Covalently bonded multimers of $Au_{25}(SBut)_{18}$ as a conjugated system

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SUPPORTING INFORMATION

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*Figure S1: NMR investigation on the disulfide formation of linker **1**. Pure **1** (red), **1** at 0h of the stability test (green) and **1** at 24h of the stability test (blue). No change is observed after 24h. The sample at 0h already shows some disulfide signals because of preparation from an original DCM solution to a DCM-d2 solution.*

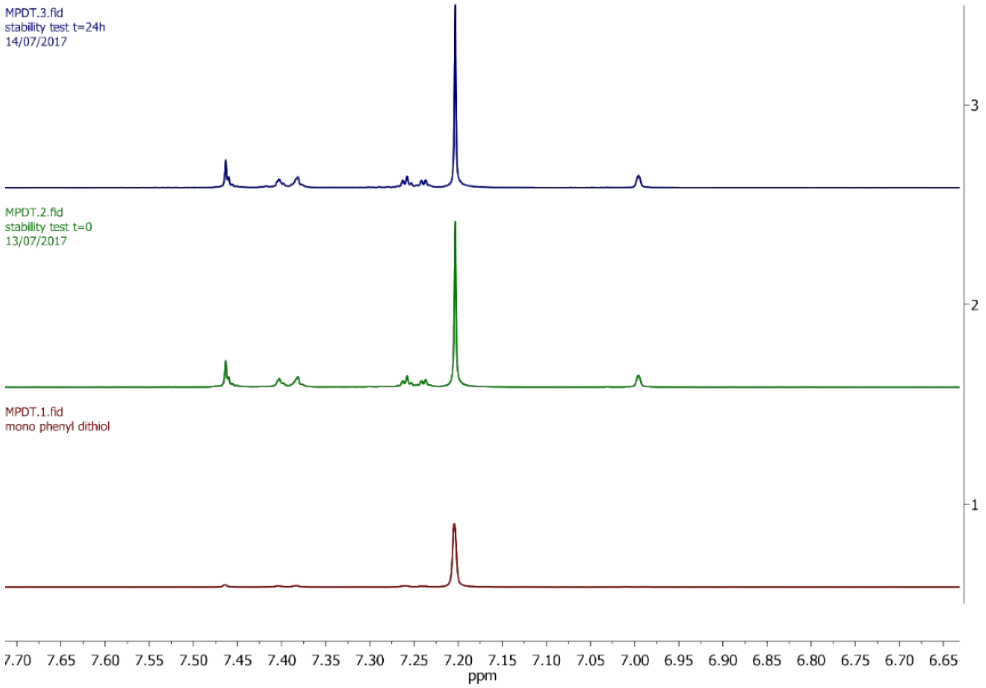


*Figure S2: SEC of 2 mg $Au_{25}(SBut)_{18}$ (left column) and 2 mg of reaction mixture $Au_{25}(SBut)_{18}$ + **1** (right column). It can be observed that the first eluting species of the multimers are eluting much faster than reference Au_{25}.*

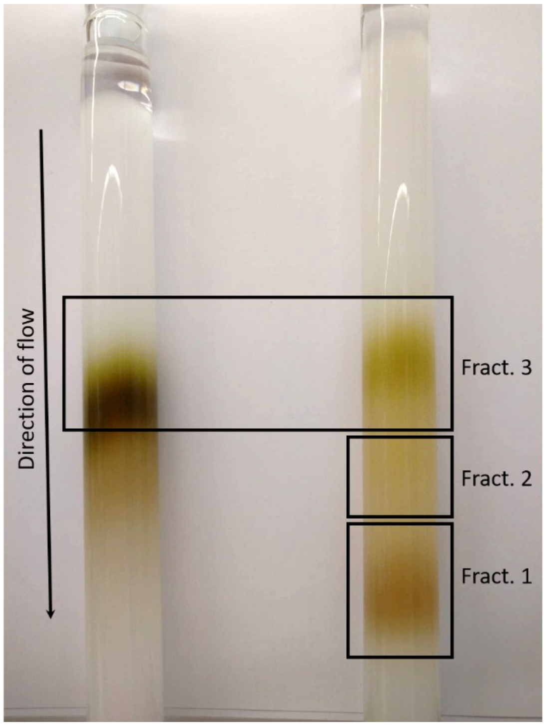


Figure S3: Reference UV (left) and MALDI (right) of pure $Au_{25}(SBut)_{18}$. The target mass peak of $Au_{25}(SBut)_{18}$ is at m/z 6529, but peaks at lower m/z present the fragmentation pattern of the loss of $Au_1(SBut)_1$

