Electronic Supplementary Material (ESI) for Polymer Chemistry.

Synthesis of Monodispersed Isomeric Oligomers Based on *meta-/para-* and *linear-/star-*Monomer Precursors with Ugi-Hydrosilylation Orthogonal Cycles

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Content

1.Materials

Tetrahydrofuran (THF) was dried by reflux over Na-benzophenone complex and then distilled under argon.4-Bromoaniline (Energy Chemical,98%),3-Bromoaniline (Energy Chemical,98%), magnesium turnings for the Grignard reaction (STREM, 99%), 4-ethynylbenzaldehyde (Bide pharm, 99%), benzoic acid (Guangfu technology development Co. ,LTD, 98%) Chlorodimethylsilane (Energy Chemical,95%) isocyanocyclohexane (TCI Chemical, 98.0%), Aniline (Energy Chemical,99.5%) and 1,3,5-Tris(4-aminophenyl) benzene (Energy Chemical,97%) were used as received.

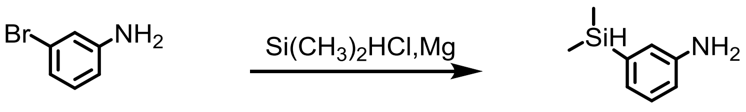
2. Analysis technique

^{1}H NMR (5wt%, $CDCl_3$) spectra were recorded on a Bruker Advance II 400MHz NMR spectrometer with $(CH_3)_4Si$ (tetramethylsilane, TMS) as an internal standard. MALDI-TOF-MS analysis was performed on a Waters MALDI micro MX mass spectrometer (Waters, Milford, CT, USA) with 2-[(2E)-3-(4-tert-butylphenyl)-2-methyprop-2-enylidene] malonitrile (DCTB) and sodium trifluoroacetate as dopants and details of the sample preparation are provided in a previous study. DSC was performed on TA Q20 at a heating rate of 10°C/min under a nitrogen atmosphere.

3. Synthetic protocols

3.1 Monomer

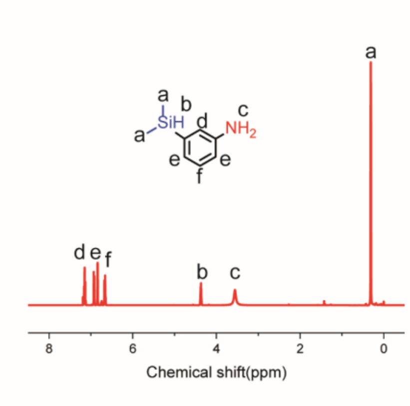
3-(dimethylsilyl)aniline



Scheme S1. Synthesis of **3-(dimethylsilyl) aniline**

To an oven-dried three-necked round-bottomed flask were added magnesium turnings (16.4g, 675mmol), then the flask was evacuated and backfilled with argon for three times. To this flask were added dimethyl chlorosilane (42.6g, 450mmol) in THF first. After that a grain of iodine and a fraction of 3-bromoaniline THF solution was added into this flask. The flask was heated until the color of iodine disappears, then the 3-bromoaniline(19.4g,112.5mmol) in

200ml THF solution was added to flask dropwise through a slow-addition apparatus. The mixture was stirred at 25°C for 18h.The mixture was then poured into n-hexane then filtered and evaporated to afford crude product. The crude product was purified through distillation to afford 3-(dimethylsilyl) aniline as colorless liquid (5.0g, yield29.4%).^{1}H NMR (500 MHz, $CDCl_3$, ppm) δ 7.18-7.11 (m, 1H), 6.97-6.80 (m, 2H), 6.71- 6.62 (m, 1H), 4.63-4.16 (m, 1H), 3.88-3.20 (m, 2H), 0.31 (dd, J = 3.8, 1.1Hz, 6H). EI-MS m/z=151.1



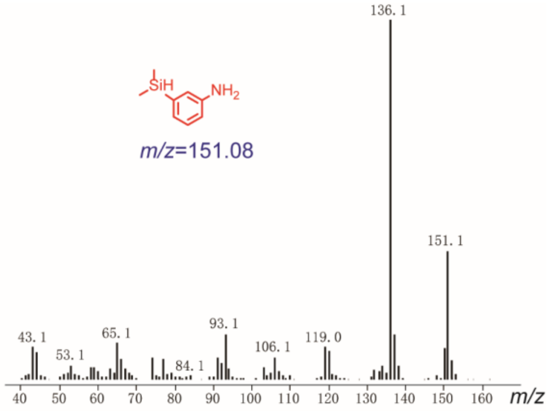
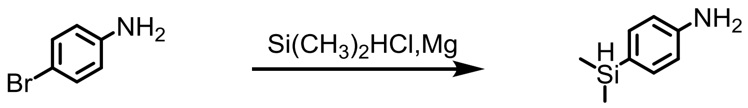


Figure S1. ^{1}H NMR spectrum of compound **3-(dimethylsilyl) aniline** in $CDCl_3$

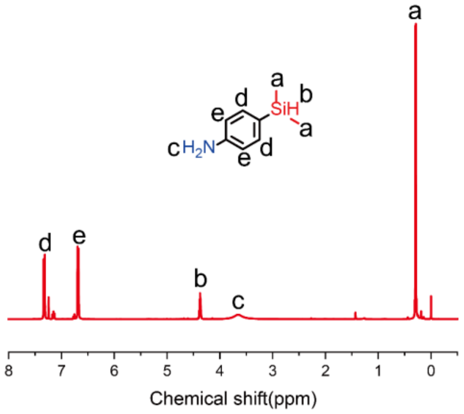
Figure S2. EI-MS spectrum of compound **3-(dimethylsilyl) aniline**

4-(dimethylsilyl)aniline



Scheme S2. Synthesis of **4-(dimethylsilyl) aniline**

To an oven-dried three-necked round-bottomed flask were added magnesium turnings (3.72g, 153mmol), then the flask was evacuated and backfilled with argon for three times. To this flask were added dimethyl chlorosilane (43.4g, 459mmol) in 100ml THF first. After that a grain of iodine and a fraction of 4-bromoaniline THF solution was added into this flask. The flask was heated until the color of iodine disappears, then the 4-bromoaniline(13.2g,76.5mmol) in 200ml THF solution was added to flask dropwise through a slow-addition apparatus. The mixture was stirred at 25°C for 18h.The mixture was then poured into n-hexane then filtered and the solvent was evaporated to afford crude product. The crude product was purified through distillation to give 4-(dimethylsilyl) aniline as colorless liquid (4,4g, yield38%). ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 7.42-7.27 (m,2H), 6.68 (d, J=8.3 Hz, 2H), 4.65-4.11 (m, 1H), 3.65 (s, 2H), 0.48-0.12 (m, 6H). EI-MS m/z=151.1



