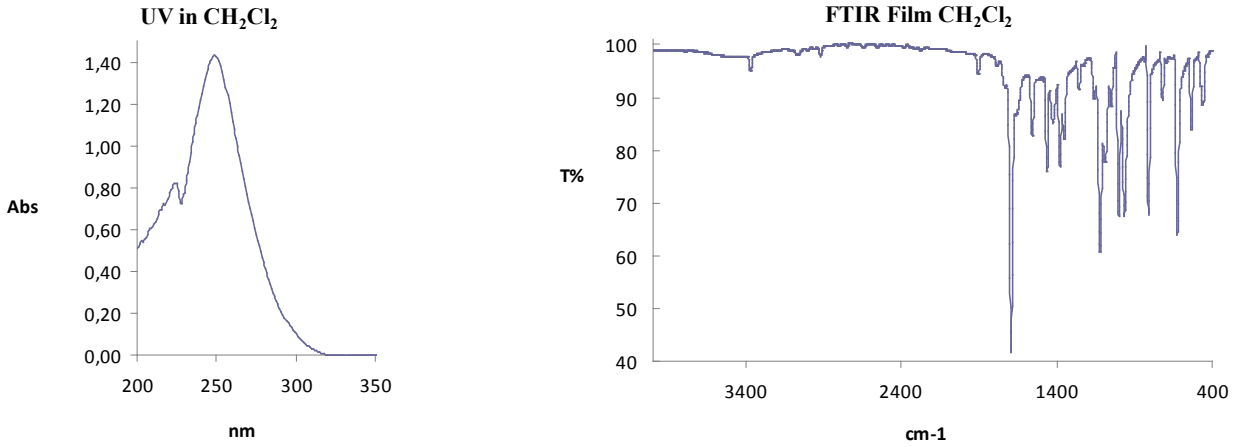


Figure 6: UV-vis and FTIR characterizations of 1-(S-acetylthio)-4-iodobenzene

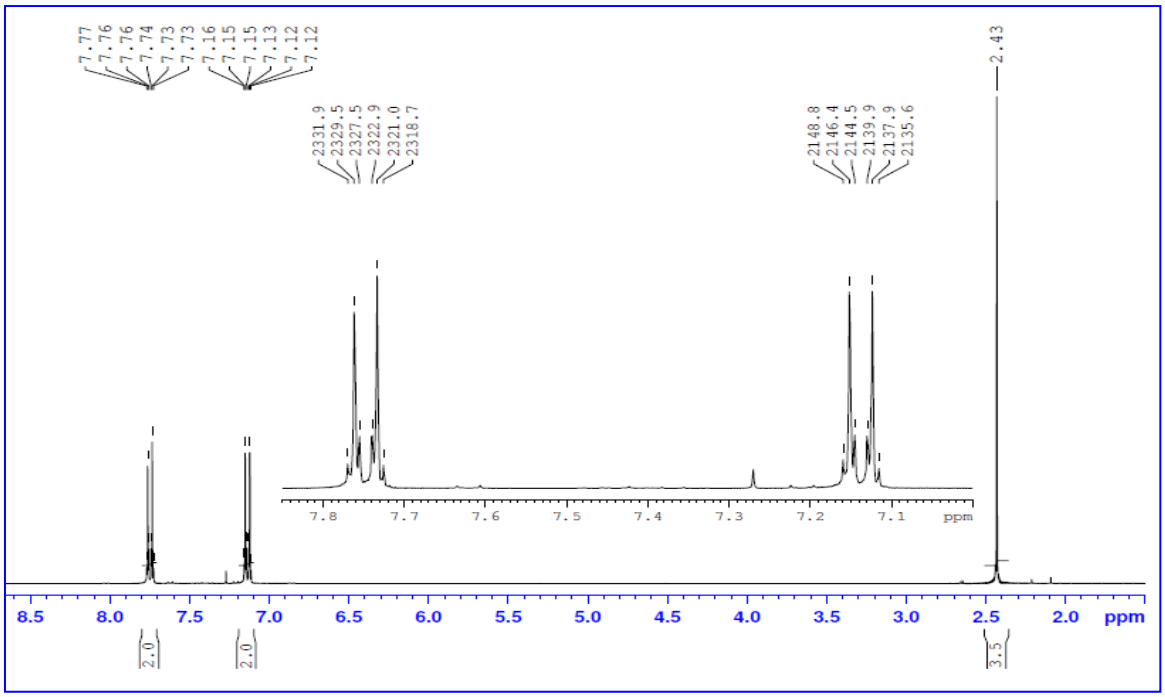


Figure 7: ^{1}H and ^{31}C NMR of 1-(S-acetylthio)-4-iodobenzene

The synthesis of fluorenyl thiolate **(2)** bearing two ethynylphenyl spacers between fluorene and the terminal thioacetyl groups is shown in Figure 2.