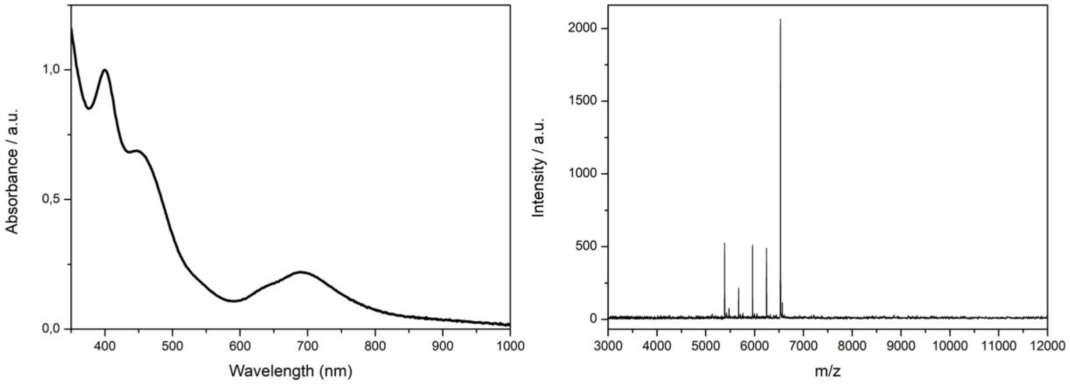


Figure S4: Full MALDI characterization of separated fractions after size exclusion chromatography

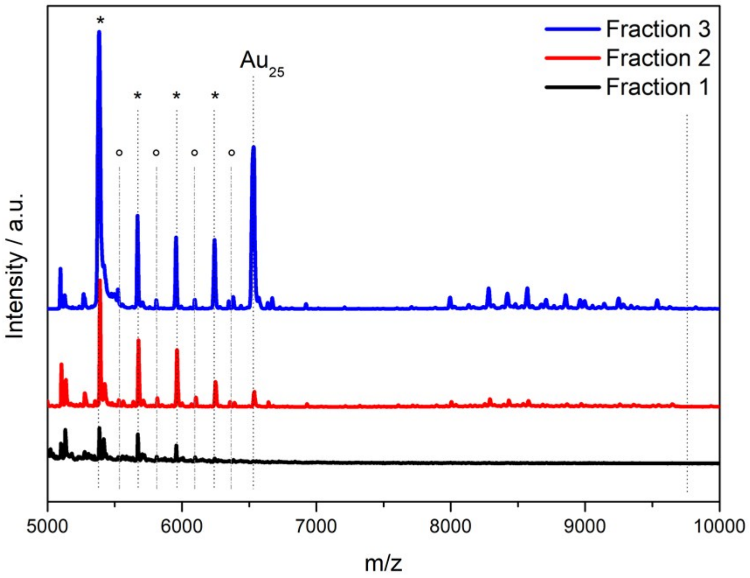
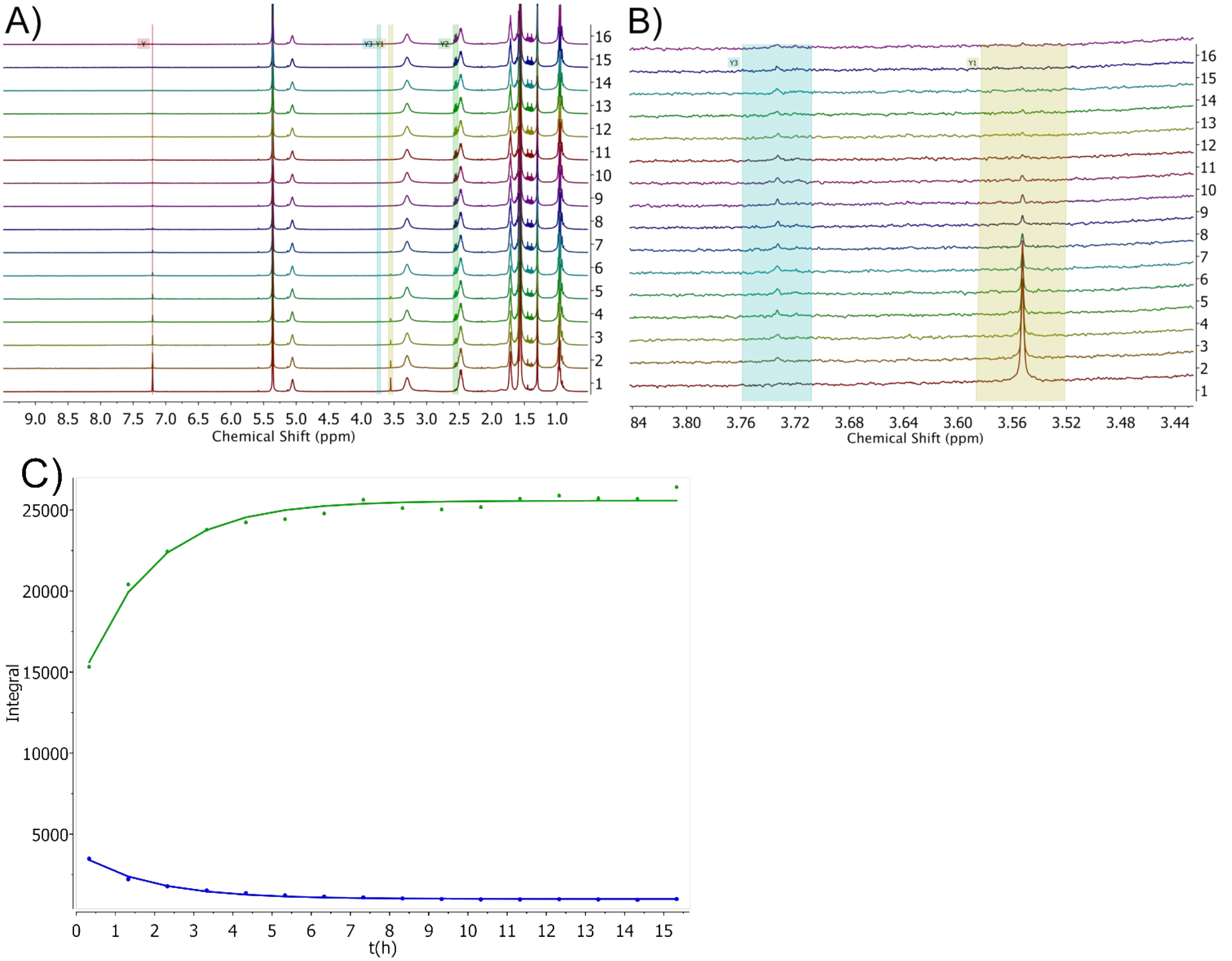