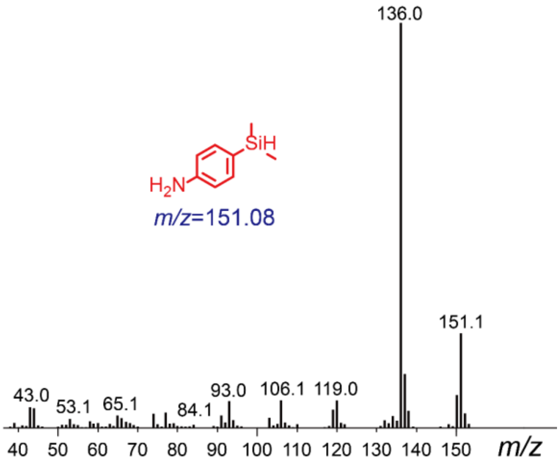


Figure S3. 1H NMR spectrum of compound **4-(dimethysilyl) aniline** in $CDCl_3$

Figure S4. EI-MS spectrum of compound **4-(dimethysilyl) aniline**

3.2 Linear Meta-oligomers

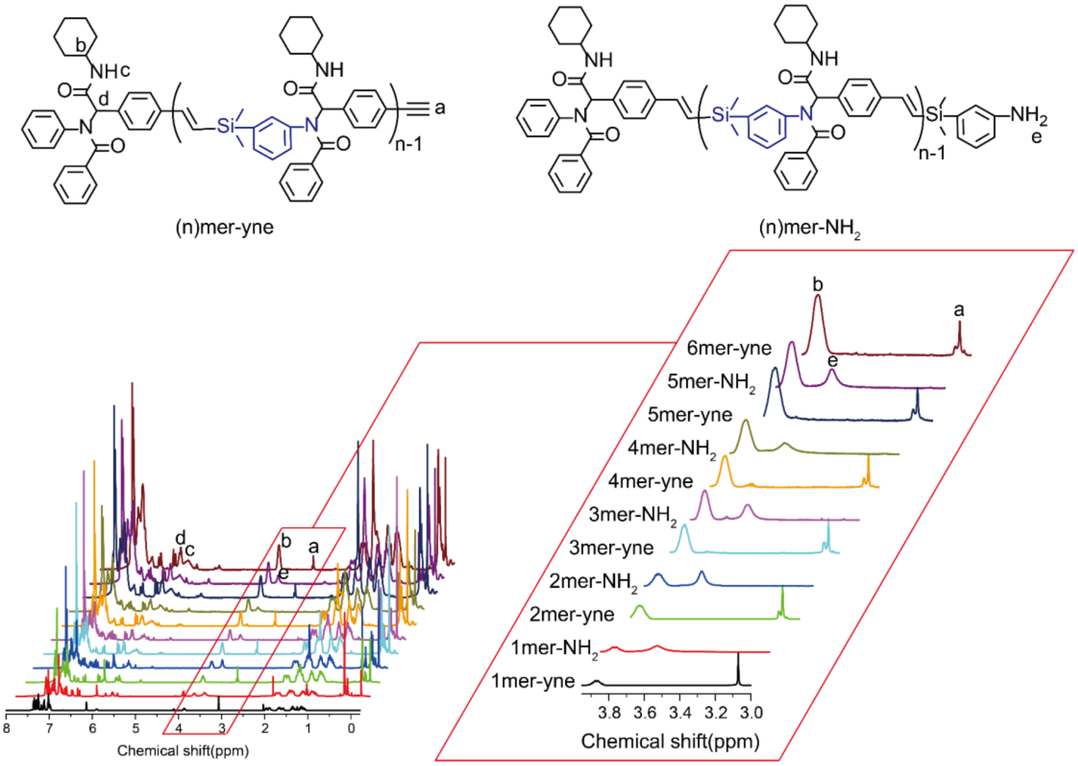


Figure S5.^{1}H NMR spectra of Meta-Oligomers

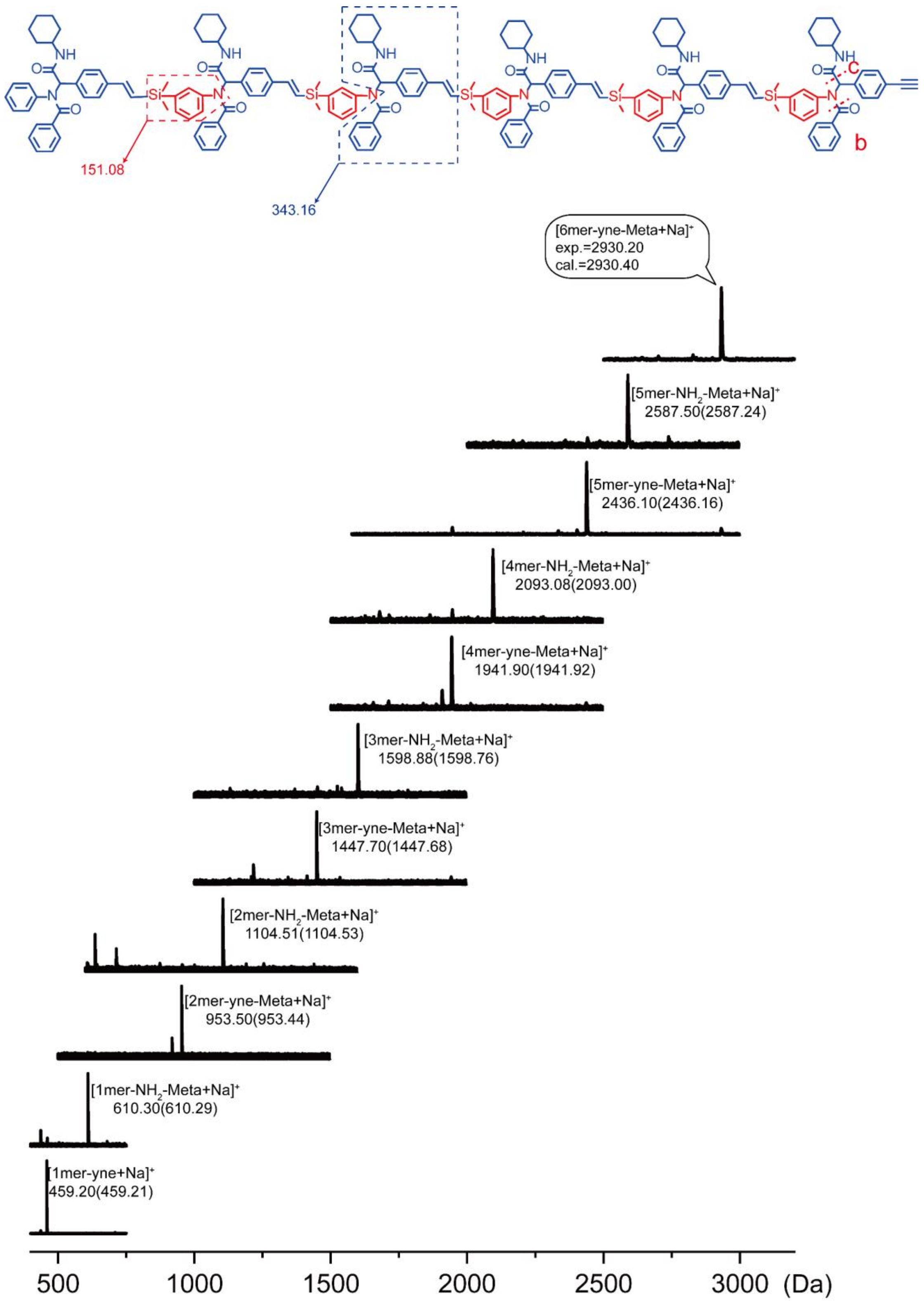
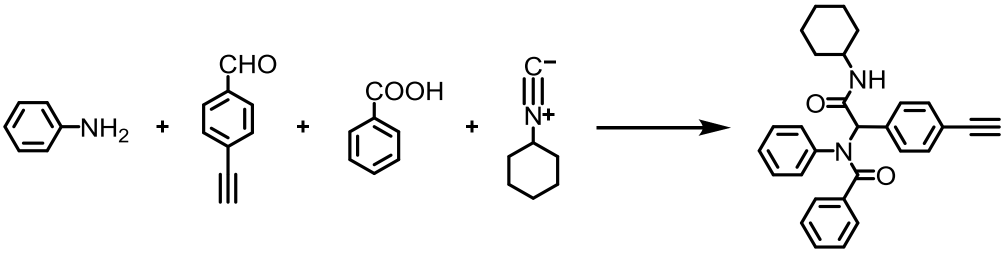


Figure S6. MALDI-TOF-MS of Meta oligomers

There are some lower peak in the spectrum. It can be attribute to the that the bond was broke down during the measurement and cut b and c down. There are also unreacted precursor and oligomer with extra amine monomer insertion.

1mer-yne



1mer-yne

Scheme S3. Synthesis of **1mer-yne**

To a round-bottomed flask were added aniline (1.00g,10.7mmol) dissolved with methanol(1.0mol/L). Then 4-ethynylbenzaldehyde(1.68g,12.9mmol) was added to the flask and stirred for 0.5h. After that benzoic acid (1.57g, 12.9mmol) was added to the flask and isocyanocyclohexane (1.76g, 16.1mol) was added to the flask lastly. The mixture was stirred at 25°C for 3d. The solvent was evaporated and the crude product was recrystallization with ethyl acetate to afford 1mer-yne as white powder (2.2g, yield47.1%).

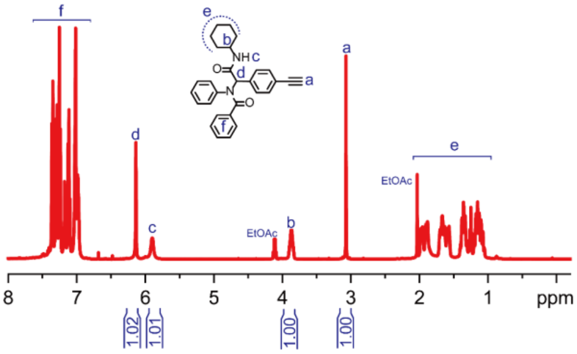
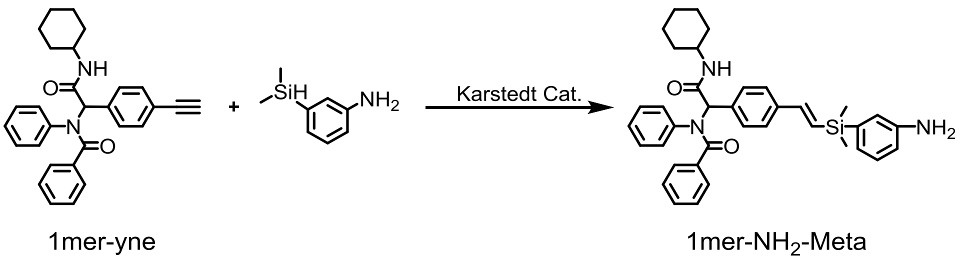


Figure S7. ^{1}H NMR spectrum of compound **1mer-yne** in $CDCl_3$

1mer-NH$_2$-Meta



Scheme S4. Synthesis of **1mer-NH$_2$-Meta**

To a round-bottomed flask filled with argon were added 1mer-yne (0.800 g, 1.83 mmol) and 3-(dimethylsilyl) aniline (0.553 g, 3.65 mmol) then the mixture was dissolved with anhydrous THF. After a drop of Karstedt catalyst was added, the solution was stirred at 25 °C for 3d. Then the solvent was evaporated to afford crude product which was purified by column chromatography over silica gel eluting with n-hexane/ethyl acetate (2/1-1/1) to give 1mer-NH$_2$-Meta as white powder (1.02 g, yield 94.8%).

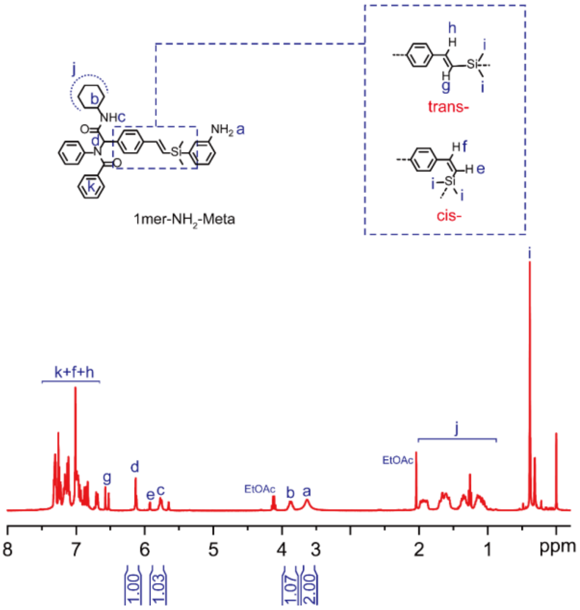
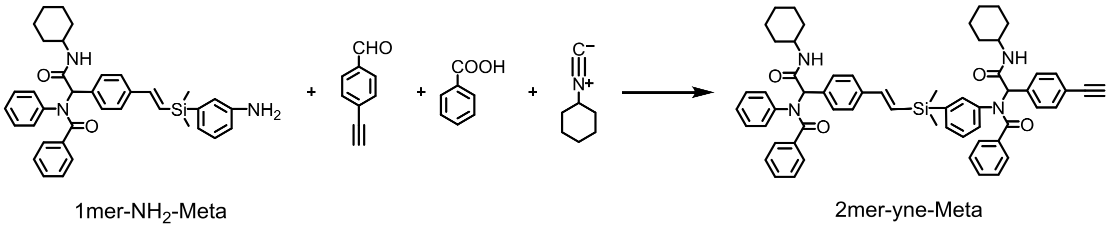


Figure S8. ^{1}H NMR spectrum of compound **1mer-NH$_2$-Meta** in CDCl$_3$

2mer-yne-Meta



Scheme S5. Synthesis of **2mer-yne-Meta**

To a round-bottomed flask were added 1mer-NH$_2$-Meta (1.00g,1.70mmol) dissolved with methanol. Then 4-ethynylbenzaldehyde (0.332g,2.55mmol) was added to the flask and stirred for 0.5h. After that benzoic acid (0.312g, 2.55mmol) was added to the flask and isocyanocyclohexane (0.371g, 3.40mmol) was added to the flask lastly. The mixture was stirred at 25^{o}C for 3d. The methanol was evaporated and the crude product was dissolved with THF and the solution was poured into n-hexane so that the crude product crash out. The crude product was precipitated using excess n-hexane and subsequently dissolved in THF, this process was repeated twice, and then the product was dried to a constant weight in a vacuum oven to afford 2mer-yne-meta as white powder (0.890g, yield59.1%).

