Supporting information

Designing Atomically Precise Gold Nanocluster Architectures with DNA-Guided Self-Assembly and Biofunctionalization Approaches

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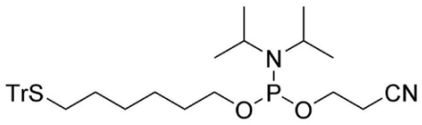
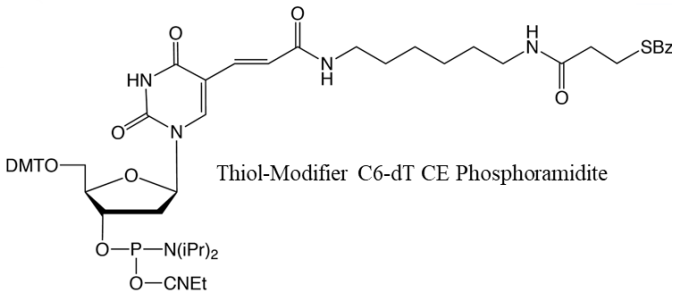
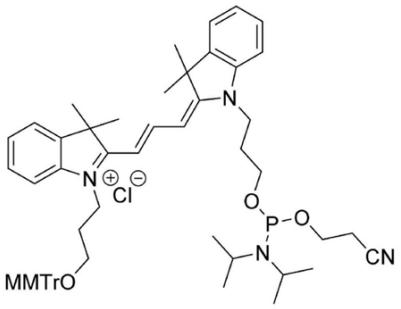


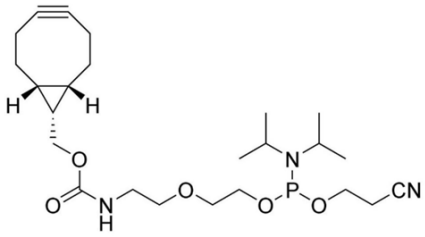
5'-Thiol Modifier C6 CE-Phosphoramidite



Thiol-Modifier C6-dT CE Phosphoramidite



Cyanine 3 CE-Phosphoramidite



5'-BCN CE-Phosphoramidite

Figure S1. Structures of linkers and dyes phosphoramidite derivatives used in this study.