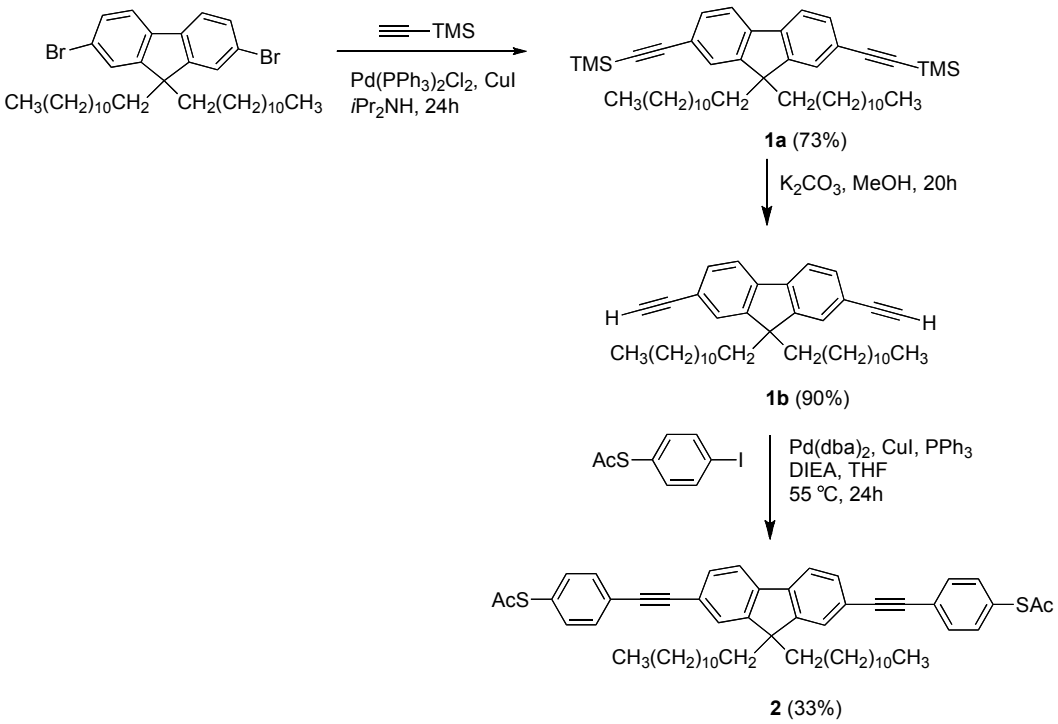


Figure 8: Reaction scheme for the preparation of compound (2)

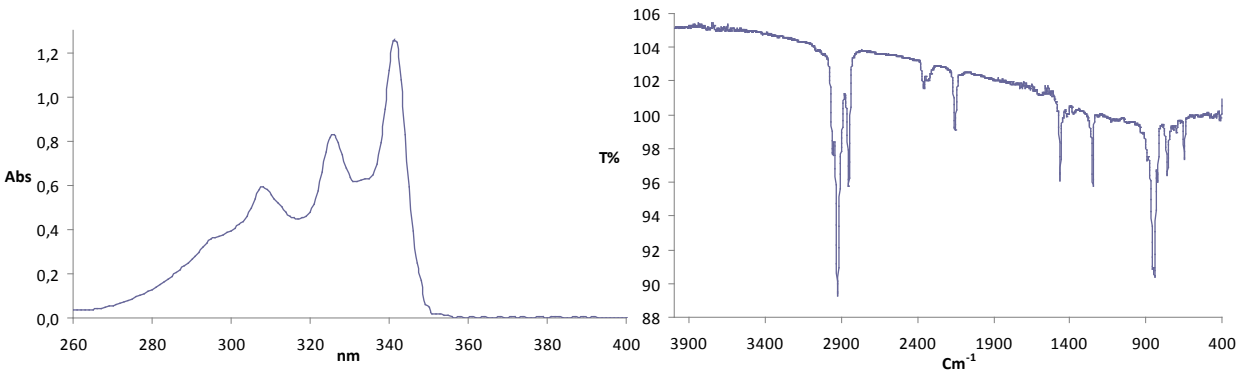


Figure 9: UV-vis and FTIR characterizations of compound (1a)