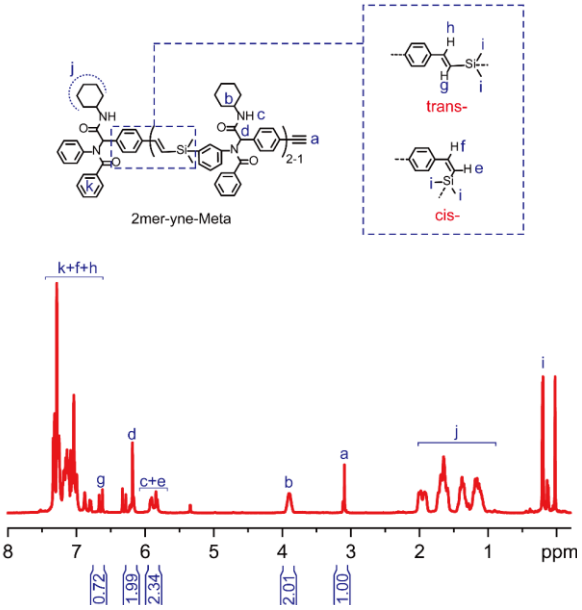
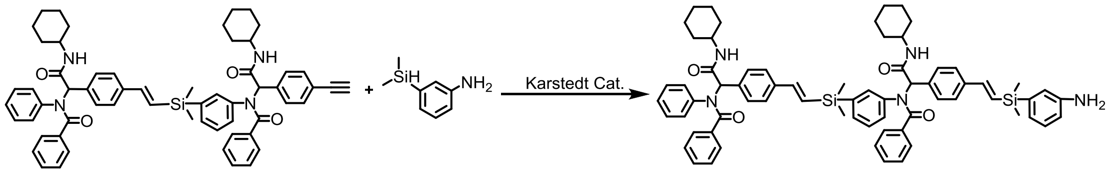


Figure S9. ^{1}H NMR spectrum of compound **2mer-yne-Meta** in CDCl$_3$

2mer-NH$_2$-Meta



2mer-yne-Meta

2mer-NH_2-Meta

Scheme S6. Synthesis of **2mer-NH_2-Meta**

To a round-bottomed flask filled with argon were added 2mer-yne-Meta (0.876g, 0.940mmol) and 3-(dimethylsilyl) aniline (0.427g, 2.82mmol) then the mixture was dissolved with anhydrous THF. After a drop of Karstedt catalyst was added, the solution was stirred at 25°C for 3d. After that the solution was poured into n-hexane so that the crude product crash out. The crude product was precipitated using excess n-hexane and subsequently dissolved in THF, this process was repeated twice, and then the product was dried to a constant weight in a vacuum oven to afford 2mer-NH_2-meta as white powder (0.690g, yield66.7%).

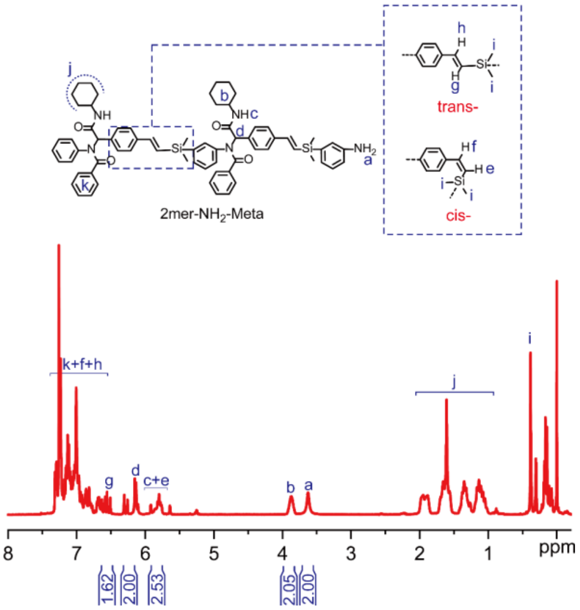
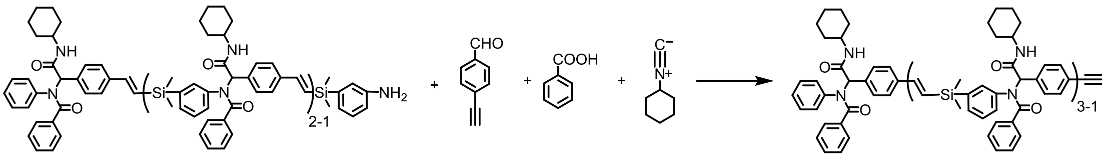


Figure S10. ^1H NMR spectrum of compound **2mer-NH_2-Meta** in $CDCl_3$

3mer-yne-Meta



2mer-NH$_2$-Meta

3mer-yne-Meta

Scheme S7. Synthesis of **3mer-yne-Meta**

To a round-bottomed flask were added 2mer-NH$_2$-Meta (0.669g,0.619mmol) dissolved with methanol. Then 4-ethynylbenzaldehyde (0.161g,1.24mmol) was added to the flask and stirred for 0.5h. After that benzoic acid (0.151g, 1.24mmol) was added to the flask and isocyanocyclohexane (0.202g, 1.85mmol) was added to the flask lastly. The mixture was stirred at 25^{o}C for 3d. The methanol was evaporated and the crude product was dissolved with THF and the solution was poured into n-hexane so that the crude product crash out. The crude product was precipitated using excess n-hexane and subsequently dissolved in THF, this process was repeated twice, and then the product was dried to a constant weight in a vacuum oven to afford 3mer-yne-meta as white powder (0.640g, yield70.4%).

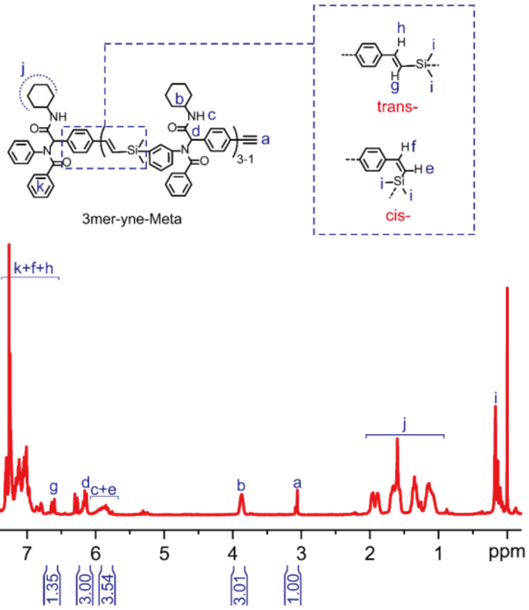
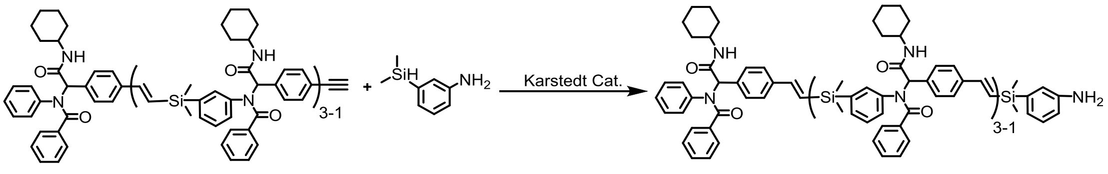


Figure S11. ^{1}H NMR spectrum of compound **3mer-yne-Meta** in CDCl$_3$

3mer-NH$_2$-Meta



3mer-yne-Meta

3mer-NH$_2$-Meta

Scheme S8. Synthesis of **3mer-NH$_2$-Meta**

To a round-bottomed flask filled with argon were added 3mer-yne-Meta (0.615g, 0.431mmol) and 3-(dimethylsilyl) aniline (0.195g, 1.29mmol) then the mixture was dissolved with anhydrous THF. After a drop of Karstedt catalyst was added, the solution was stirred at 25°C for 3d. After that the solution was poured into n-hexane so that the crude product crash out. The crude product was precipitated using excess n-hexane and subsequently dissolved in THF, this process was repeated twice, and then the product was dried to a constant weight in a vacuum oven to afford 3mer-NH$_2$-meta as white powder (0.520g, yield73.5%).