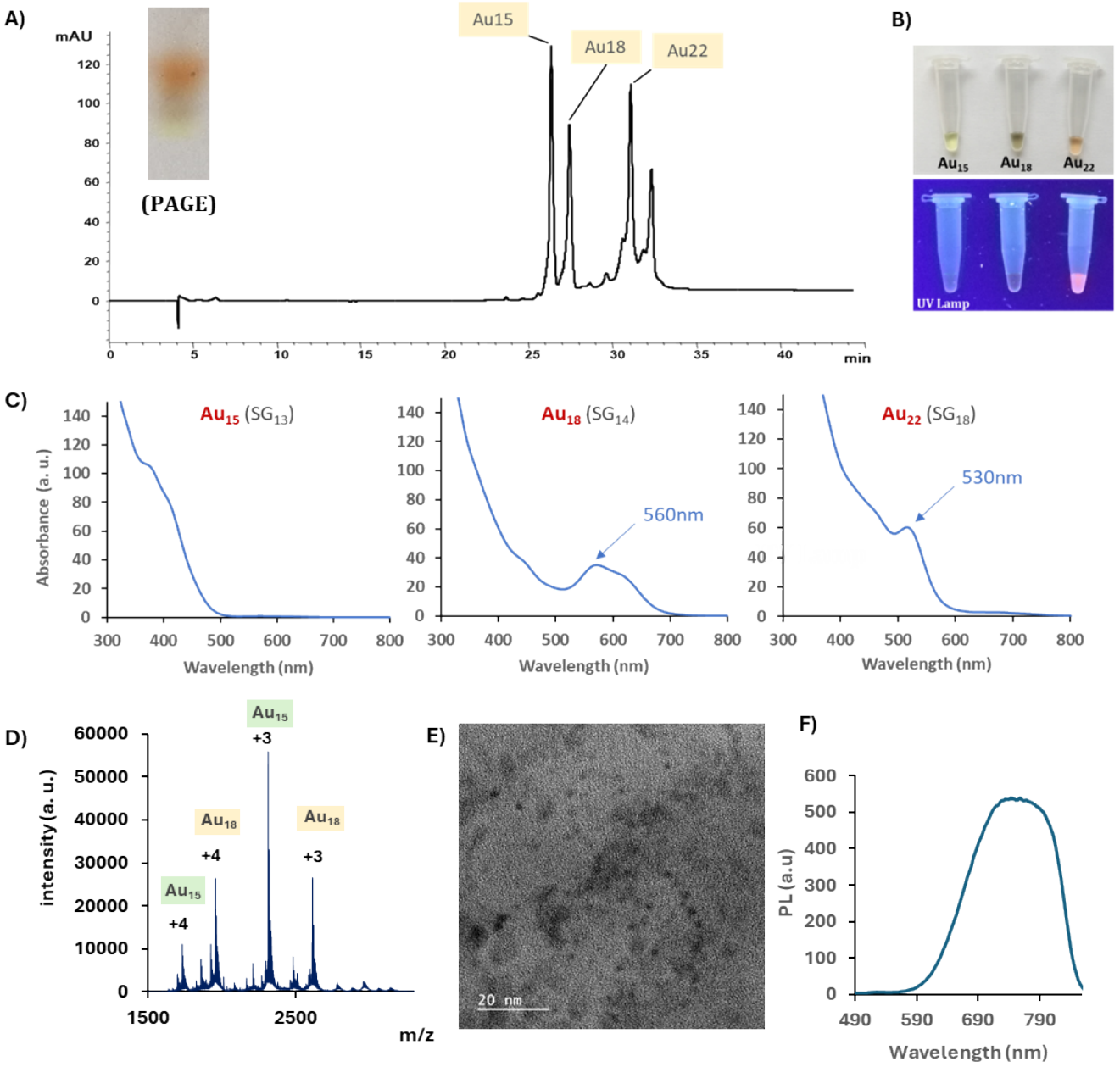


Figure S2. **A**) RP-HPLC analysis coupled with absorbance measurements of the AuSG NCs crude reaction mixture, eluted on a gradient from 0% to 6% of acetonitrile in 10 mM TEAA buffer, showing different AuNCs eluted at different retention times. Inset, photograph of PAGE analysis of the same Au(SG) crude reaction mixture. **B**) Photograph of collected AuNCs at different elution times and under UV irradiation. **C**) Corresponding absorbance measurements of each collected peak. **D**) Native ESI-MS measurement of purified $Au_{18}(SG)_{14}$. **E**) HRTEM image of $Au_{18}(SG)_{14}$. F) PL spectrum of $Au_{18}(SG)_{14}$.