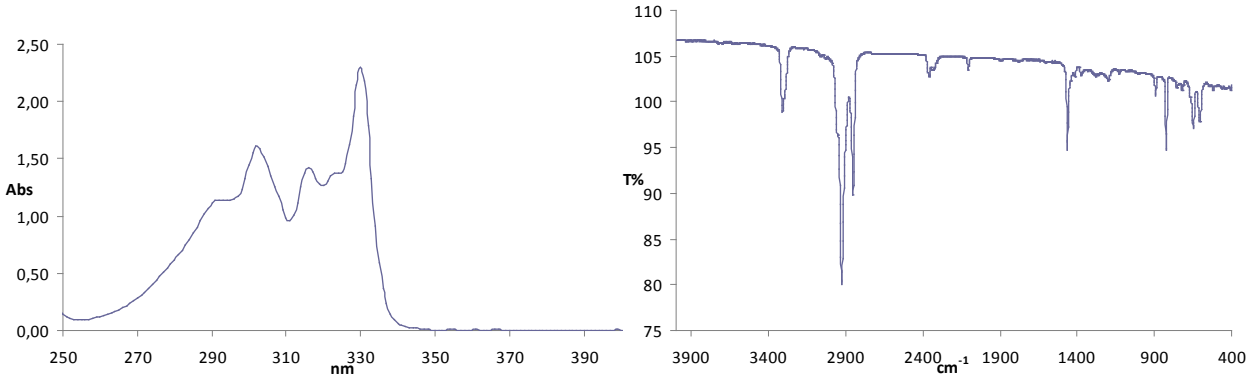


Figure 10: UV-vis and FTIR characterizations of compound (1b)

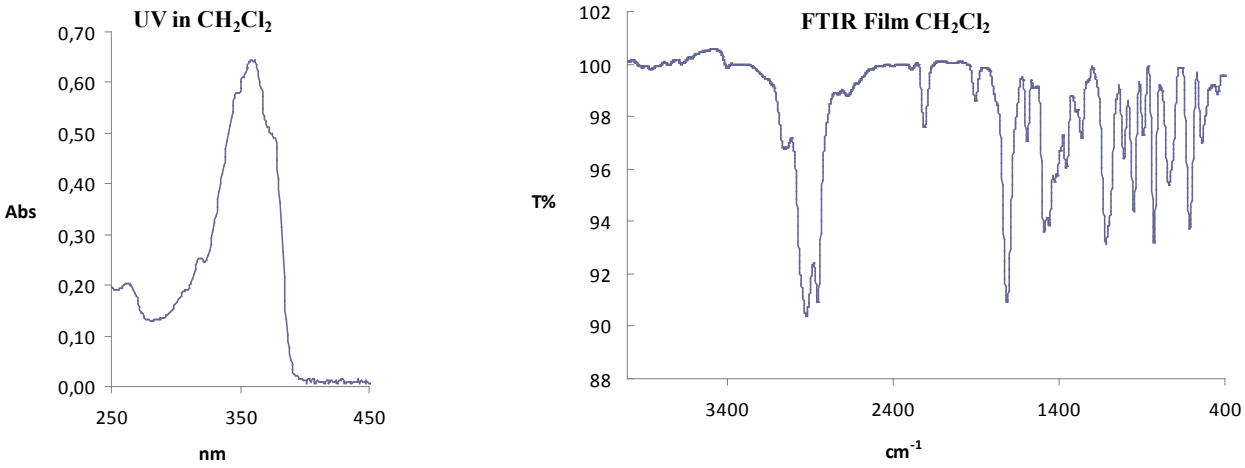


Figure 11: UV-vis and FTIR characterizations of compound (2)