Figure S5: Full NMR spectrum after kinetics 3. Red and yellow are signals resulting from linker ***1****; green and blue are signals originating from butanethiol. Linking reaction with addition of 0.5 equiv of* ***1****, 5 mg/ mL in DCM-2d.*



$y=B + F \exp^{(-xG)}$	Entering PhSH (3.55 ppm)	Leaving ButSH (2.55 ppm)
B	1002.9	25573.6
F	2881.03	-12011
G	0.551453	0.568001
Sum of B	26576.5	
Ratio at equilibrium	**0.038**	**0.962**

Figure S6: NMR (A, B), kinetics (C) and MALDI (D)of thiophenol exchange reaction. Exchange reaction was performed with 0.1 equiv of thiophenol, 4 mg/ mL in DCM-2d. NMR comparison (E) of pure $Au_{25}(SBut)_{18}$ *with* $Au_{25}(SBut)_{18-x}(SPh)_x$ *after exchange reaction confirms thiophenol exchanged species which can be the only reason for the NMR signal at 9 ppm.*

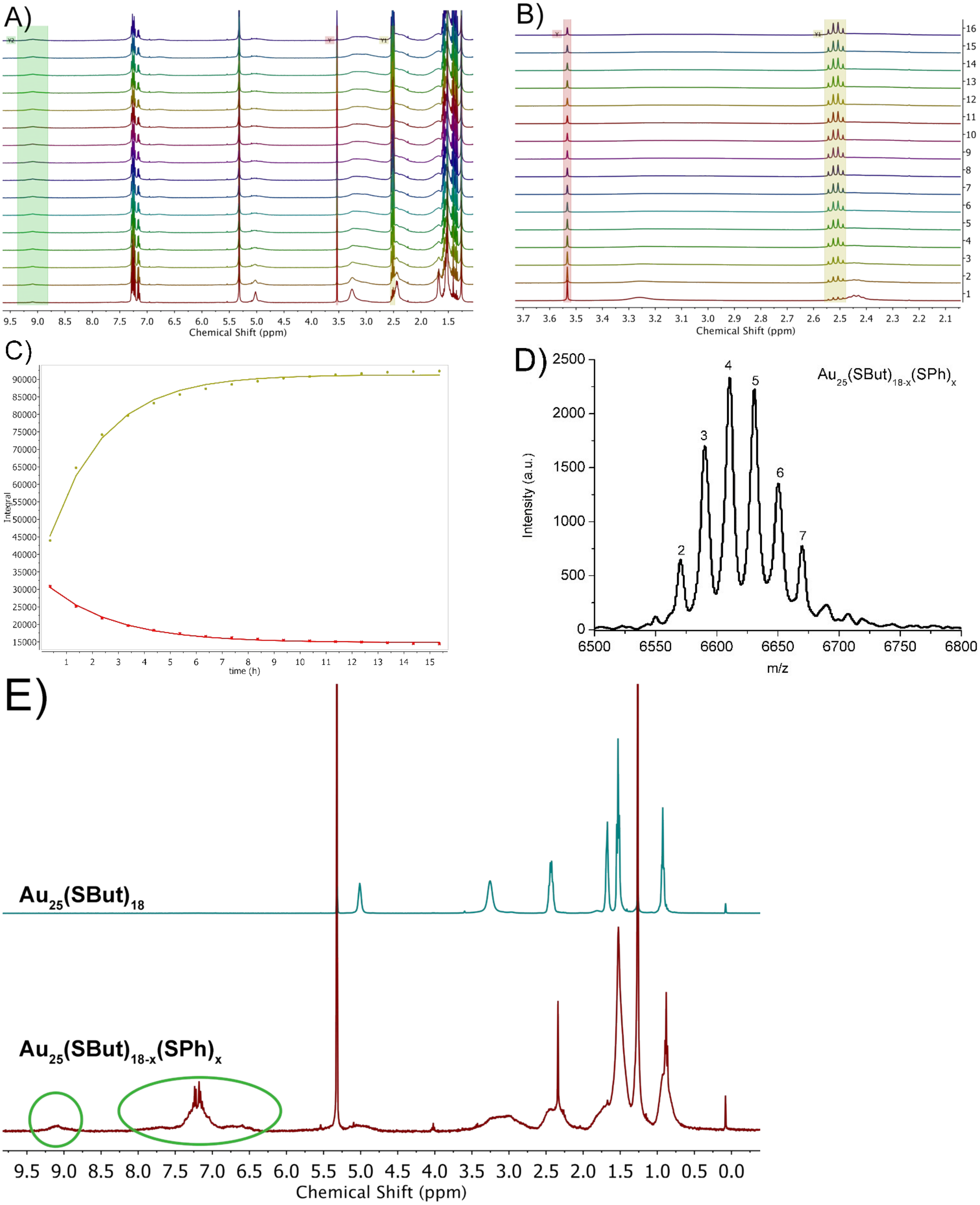


Figure S7: Full UV-vis spectra (A) of the unlinking reaction after addition of 1 equiv butanethiol to a multimers solution of approximately 0.23 mg/ mL in THF (concentration approximated by UV-vis calibration) and MALDI (B) of the separated fractions afterwards.

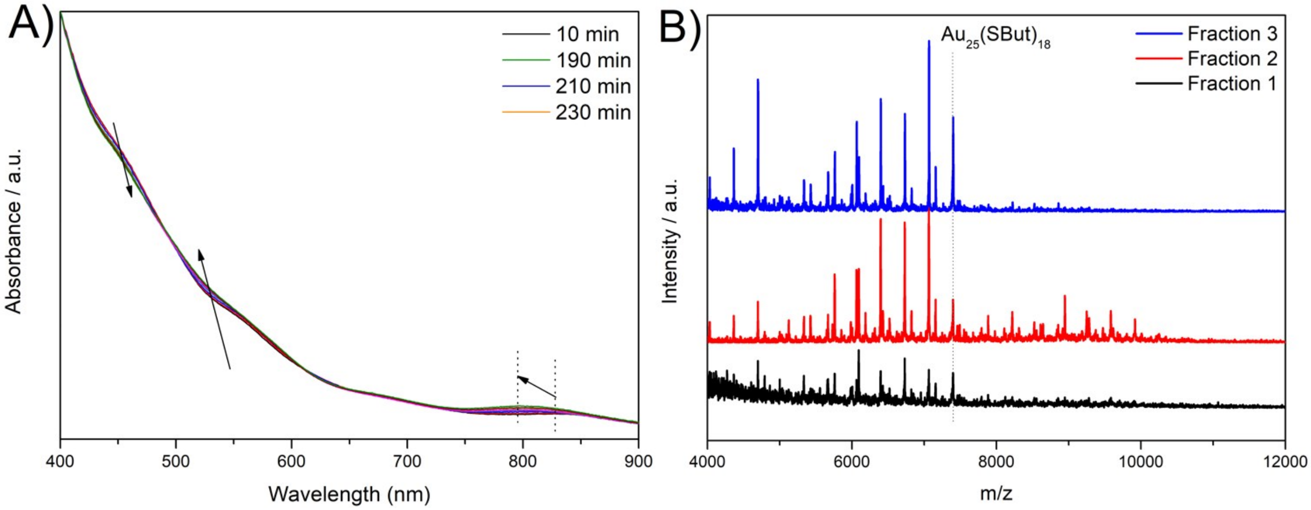


Figure S8: Unlinking reaction with the precipitated multimers. UV-vis analysis of the suspension of precipitated $Au_{25}(SBut)_{18}$-multimers (0h) and after addition of butanethiol (0,1 mL). UV-vis taken after 2h 20 min, 4h 30 min and 72h of reaction. After 72h the precipitate dissolved and UV-vis shows again the typical features (800-840 nm) of a multimer solution.