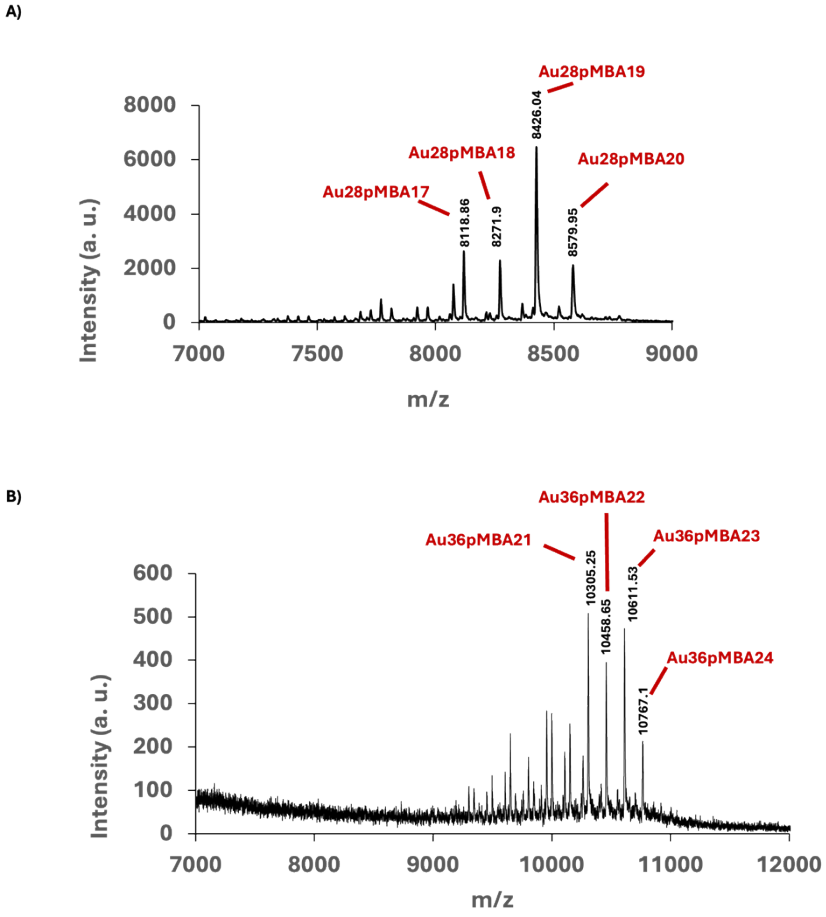


Figure S3. MALDI-ToF Mass spectrometry of purified **A**) $Au_{28}pMBA_{20}$, and **B**) $Au_{36}pMBA_{24}$.

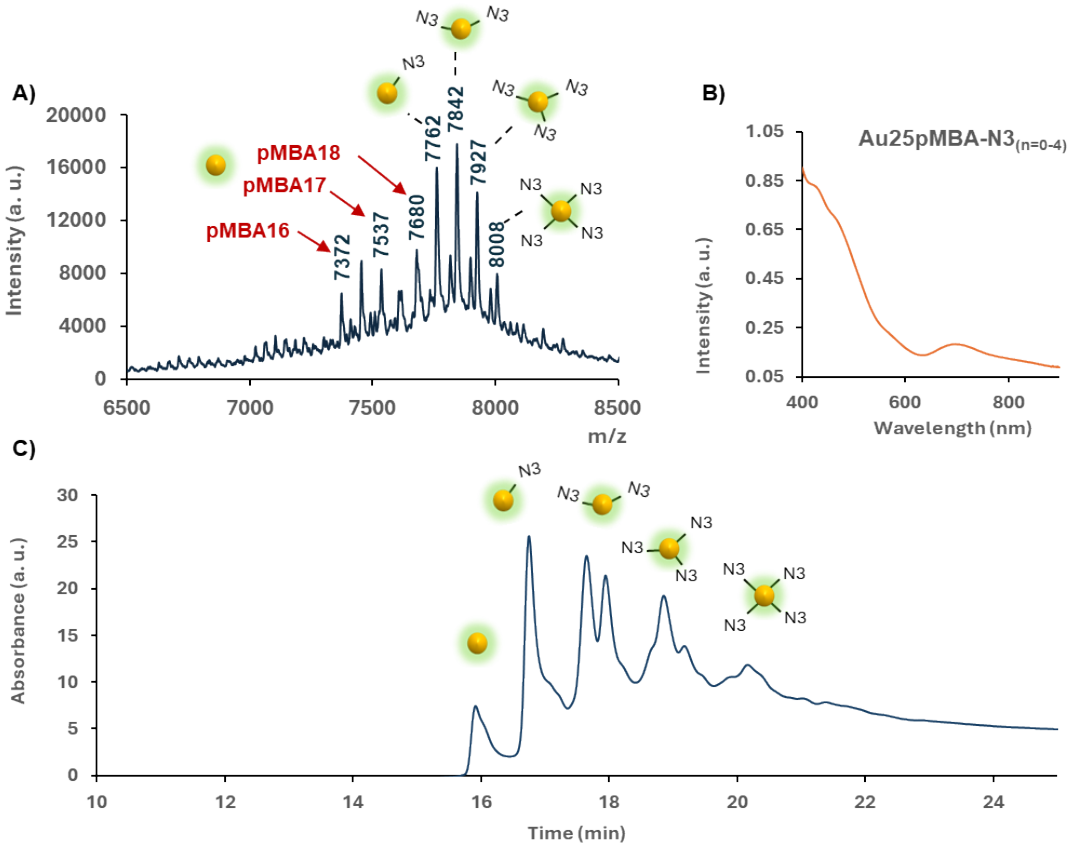


Figure S4. MALDI-ToF Mass spectrometry (**A**), absorbance spectrum (**B**), and RP-HPLC analysis (**C**) of $Au_{25}(pMBA)_{18}$ functionalized with azide (N_3) through ligand exchange with a thiol-PEG_3-N_3 linker.