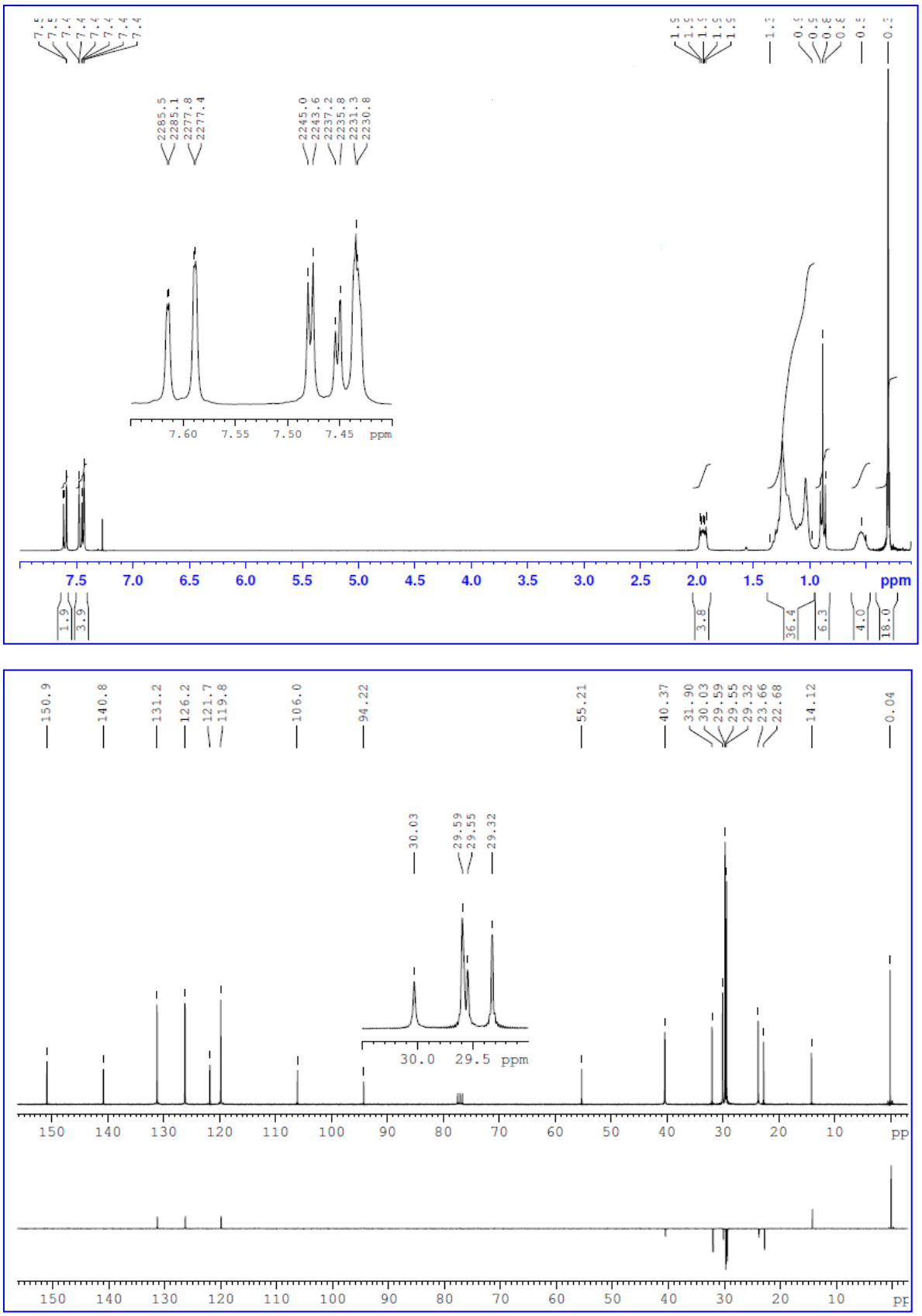
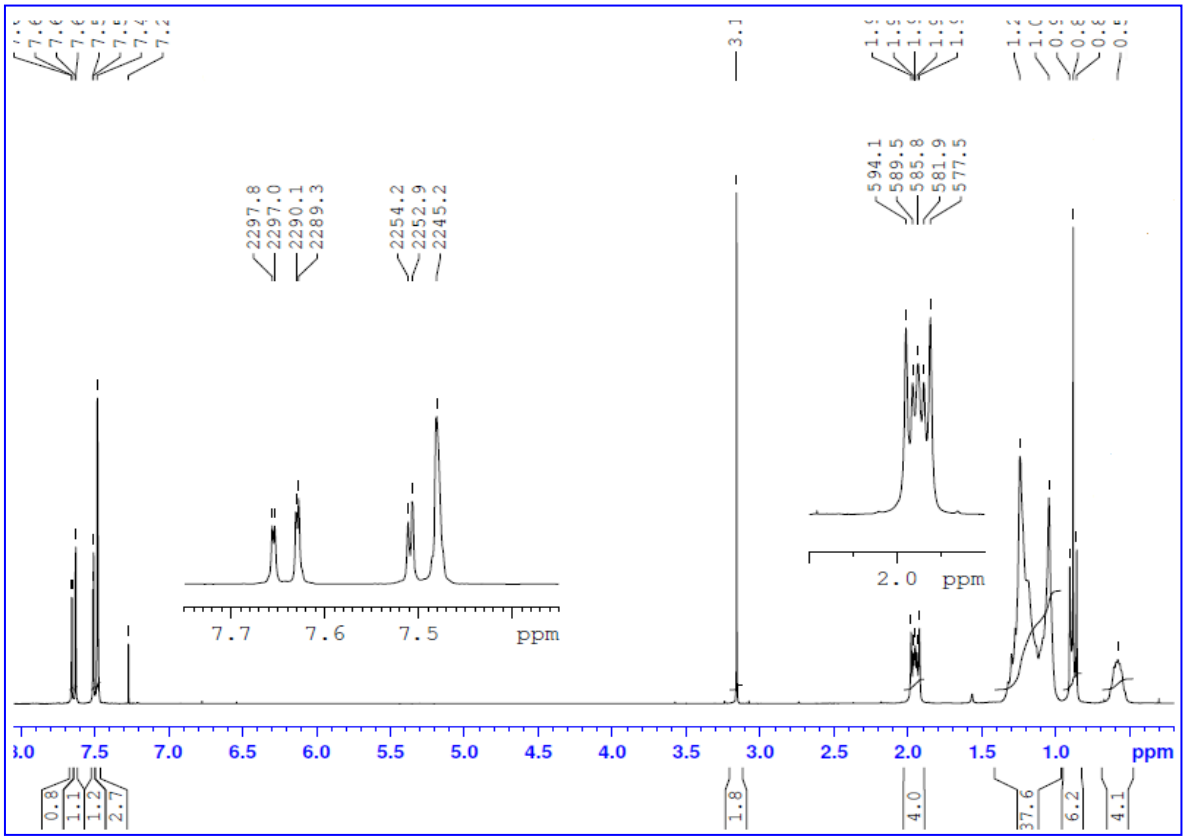