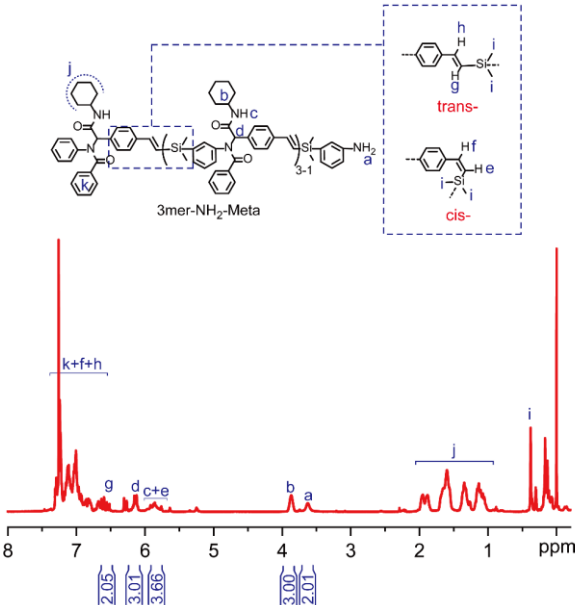
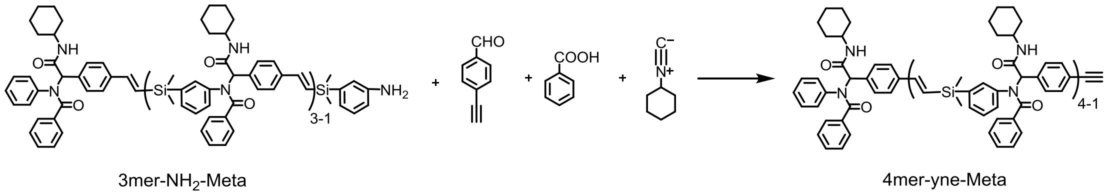


Figure S12. ^{1}H NMR spectrum of compound **3mer-NH$_2$-Meta** in CDCl$_3$

4mer-yne-Meta



Scheme S9. Synthesis of **4mer-yne-Meta**

To a round-bottomed flask were added 3mer-NH$_2$-Meta (0.500g,0.329mmol) dissolved with methanol. Then 4-ethynylbenzaldehyde (0.213g,1.64mmol) was added to the flask and stirred for 0.5h. After that benzoic acid (0.200g, 1.64mmol) was added to the flask and isocyanocyclohexane (0.359g, 3.29mmol) was added to the flask lastly. The mixture was stirred at 25°C for 3d. The methanol was evaporated and the crude product was dissolved with THF and the solution was poured into n-hexane so that the crude product crash out. The crude product was precipitated using excess n-hexane and subsequently dissolved in THF, this process was repeated twice, and then the product was dried to a constant weight in a vacuum oven to afford 4mer-yne-meta as white powder (0.490g, yield77.4%).

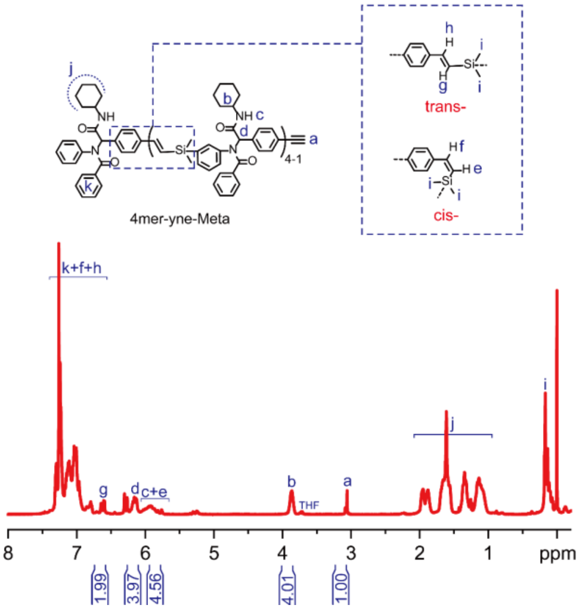
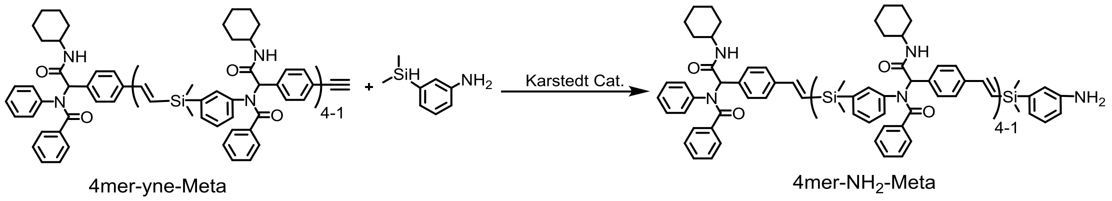


Figure S13. ^{1}H NMR spectrum of compound **4mer-yne-Meta** in $CDCl_3$

4mer-NH$_2$-Meta



Scheme S10. Synthesis of **4mer-NH$_2$-Meta**

To a round-bottomed flask filled with argon were added 4mer-yne-Meta (0.467g, 0.243mmol) and 3-(dimethylsilyl) aniline (0.110g, 0.729mmol) then the mixture was dissolved with anhydrous THF. After a drop of Karstedt catalyst was added, the solution was stirred at 25°C for 3d. After that the solution was poured into n-hexane so that the crude product crash out. The crude product was precipitated using excess n-hexane and subsequently dissolved in THF, this process was repeated twice, and then the product was dried to a constant weight in a vacuum oven to afford 4mer-NH_2-meta as white powder (0.400g, yield75.7%).

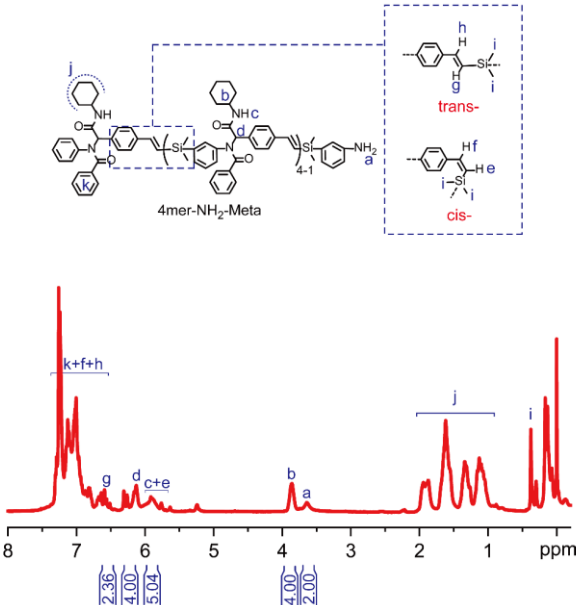
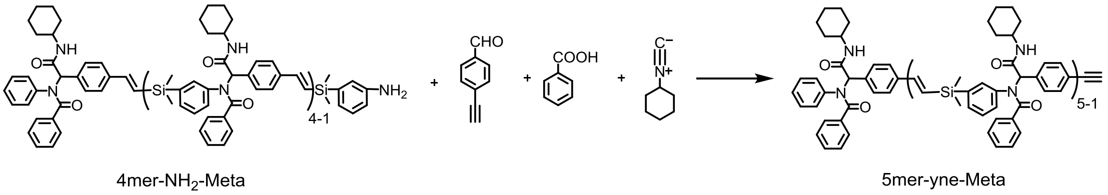


Figure S14. ^1H NMR spectrum of compound **4mer-NH_2-Meta** in $CDCl_3$

5mer-yne-Meta



Scheme S11. Synthesis of **5mer-yne-Meta**

To a round-bottomed flask were added 4mer-NH_2-Meta (0.378g,0.182mmol) dissolved with methanol. Then 4-ethynylbenzaldehyde (0.118g,0.911mmol) was added to the flask and stirred for 0.5h. After that benzoic acid (0.111g, 0.911mmol) was added to the flask and isocyanocyclohexane (0.198g, 1.82mmol) was added to the flask lastly. The mixture was stirred at 25°C for 3d. The methanol was evaporated and the crude product was dissolved with THF and the solution was poured into n-hexane so that the crude product crash out. The crude product was precipitated using excess n-hexane and subsequently dissolved in THF, this process was repeated twice, and then the product was dried to a constant weight in a vacuum oven to afford 5mer-yne-meta as white powder (0.320g, yield68.6%).

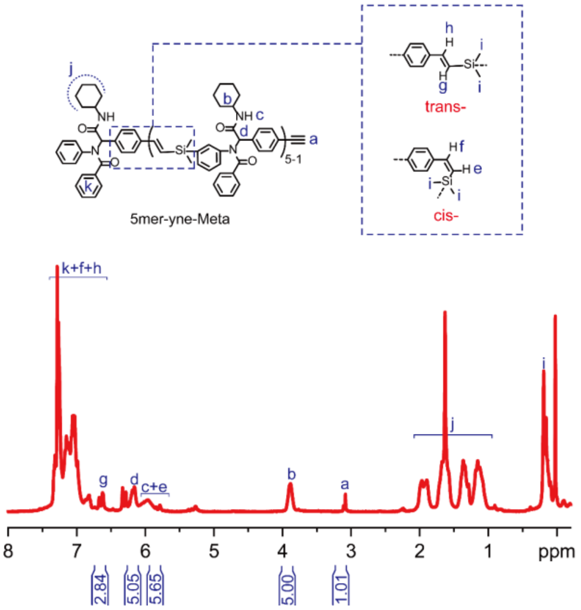
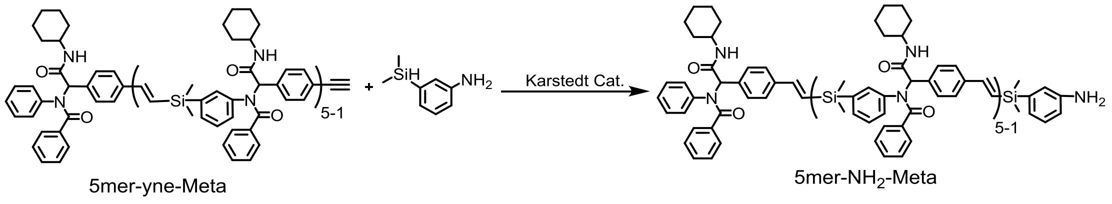


Figure S15. ^{1}H NMR spectrum of compound **5mer-yne-Meta** in $CDCl_3$

5mer-NH$_2$-Meta



Scheme S12. Synthesis of **5mer-NH$_2$-Meta**

To a round-bottomed flask filled with argon were added 5mer-yne-Meta (0.300g, 0.124mmol) and 3-(dimethylsilyl) aniline (0.0560g, 0.372mmol) then the mixture was dissolved with anhydrous THF. After a drop of Karstedt catalyst was added, the solution was stirred at 25°C for 3d. After that the solution was poured into n-hexane so that the crude product crash out. The crude product was precipitated using excess n-hexane and subsequently dissolved in THF, this process was repeated twice, and then the product was dried to a constant weight in a vacuum oven to afford 5mer-NH$_2$-meta as white powder (0.222g, yield64.7%).