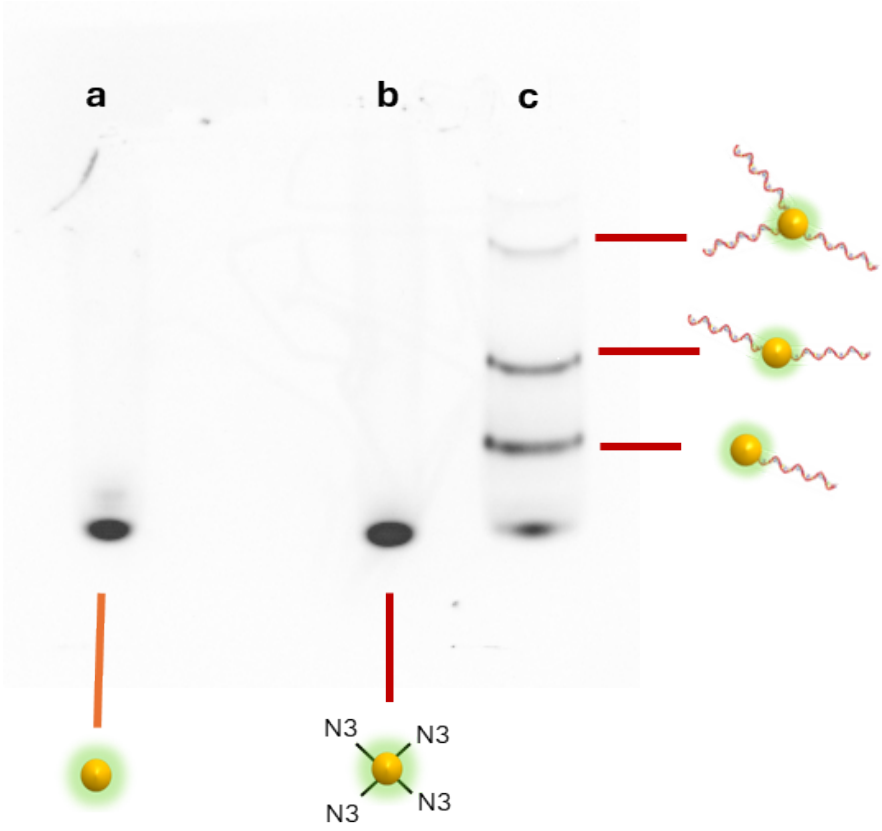


Figure S5. Native PAGE analysis for Au_{25}(pMBA)-N_3(n) clicked to 5'-BCN-15mer ODN taken by NIR-II imaging ($\lambda_{exc.}$ 808 nm; $\lambda_{em.}$ =1064-1700 nm).

Figure S6. Native PAGE analysis of ligand exchange reaction mixture of $Au_{25}(pMBA)_{18}$ conjugated with thiol-5mer.

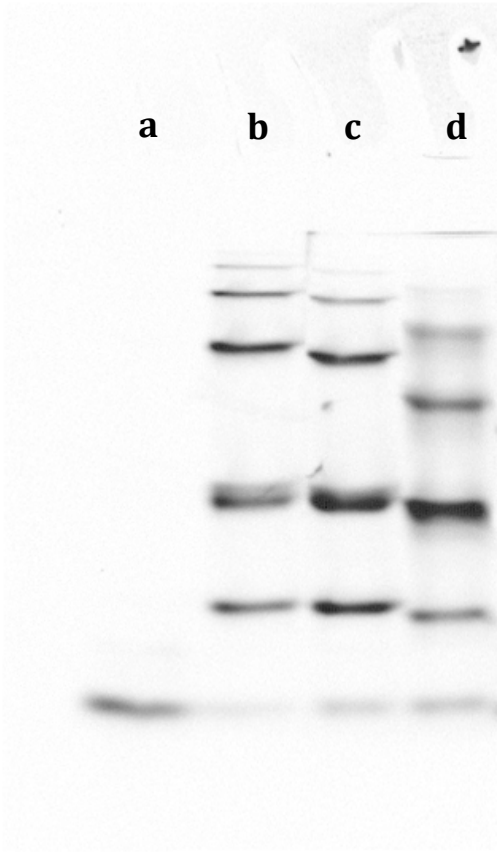


Figure S7. Native PAGE analysis of $Au_{25}(pMBA)_{18}$ conjugated with thiol-17mer (A), its complementary strand thiol-17mer (A'), and the (mid-sequence) thiol-modified-17mer (A'').