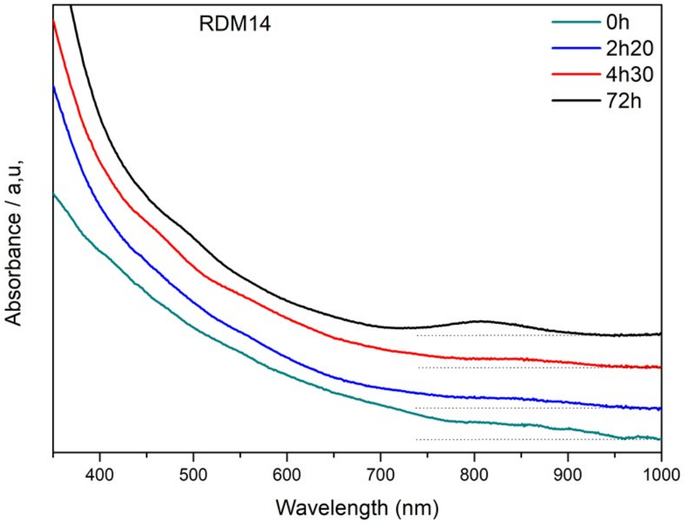


*Figure S9: Linking reaction of $Au_{25}(PET)_{18}^{0}$ with **2** (left) and **1** (right) (0.5 equiv dithiol, 0.5 mg/ mL in THF).*

*SEC of $Au_{25}(PET)_{18-x}(\mathbf{2})_x$ (left) confirmed presence of larger species, eluting faster than Au_{25}. Although MALDI does not show any additional peaks at higher mass range, UV-vis indeed shows a new feature at 840nm for Fraction 1. SEC of $Au_{25}(PET)_{18-x}(\mathbf{1})_x$ (right) confirms presence of mostly unreacted Au_{25} as no clear fraction of linked clusters could be observed. It looks like PET-protected Au_{25} cluster does not form multimers using linker **1**. We think this results from a more sterically hindered PET ligand compered to butanethiol.*