Figure 12: ^{1}H and ^{31}C NMR of compound (1a)



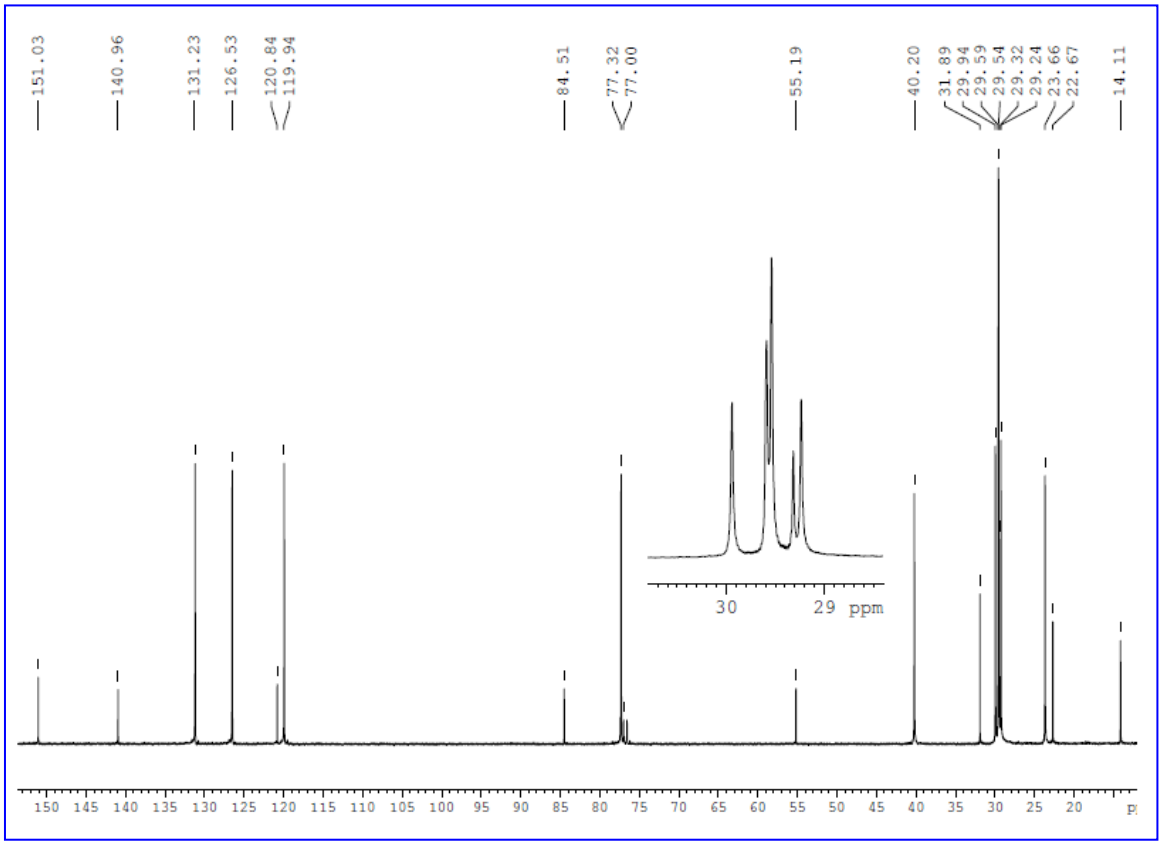


Figure 13: ^{1}H and ^{31}C NMR of compound (1b)

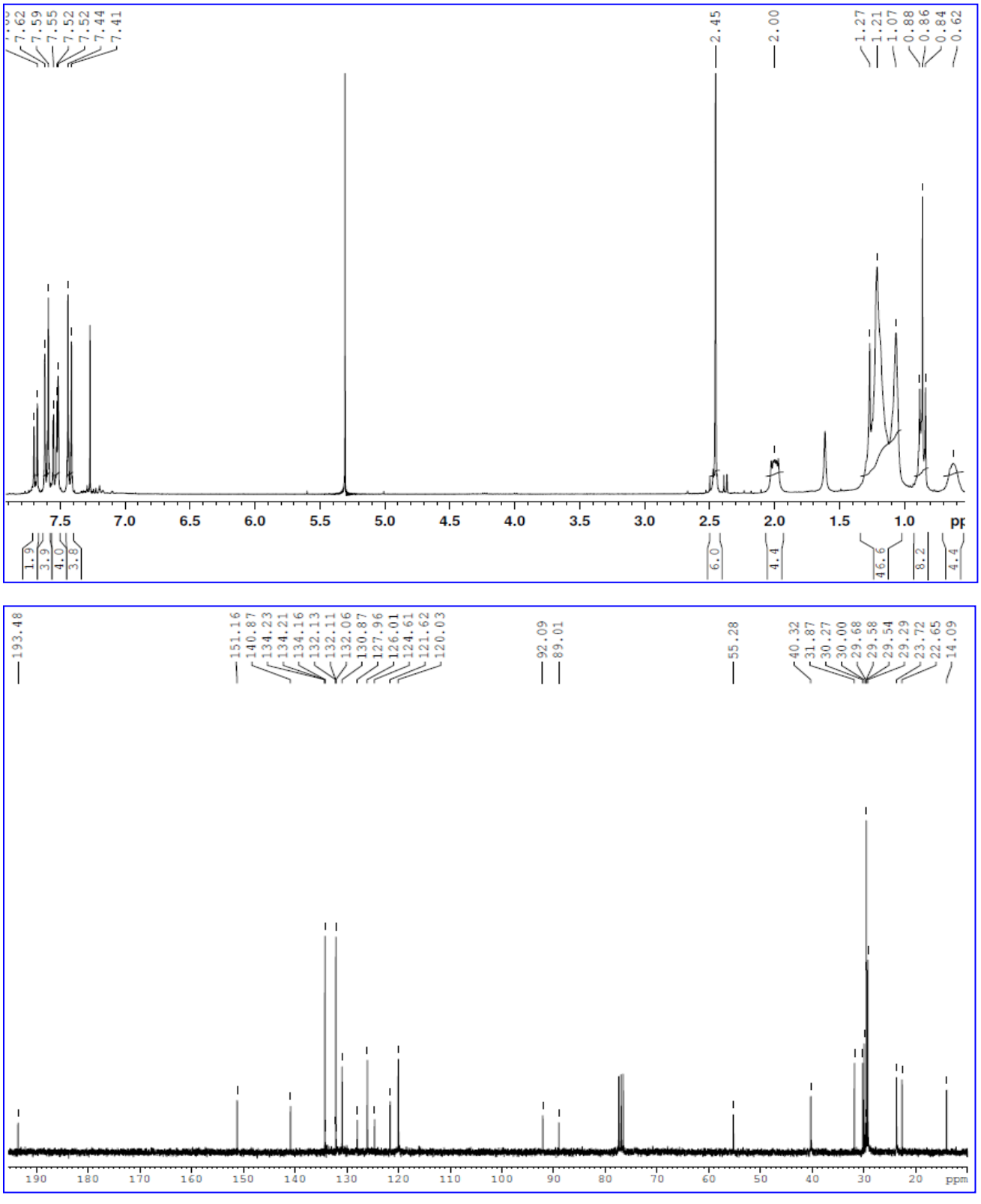


Figure 14: ^{1}H and ^{31}C NMR of compound (2)