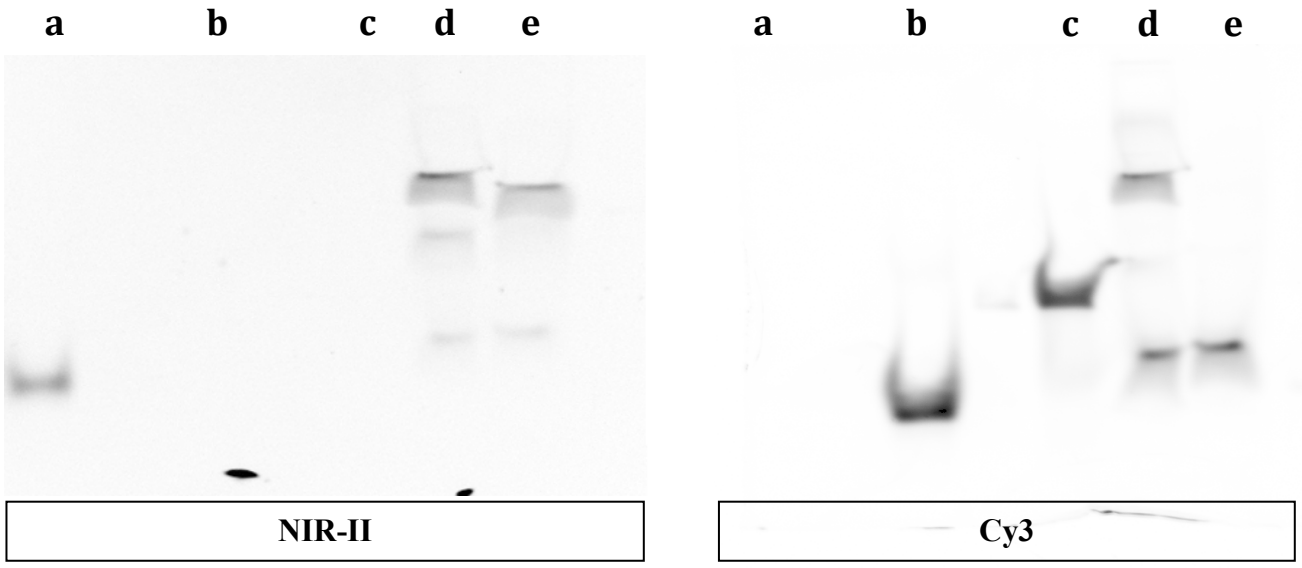


Figure S8. Native PAGE analysis of the coupling between Cy3 dye and AuNCs through DNA hybridization (17-mer). Gel imaging was recorded on the NIR-II camera (**on the left**) and on a BioRad gel imager with Cy3 filter (**on the right**).