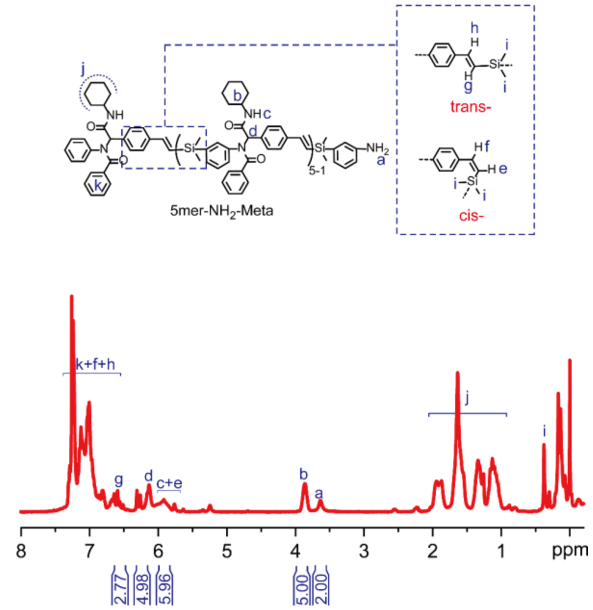
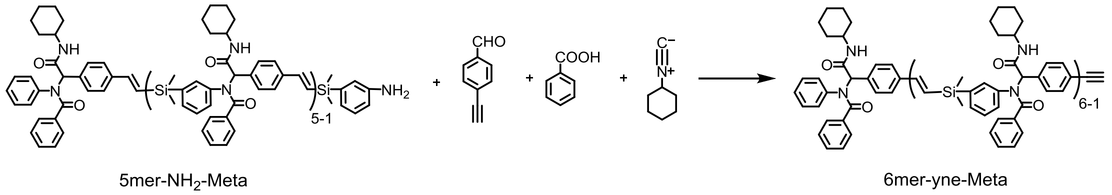


Figure S16. ^{1}H NMR spectrum of compound **5mer-NH$_2$-Meta** in CDCl$_3$

6mer-yne-Meta



Scheme S13. Synthesis of **6mer-yne-Meta**

To a round-bottomed flask were added 5mer-NH$_2$-Meta (0.202g,0.0787mmol) dissolved with methanol. Then 4-ethynylbenzaldehyde (0.0510g,0.394mmol) was added to the flask and stirred for 0.5h. After that benzoic acid (0.0480g, 0.394mmol) was added to the flask and isocyanocyclohexane (0.0860g, 0.787mmol) was added to the flask lastly. The mixture was stirred at 25^{o}C for 3d. The methanol was evaporated and the crude product was dissolved with THF and the solution was poured into n-hexane so that the crude product crash out. The crude product was precipitated using excess n-hexane and subsequently dissolved in THF, this process was repeated twice, and then the product was dried to a constant weight in a vacuum oven to afford 6mer-yne-meta as white powder (0.180g, yield72.2%).

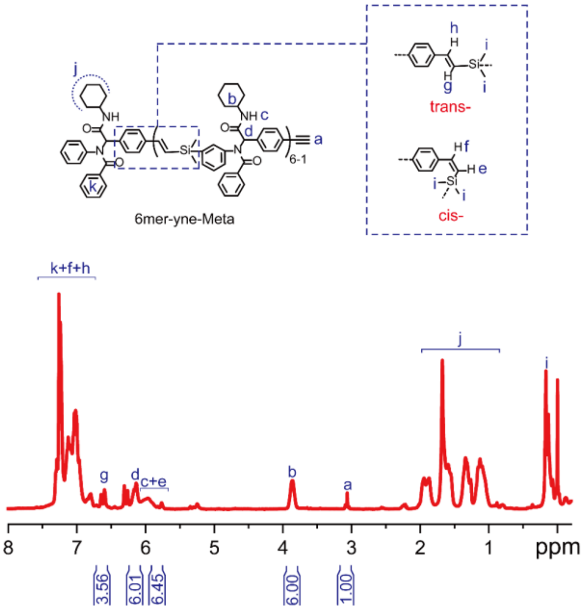


Figure S17. ^{1}H NMR spectrum of compound **6mer-yne-Meta** in $CDCl_3$

3.3 Linear Para-oligomers

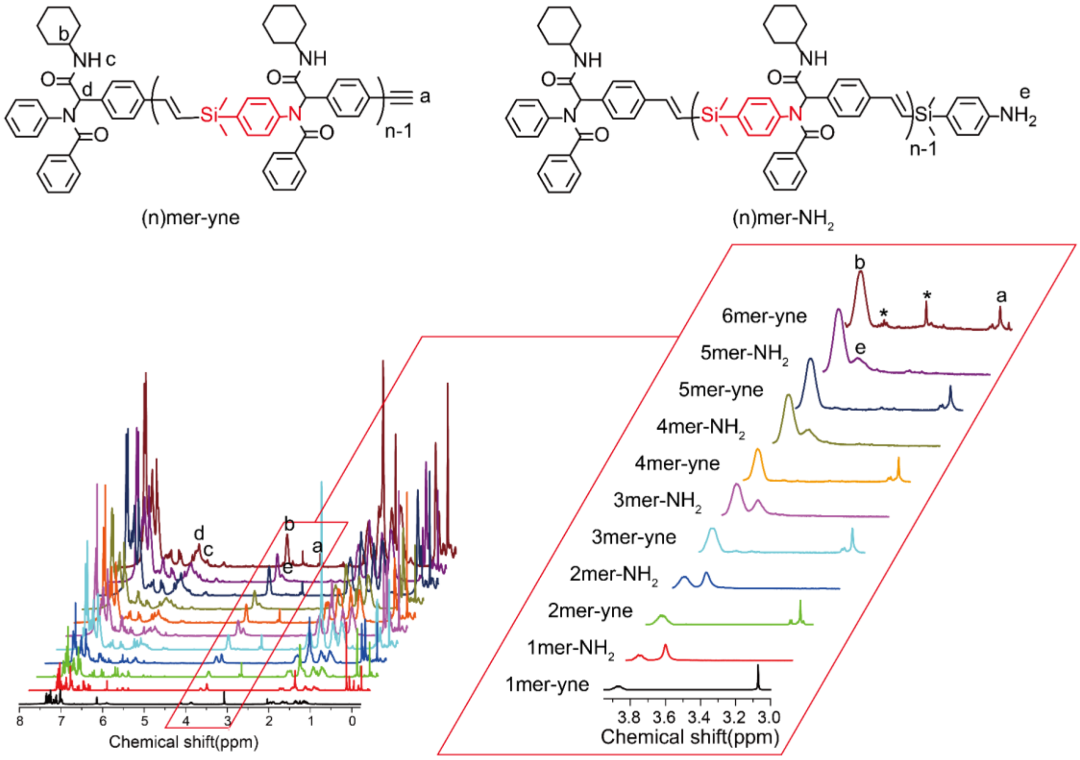


Figure S18.^{1}**H NMR spectra of Para-Oligomers**

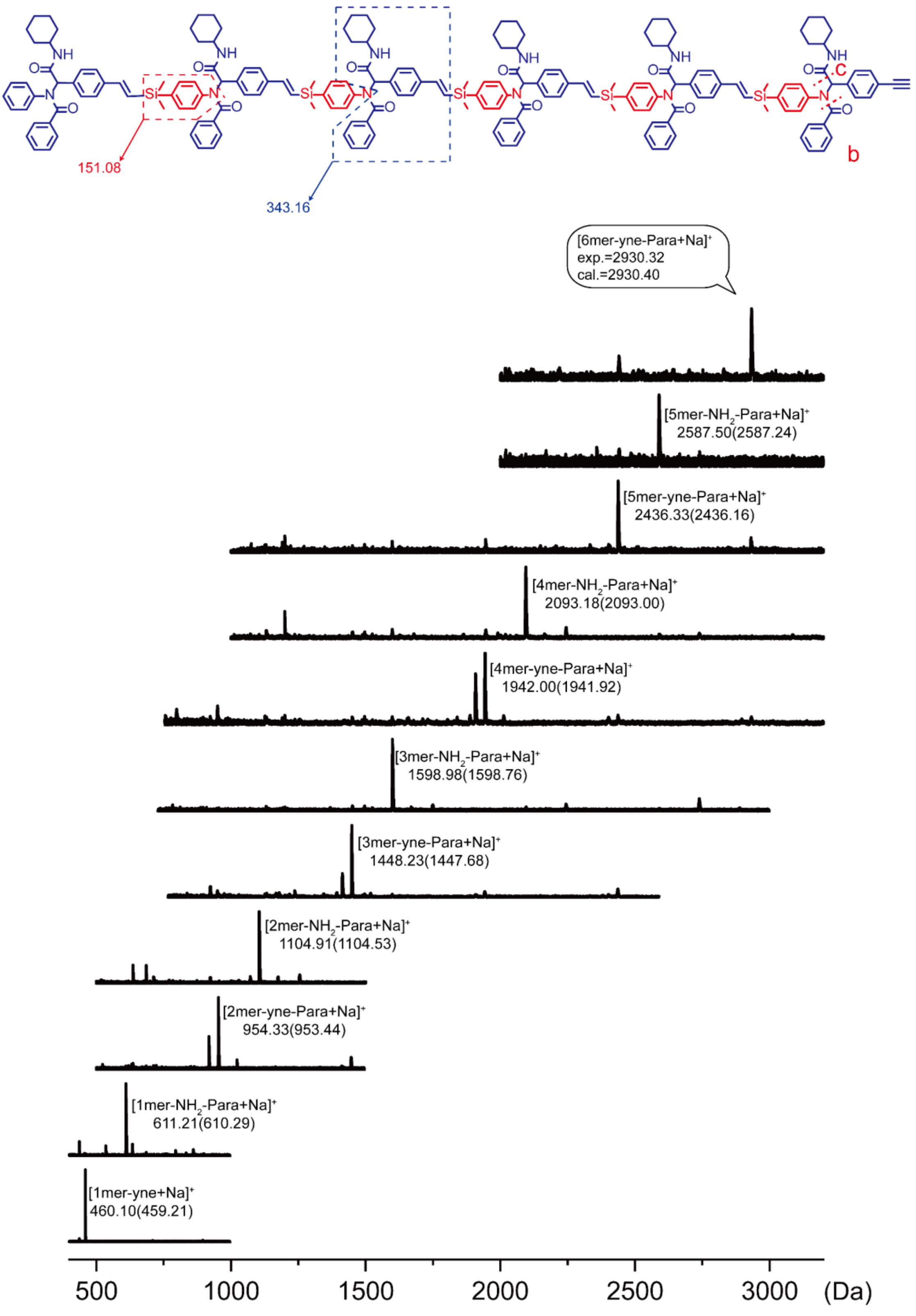
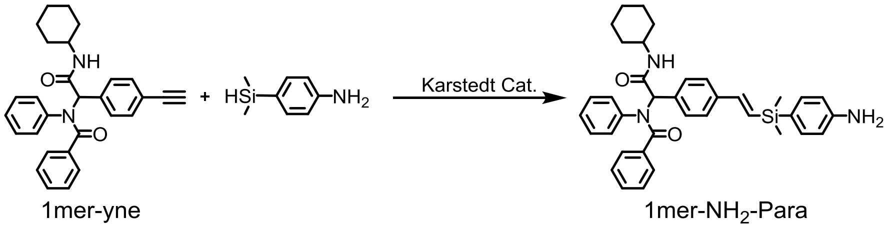