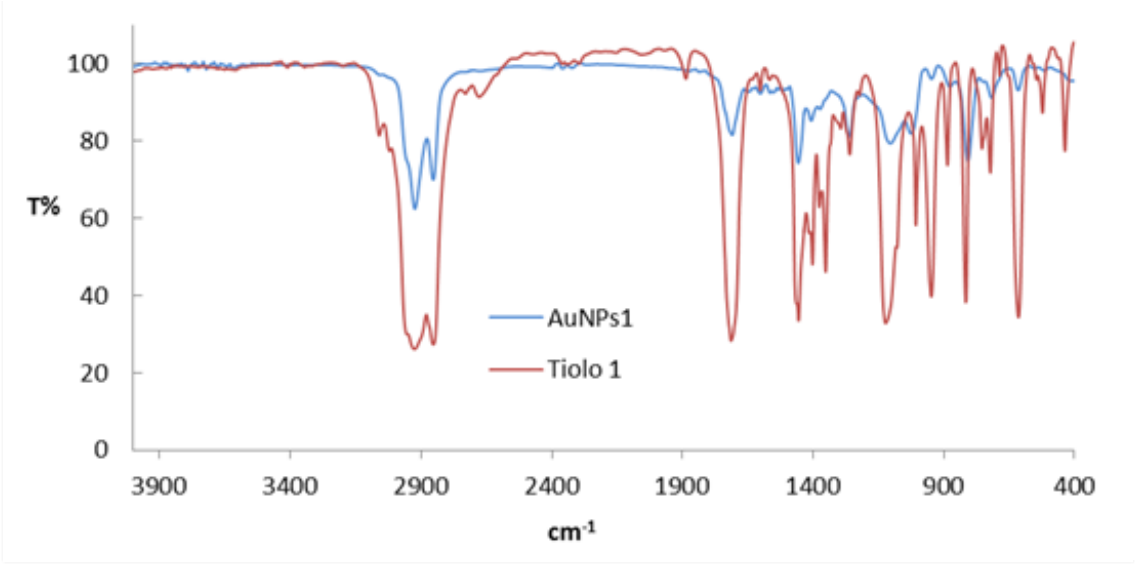


Figure 15: FTIR of compound (1) and AuNPs-1 (film)