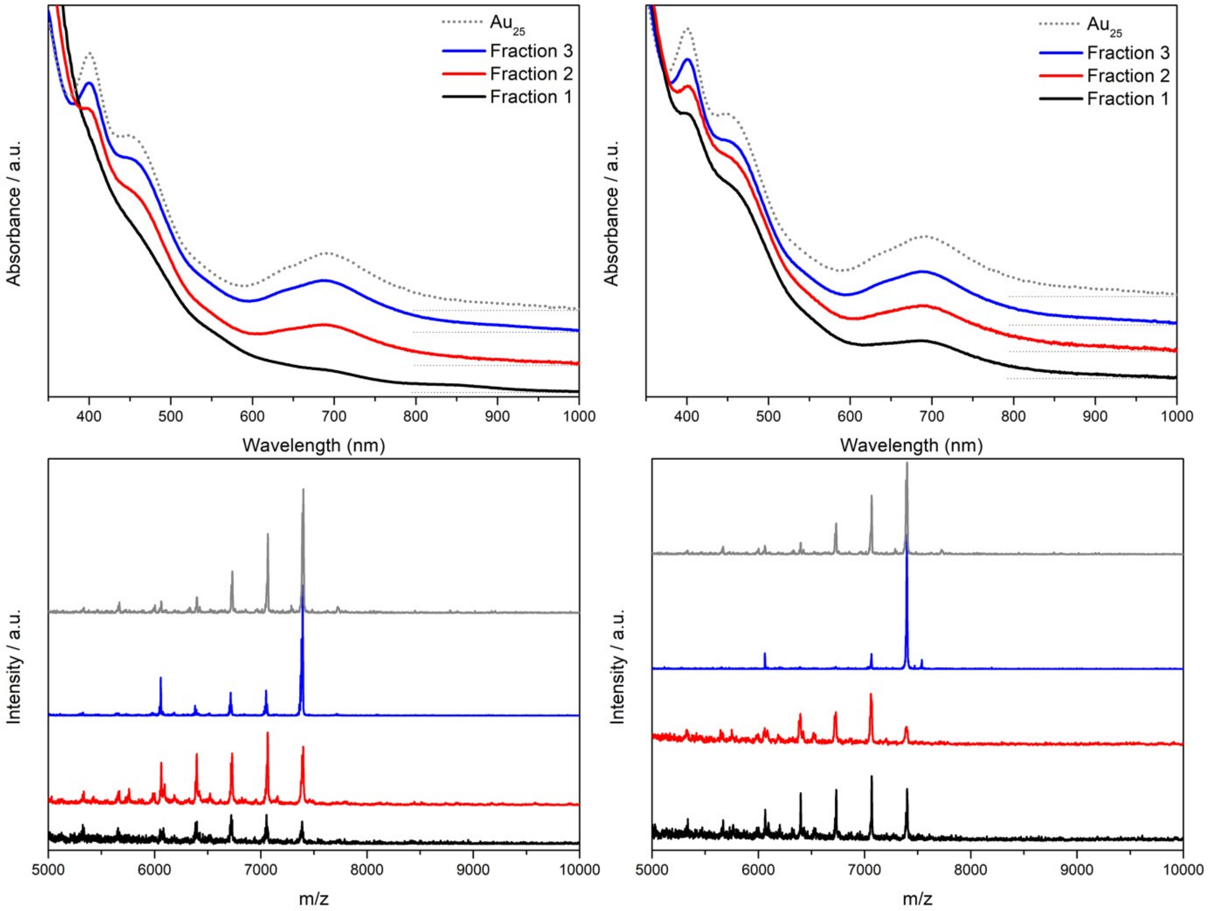


Figure S10: Linking reaction of $Au_{25}(Sbut)_{18}{}^{0}$ *with 1,4-Benzenedimethanethiol. A non-conjugated linker, 1,4-Benzenedimethanethiol was chosen in order to confirm the origin of the new peak (840 nm) in UV-Vis absorption spectra. (A) SEC of* $Au_{25}(SBut)_{18-x}(\mathbf{3})_x$ *confirmed presence of larger species, eluting faster than* Au_{25}*. UV-Vis of the separated fractions all show typical* Au_{25} *features, also the first eluting species do not show the UV-vis feature of 840 nm. (B) MALDI of the last fraction shows the ligand exchange product of 1 exchanged dithiol.(D) MALDI of the first fraction gives indication of presence of larger species, however no clear peak can be observed. (C)*