Figure S19. MALDI-TOF-MS of Para oligomers

There are some lower peak in the spectrum. It can be attribute to the that the bond was broke down during the measurement and cut b and c down. There are also unreacted precursor and oligomer with extra amine monomer insertion.

1mer-NH$_2$-Para



Scheme S14. Synthesis of **1mer-NH$_2$-Para**

To a round-bottomed flask filled with argon were added 1mer-yne (0.800g, 1.83mmol) and 4-(dimethylsilyl) aniline (0.832g, 5.50mmol) then the mixture was dissolved with anhydrous THF. After a drop of Karstedt catalyst was added, the solution was stirred at 25°C for 3d. Then the solvent was evaporated to afford crude product which was purified by column chromatography over silica gel eluting with n-hexane/ethyl acetate (2/1-1/1) to give 1mer-NH$_2$-Para as white powder (0.740g, yield68.7%).

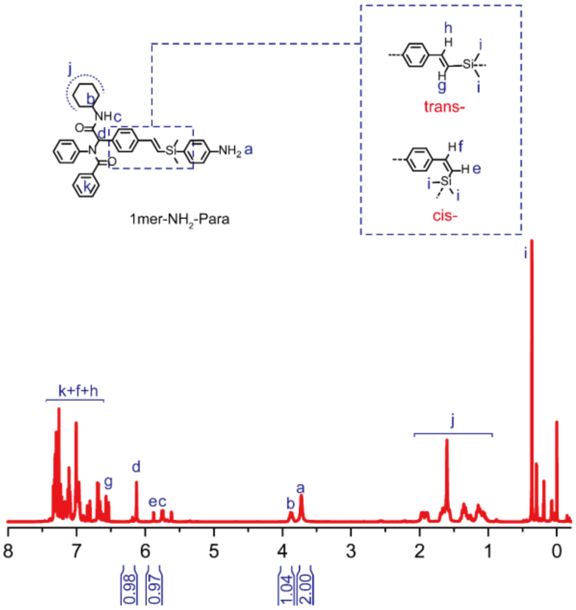
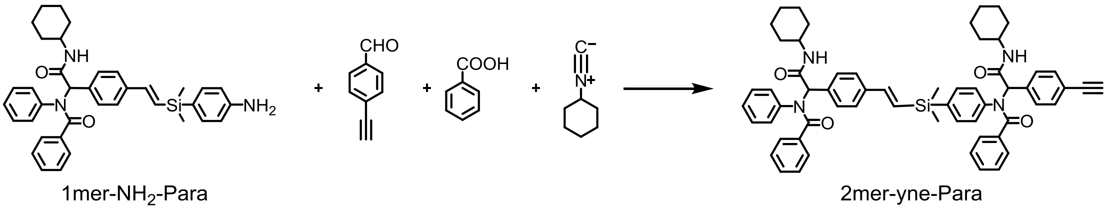


Figure S20. ^{1}H NMR spectrum of compound **1mer-NH$_2$-Para** in CDCl$_3$

2mer-yne-Para



Scheme S15. Synthesis of **2mer-yne-Para**

To a round-bottomed flask were added 1mer-NH_2-Para (0.717g,1.22mmol) dissolved with methanol. Then 4-ethynylbenzaldehyde (0.318g,2.44mmol) was added to the flask and stirred for 0.5h. After that benzoic acid (0.298g, 2.44mmol) was added to the flask and isocyanocyclohexane (0.399g, 3.66mmol) was added to the flask lastly. The mixture was stirred at 25^{o}C for 3d. The methanol was evaporated and the crude product was dissolved with THF and the solution was poured into n-hexane so that the crude product crash out. The crude product was precipitated using excess n-hexane and subsequently dissolved in THF, this process was repeated twice, and then the product was dried to a constant weight in a vacuum oven to afford 2mer-yne-para as white powder (0.720g, yield61.4%).

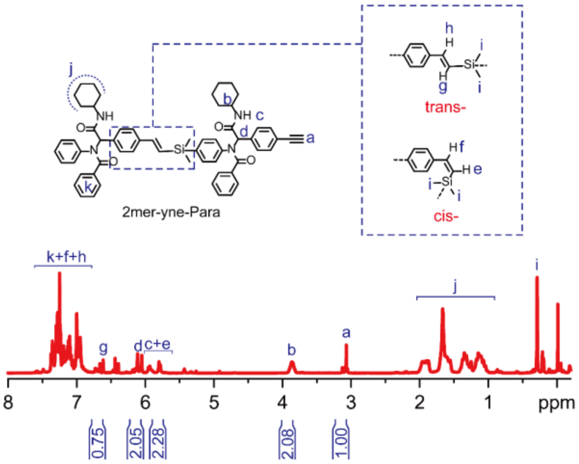
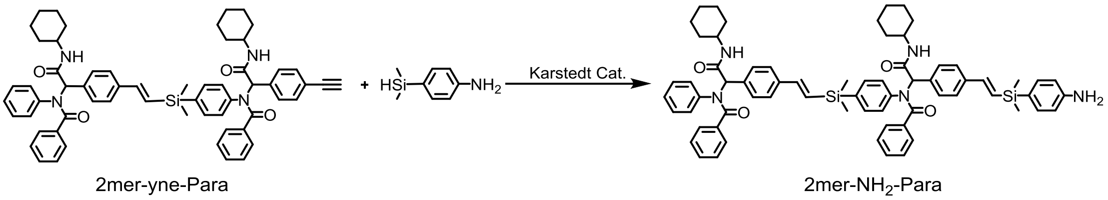


Figure S21. ^{1}H NMR spectrum of compound **2mer-yne-Para** in $CDCl_3$

2mer-NH$_2$-Para



Scheme S16. Synthesis of **2mer-NH$_2$-Para**

To a round-bottomed flask filled with argon were added 2mer-yne-Para (0.699g, 0.750mmol) and 4-(dimethylsilyl) aniline (0.340g, 2.25mmol) then the mixture was dissolved with anhydrous THF. After a drop of Karstedt catalyst was added, the solution was stirred at 25 °C for 3d. After that the solution was poured into n-hexane so that the crude product crash out. The crude product was precipitated using excess n-hexane and subsequently dissolved in THF, this process was repeated twice, and then the product was dried to a constant weight in a vacuum oven to afford 2mer-NH_2-para as white powder (0.461g, yield55.0%).

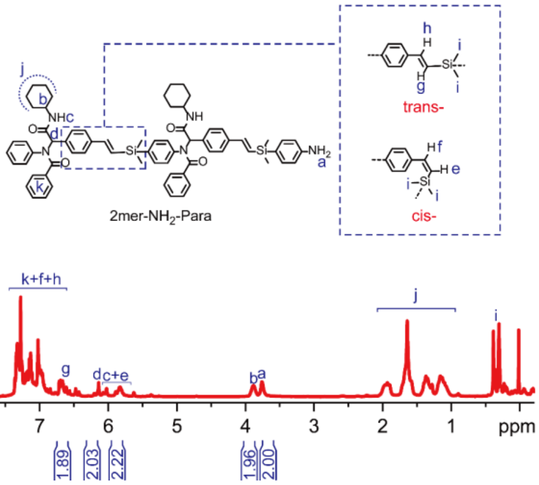
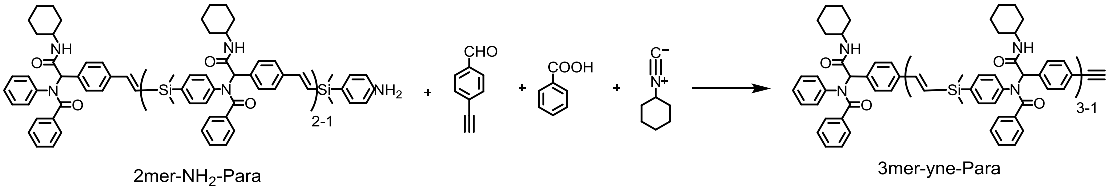


Figure S22. ^{1}H NMR spectrum of compound **2mer-NH_2-Para** in $CDCl_3$

3mer-yne-Para



Scheme S17. Synthesis of **3mer-yne-Para**

To a round-bottomed flask were added 2mer-NH_2-Para (0.443g,0.410mmol) dissolved with methanol. Then 4-ethynylbenzaldehyde (0.106g,0.819mmol) was added to the flask and stirred for 0.5h. After that benzoic acid (0.100g, 0.819mmol) was added to the flask and isocyanocyclohexane (0.134g, 1.23mmol) was added to the flask lastly. The mixture was stirred at 25°C for 3d. The methanol was evaporated and the crude product was dissolved with THF and the solution was poured into n-hexane so that the crude product crash out. The crude product was precipitated using excess n-hexane and subsequently dissolved in THF, this process was repeated twice, and then the product was dried to a constant weight in a vacuum oven to afford 3mer-yne-para as white powder (0.432g, yield71.0%).^{1}H NMR (400 MHz, $CDCl_3$).