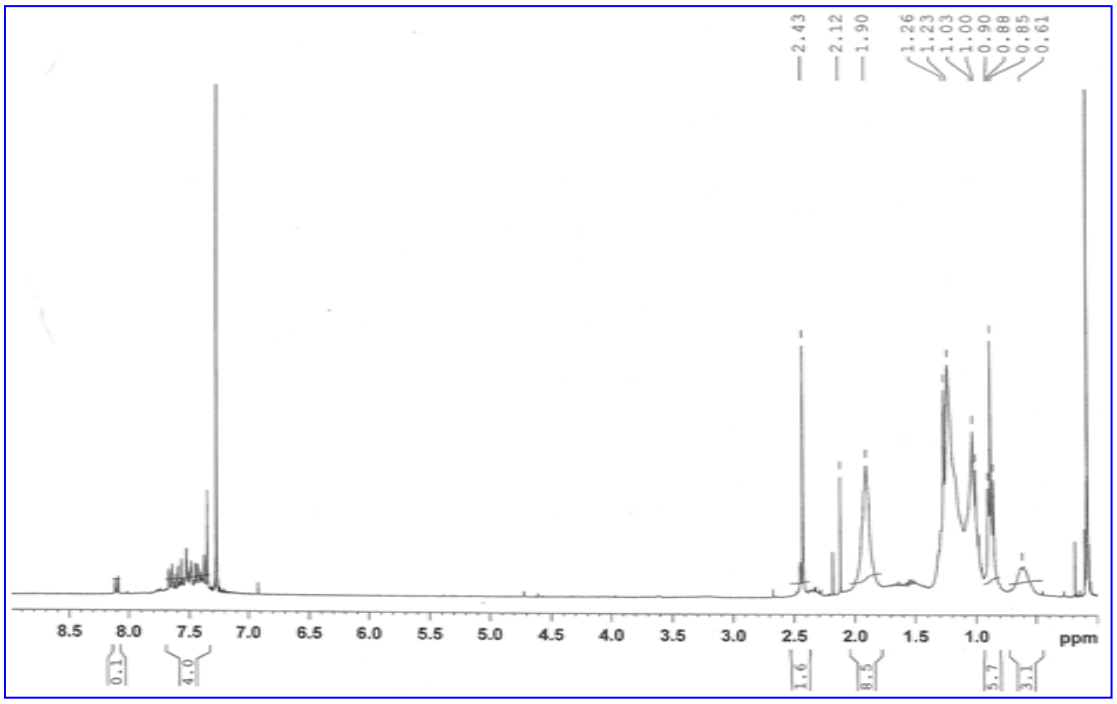


Figure 16: ^{1}H NMR of AuNPs-1

Table 1: XPS core levels data collected on fluorene thiolates 1 and 2, AuNPs-1 and AuNPs-2.

SAMPLE	Signal	BE (eV)	FWHM (eV)	Assignment | % on the same signal
Thiolate 1	C1s	285.00	1.79	C*-C | 80%
		286.59	1.79	C*-S; COC*H_3 | 12.8%
		288.42	1.79	C*OCH_3 | 7.2%
		292.79	1.79	Shake-up?
	$S2p_{3/2}$	163.36	1.75	S*$COCH_3$
AuNPs-1 0.25/1	C1s	285.00	1.48	C*-C | 86%
		286.36	1.48	C*-S; COC*H_3 | 9.8%
		287.98	1.48	C*OCH_3 | 4.2%
	$S2p_{3/2}$	162.61	1.62	S*-Au | 26%
		163.95	1.62	S*$COCH_3$ | 74%
	$Au4f_{7/2}$	84.08	1.26	Au(0) | 90%
		84.99	1.26	Au*-S | 10%
AuNPs-1 1.0/1	C1s	285.00	1.55	C*-C | 85%
		286.47	1.55	C*-S; COC*H_3 | 9%
		287.87	1.55	C*OCH_3 | 1%
	$S2p_{3/2}$	162.65	1.88	S*-Au | 31%
		164.30	1.88	S*$COCH_3$ | 69%
	$Au4f_{7/2}$	83.90	1.27	Au(0) | 88.7%
		84.78	1.27	Au*-S | 11.3%
AuNPs-1 0.7/1	C1s	285.00	1.59	C*-C | 83%
		286.41	1.59	C*-S; COC*H_3 | 12%
		288.03	1.59	C*OCH_3 | 5%
	$S2p_{3/2}$	162.45	1.40	S*-Au | 32%
		163.91	1.40	S*$COCH_3$ | 68%
	$Au4f_{7/2}$	84.04	1.28	Au(0) | 86%
		85.00	1.28	Au*-S | 14%
Thiolate 2	C1s	285.00	1.62	C*-C | 79.0%
		286.31	1.62	C*-S; COC*H_3 | 15.5%
		288.24	1.62	C*OCH_3 | 5.5%
		292.65	1.62	Shake-up
	S2p	164.06	1.56	S*$COCH_3$
AuNPs-2 1.0/1	C1s	285.00	1.81	C*-C | 66.70%
		286.86	1.81	C*-S; COC*H_3 | 21.10%
		288.54	1.81	C*OCH_3 | 12.20%
	S2p	161.80	1.77	S*-Au | 100%
	$Au4f_{7/2}$	84.00	1.27	Au(0) | 75.70%
		84.67	1.27	Au*-S | 24.30%

Table 2: Photophysical parameters of **1**, **2**, **AuNPs-1** and **AuNPs-2**.

Sample	**Concentration**	**Absorption** λ_{max} **(nm)**	**Emission** λ_{max} **(nm)**
1	1.95 x 10^{-6}M (1.27 x10^{-3}mg/mL) ($CHCl_3$)	293 (4.3), 317 (4.4)	λ_{exc320} = 355, 390(s)
2	1.75 x 10^{-6}M ($CHCl_3$)	360 (4.9)	λ_{exc360} = 385, 405
AuNPs-1	2.3 x 10^{-3} mg/mL (CH_2Cl_2)	323 (s) 330 530	λ_{exc330} = 387, 409 λ_{exc530} = 792
AuNPs-2	2.0 x 10^{-3} mg/mL (DMF)	365 593	λ_{exc360} = 381, 402 λ_{exc580} = 765, 820