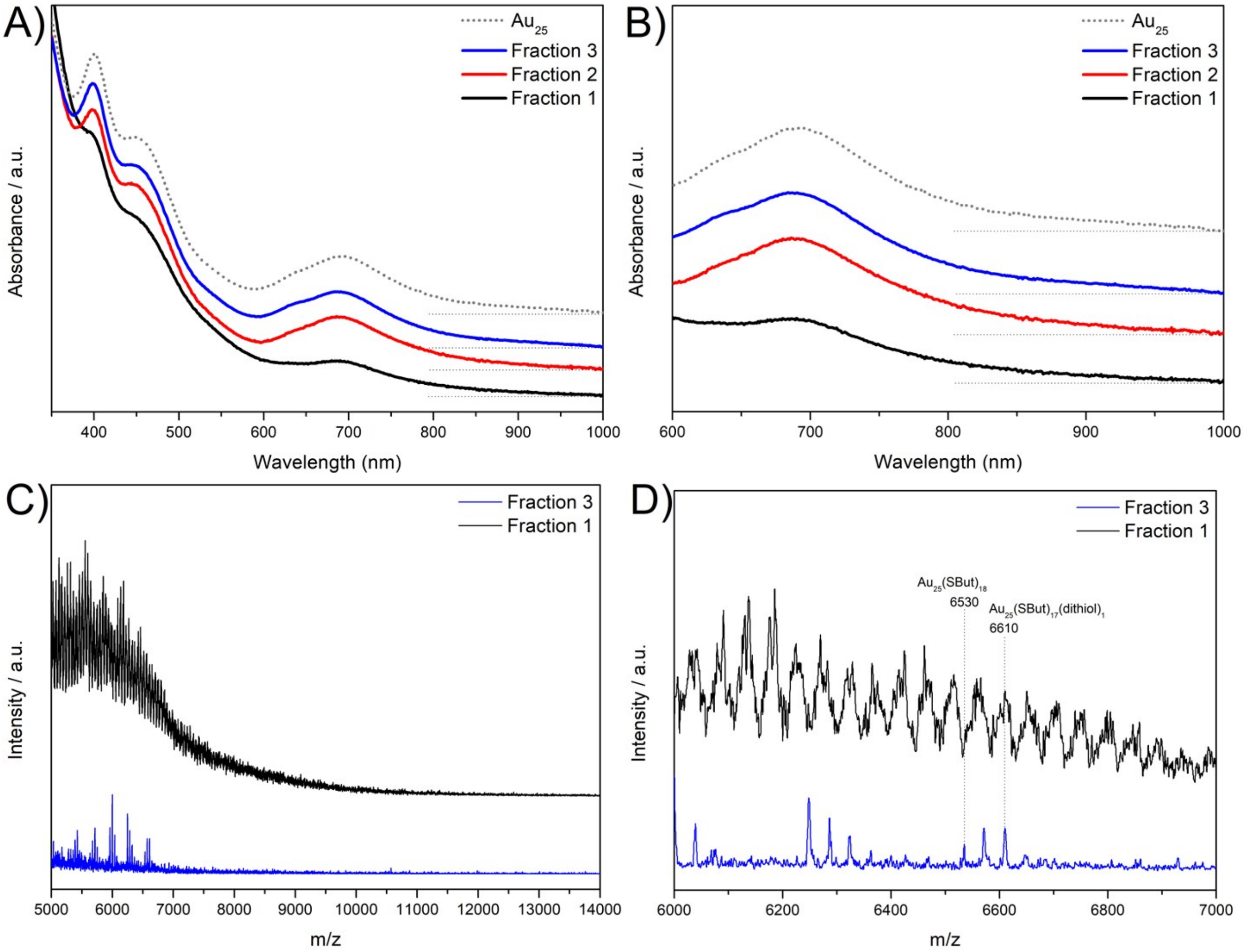


Figure S11: UV-Vis comparison of the first eluting fractions after linking. In both linking reactions using linker 1 and 2, a new feature at 840 nm appears at the same position. The first fraction with linker 3 shows only the typical Au_{25} feature (690 nm). The absorption spectra were not normalized, therefore intensities should not be considered significant.

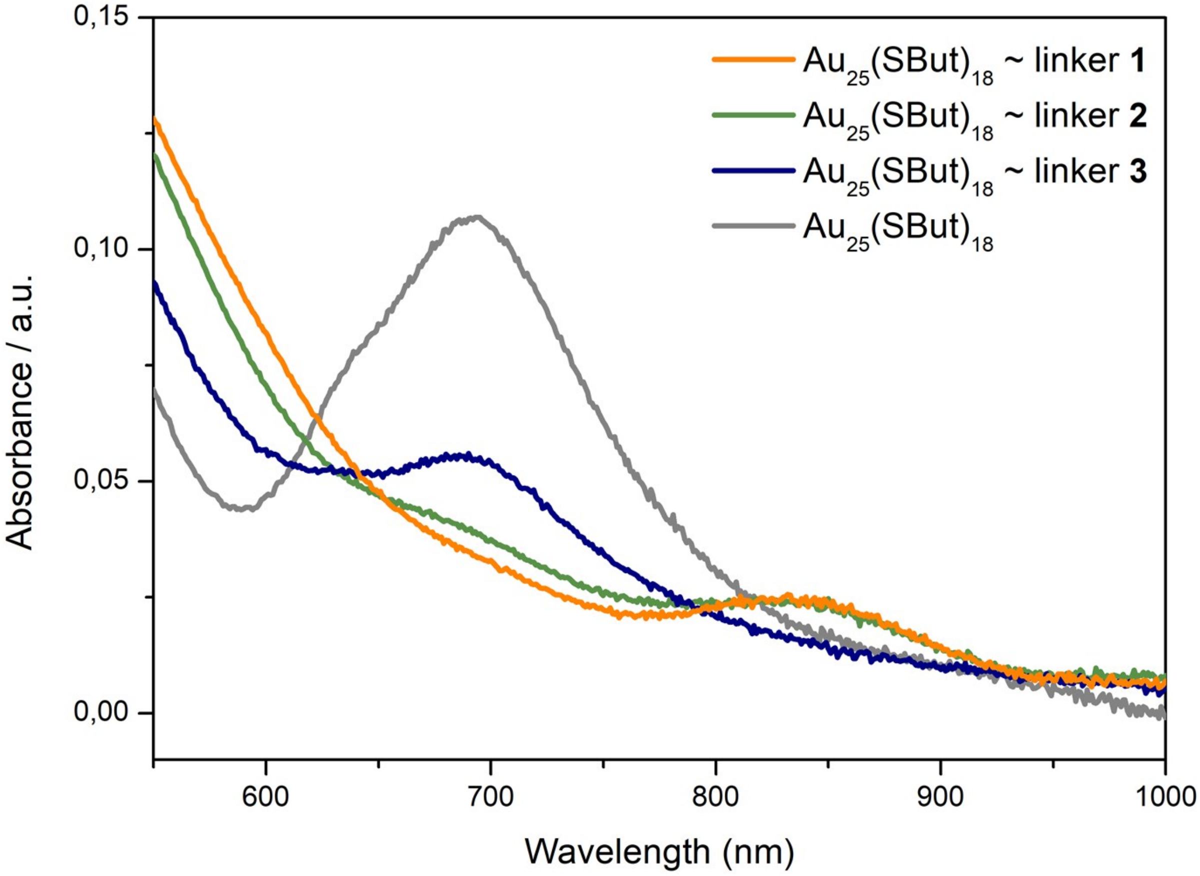


Figure S12: UV-vis of isolated fractions measured by SAXS. Fractions 1 (A) and zoom at higher wavelengths (B). All fractions show no longer the typical Au_{25} *features but all show a signal at 840 nm. Fractions 2 (C) and zoom at higher wavelengths (D). All fractions have still some* Au_{25} *features, except the fraction of PET-protected* Au_{25} *linked with* ***2*** *who appears to show the UV-vis feature at 840 nm.*