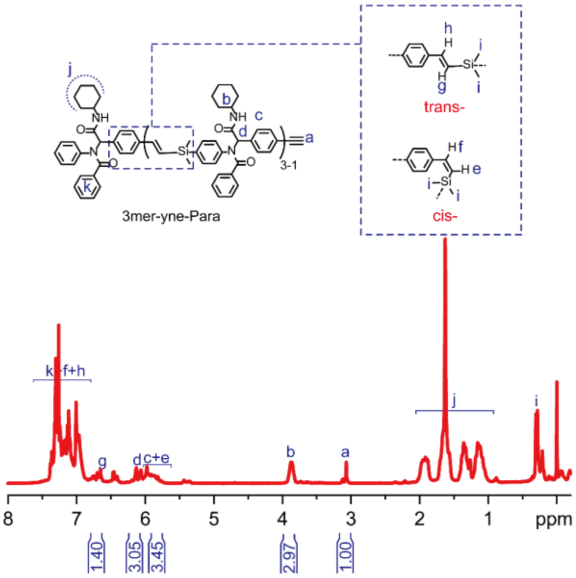
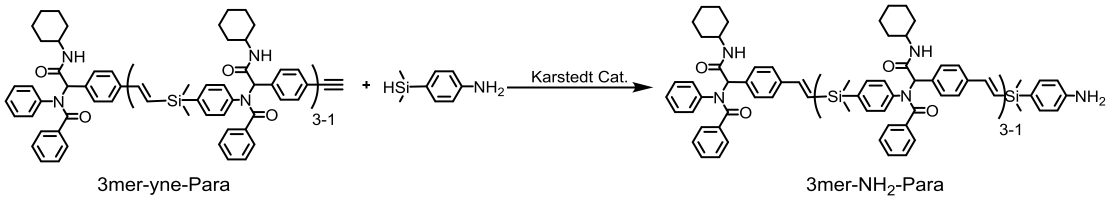


Figure S23. ^{1}H NMR spectrum of compound **3mer-yne-Para** in $CDCl_3$

3mer-NH_2-Para



Scheme S18. Synthesis of **3mer-NH_2-Para**

To a round-bottomed flask filled with argon were added 3mer-yne-Para (0.410g, 0.287mmol) and 4-(dimethylsilyl) aniline (0.130g, 0.862mmol) then the mixture was dissolved with anhydrous THF. After a drop of Karstedt catalyst was added, the solution was stirred at 25°C for 3d. After that the solution was poured into n-hexane so that the crude product crash out. The crude product was precipitated using excess n-hexane and subsequently dissolved in THF, this process was repeated twice, and then the product was dried to a constant weight in a vacuum oven to afford 3mer-NH_2-para as white powder (0.319g, yield67.3%).^{1}H NMR (400 MHz, $CDCl_3$).

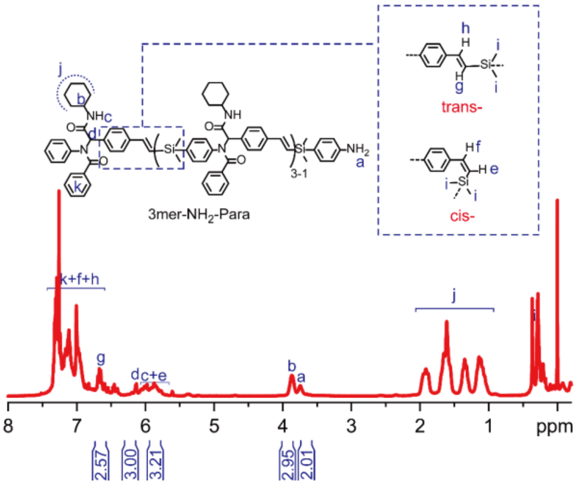
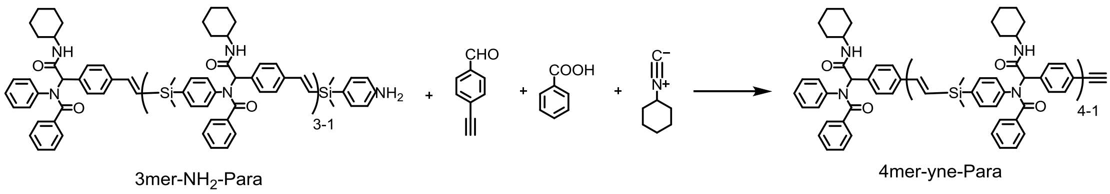


Figure S24. ${}^1H$ NMR spectrum of compound **3mer-NH$_2$-Para** in $CDCl_3$

4mer-yne-Para



Scheme S19. Synthesis of **4mer-yne-Para**

To a round-bottomed flask were added 3mer-NH$_2$-Para (0.300g,0.197mmol) dissolved with methanol. Then 4-ethynylbenzaldehyde (0.128g,0.987mmol) was added to the flask and stirred for 0.5h. After that benzoic acid (0.120g, 0.987mmol) was added to the flask and isocyanocyclohexane (0.215g, 1.97mmol) was added to the flask lastly. The mixture was stirred at 25°C for 3d. The methanol was evaporated and the crude product was dissolved with THF and the solution was poured into n-hexane so that the crude product crash out. The crude product was precipitated using excess n-hexane and subsequently dissolved in THF, this process was repeated twice, and then the product was dried to a constant weight in a vacuum oven to afford 4mer-yne-para as white powder (0.272g, yield69.3%).

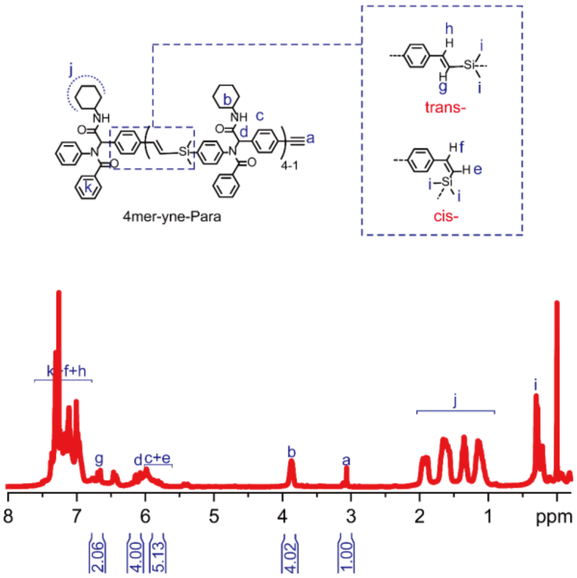
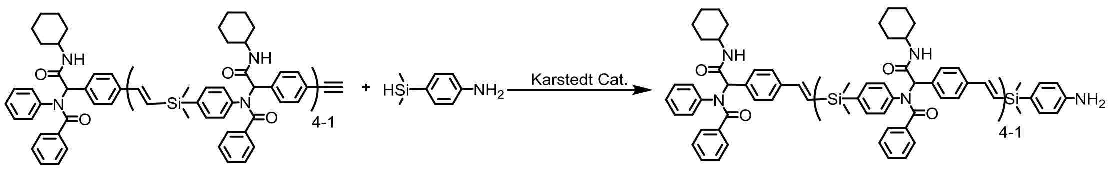


Figure S25. ^1H NMR spectrum of compound **4mer-yne-Para** in $CDCl_3$

4mer-NH$_2$-Para



Scheme S20. Synthesis of **4mer-NH$_2$-Para**

To a round-bottomed flask filled with argon were added 4mer-yne-Para (0.250g, 0.130mmol) and 4-(dimethylsilyl) aniline (0.0590g, 0.390mmol) then the mixture was dissolved with anhydrous THF. After a drop of Karstedt catalyst was added, the solution was stirred at 25°C for 3d. After that the solution was poured into n-hexane so that the crude product crash out. The crude product was precipitated using excess n-hexane and subsequently dissolved in THF, this process was repeated twice, and then the product was dried to a constant weight in a vacuum oven to afford 4mer-NH$_2$-para as white powder (0.203g, yield68.7%).

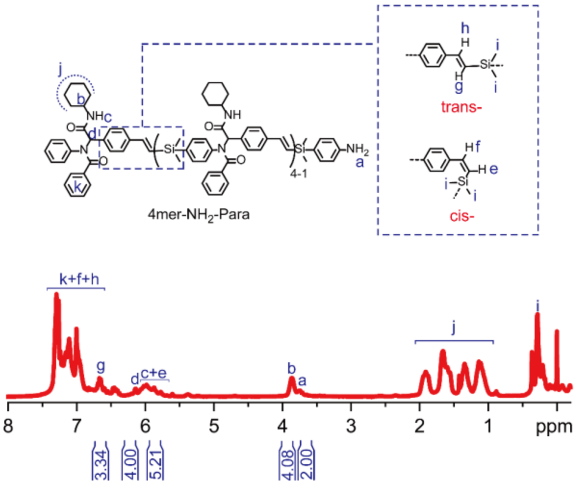
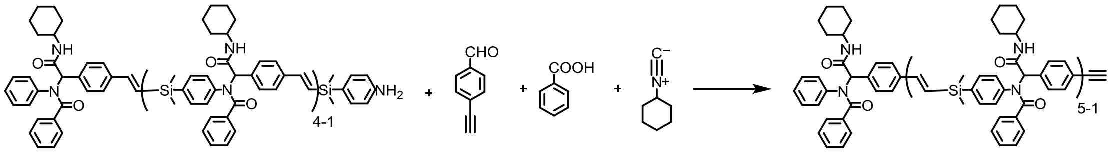


Figure S26. ^{1}H NMR spectrum of compound **4mer-NH$_2$-Para** in $CDCl_3$

5mer-yne-Para



4mer-NH$_2$-Para

5mer-yne-Para

Scheme S21. Synthesis of **5mer-yne-Para**

To a round-bottomed flask were added 4mer-NH$_2$-Para (0.173g,0.0836mmol) dissolved with methanol. Then 4-ethynylbenzaldehyde (0.0544g,0.418mmol) was added to the flask and stirred for 0.5h. After that benzoic acid (0.0510g, 0.418mmol) was added to the flask and isocyanocyclohexane (0.0913g, 0.836mmol) was added to the flask lastly. The mixture was stirred at 25^{o}C for 3d. The methanol was evaporated and the crude product was dissolved with THF and the solution was poured into n-hexane so that the crude product crash out. The crude product was precipitated using excess n-hexane and subsequently dissolved in THF, this process was repeated twice, and then the product was dried to a constant weight in a vacuum oven to afford 5mer-yne-para as white powder (0.138g, yield60.0%).