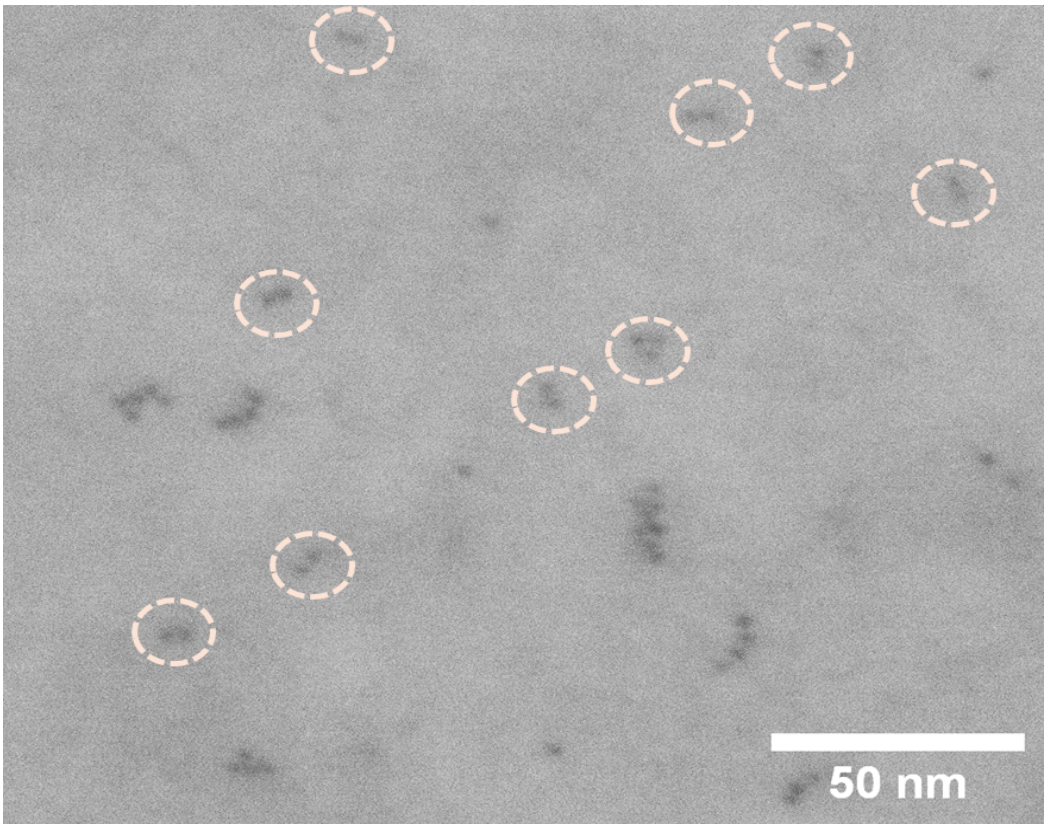


Figure S9. STEM image of Au_{25}(pMBA)-17mer dimers.

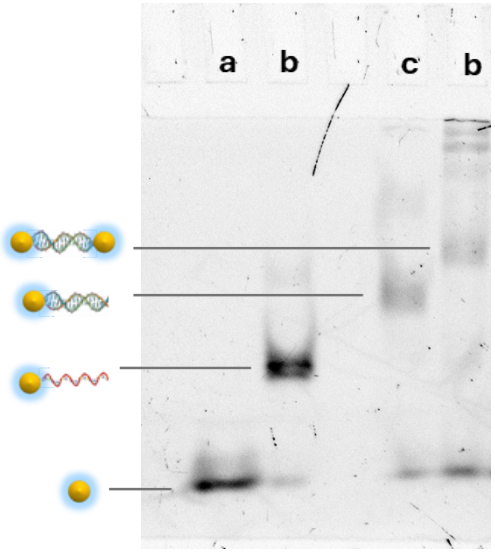


Figure S10. Native PAGE analysis of the hybridization reaction resulting in Au_{18}SG-17mer dimer structure. Image taken by BioRad gel imager with QDots705 filter.

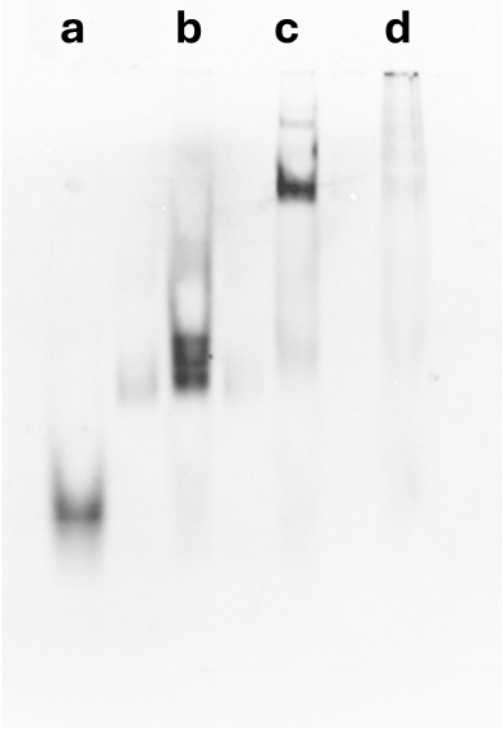


Figure S11. Native PAGE analysis of the hybridization reaction resulting in Au_{25}(pMBA)-17mer dimer and trimer structures, image taken by the NIR-II camera.