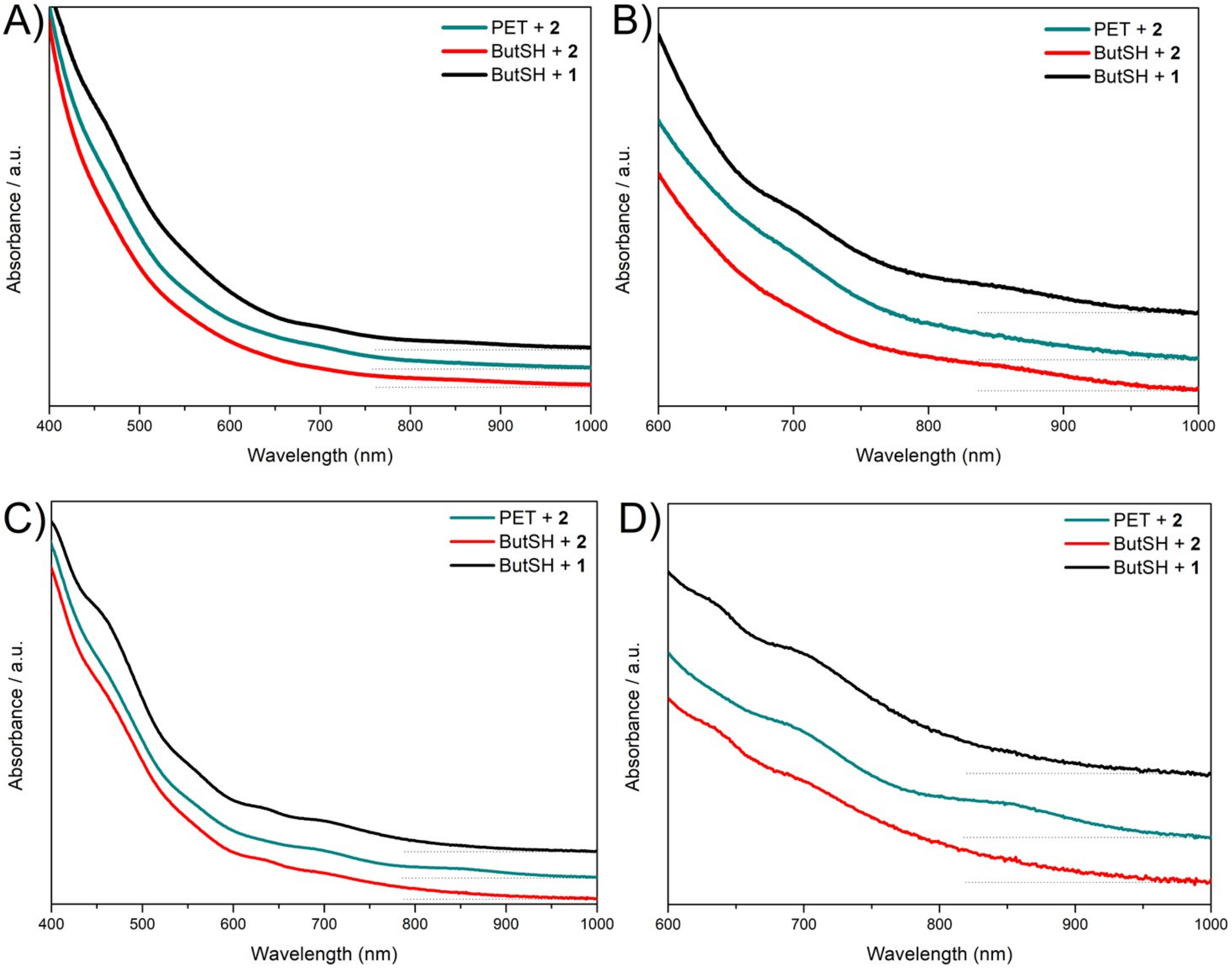


Figure S13: Non-normalized fitting of SAXS curves by SASVIEW (second fractions). $Au_{25}(SBut)_{18}$*~1 is Sample 7;* $Au_{25}(SBut)_{18}$*~2 is Sample 6;* $Au_{25}(PET)_{18}$*~2 is Sample 5*