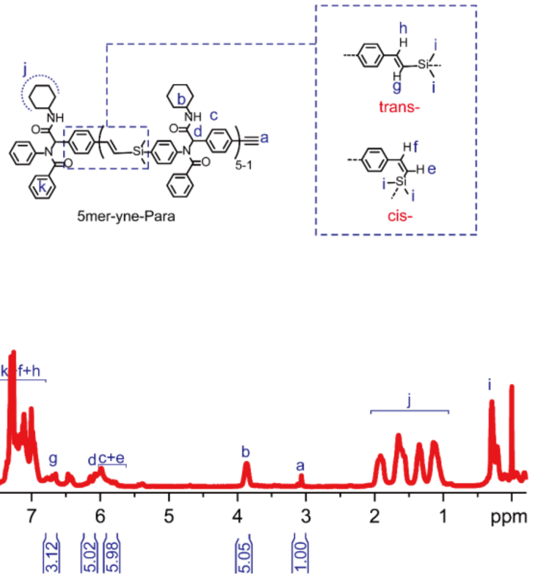
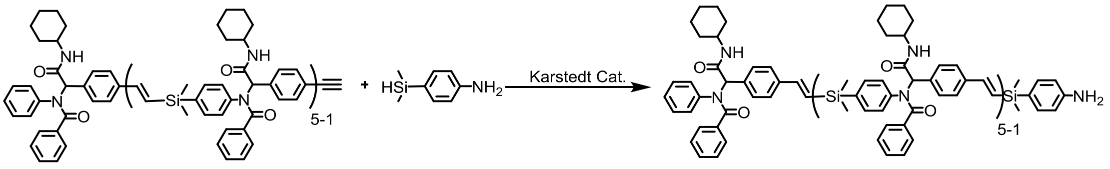


Figure S27. ^{1}H NMR spectrum of compound **5mer-yne-Para** in $CDCl_3$

5mer-NH$_2$-Para



5mer-yne-Para

5mer-NH$_2$-Para

Scheme S22. Synthesis of **5mer-NH$_2$-Para**

To a round-bottomed flask filled with argon were added 5mer-yne-Para (0.116g, 0.0480mmol) and 4-(dimethylsilyl) aniline (0.0218g, 0.144mmol) then the mixture was dissolved with anhydrous THF. After a drop of Karstedt catalyst was added, the solution was stirred at 25°C for 3d. After that the solution was poured into n-hexane so that the crude product crash out. The crude product was precipitated using excess n-hexane and subsequently dissolved in THF, this process was repeated twice, and then the product was dried to a constant weight in a vacuum oven to afford 5mer-NH$_2$-para as white powder (0.103g, yield67.2%).

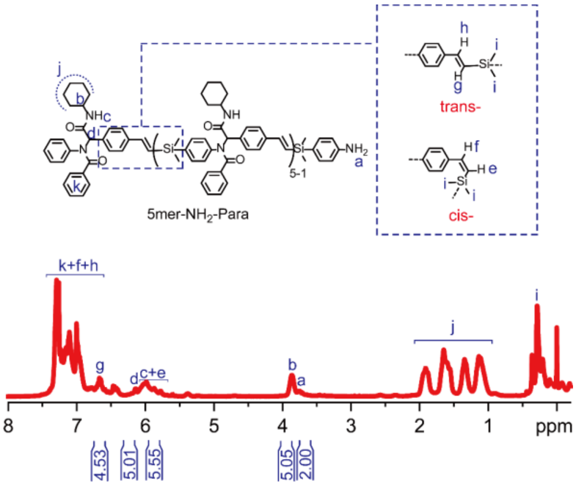
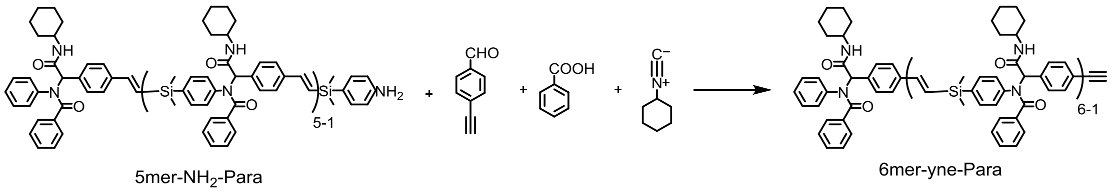


Figure S28. ^1H NMR spectrum of compound **5mer-NH$_2$-Para** in $CDCl_3$

6mer-yne-Para



Scheme S23. Synthesis of **6mer-yne-Para**

To a round-bottomed flask were added 5mer-NH$_2$-Para (0.0777g,0.030mmol) dissolved with methanol. Then 4-ethynylbenzaldehyde (0.0078g,0.060mmol) was added to the flask and stirred for 0.5h. After that benzoic acid (0.0074g, 0.060mmol) was added to the flask and isocyanocyclohexane (0.0098g, 0.090mmol) was added to the flask lastly. The mixture was stirred at 25^{o}C for 3d. The methanol was evaporated and the crude product was dissolved with THF and the solution was poured into n-hexane so that the crude product crash out. The crude product was precipitated using excess n-hexane and subsequently dissolved in THF, this process was repeated twice, and then the product was dried to a constant weight in a vacuum oven to afford 6mer-yne-para as white powder (0.0628g, yield72.2%).

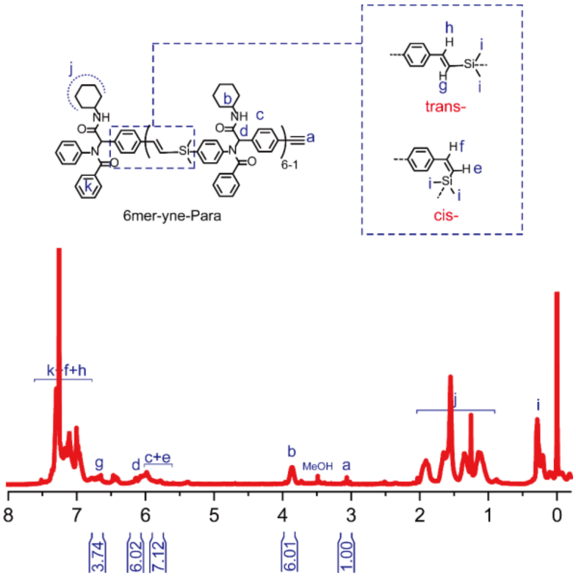
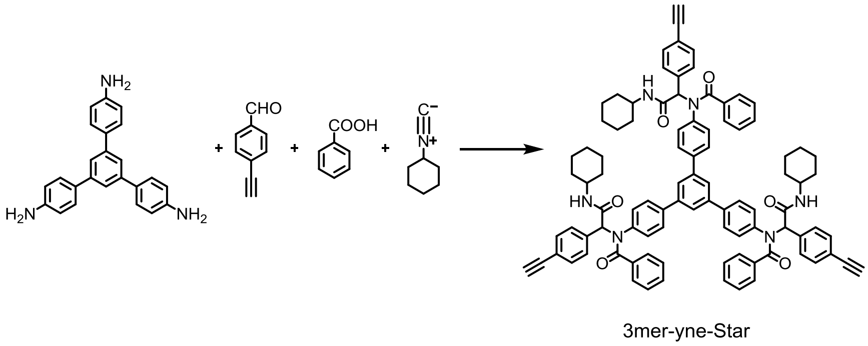


Figure S29. ^{1}H NMR spectrum of compound **6mer-yne-Para** in $CDCl_3$

3.4 Star-shaped Meta-oligomers

3mer-yne-Star



Scheme S24. Synthesis of **3mer-yne-Star**

To a round-bottomed flask were added 1,3,5-Tris(4-aminophenyl) benzene (0.500g,1.42mmol) dissolved with methanol and DMF. Then 4-ethynylbenzaldehyde (0.831g,6.39mmol) was added to the flask and stirred for 0.5h. After that benzoic acid (0.780g, 6.39mmol) was added to the flask and isocyanocyclohexane (0.930g, 8.52mmol) was added to the flask lastly. The mixture was stirred at 25°C for 3d. The methanol was evaporated and DMF was evacuated by vacuum pump. After that the crude product was dissolved with THF and the solution was poured into n-hexane so that the crude product crash out. The crude product was precipitated using excess n-hexane and subsequently dissolved in THF, this process was repeated twice, and then the product was dried to a constant weight in a vacuum oven to afford 3mer-yne-Star as white powder (1.80g, yield91.8%).

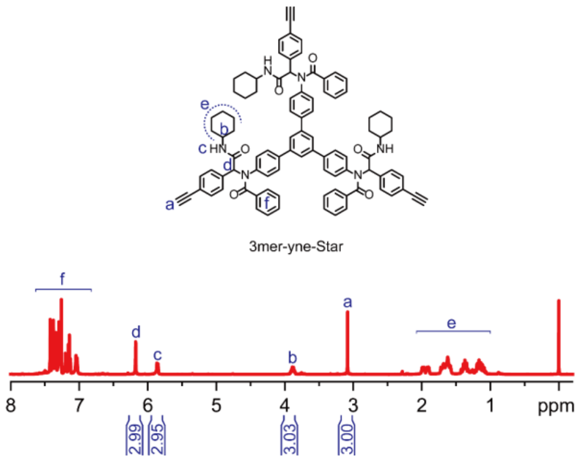
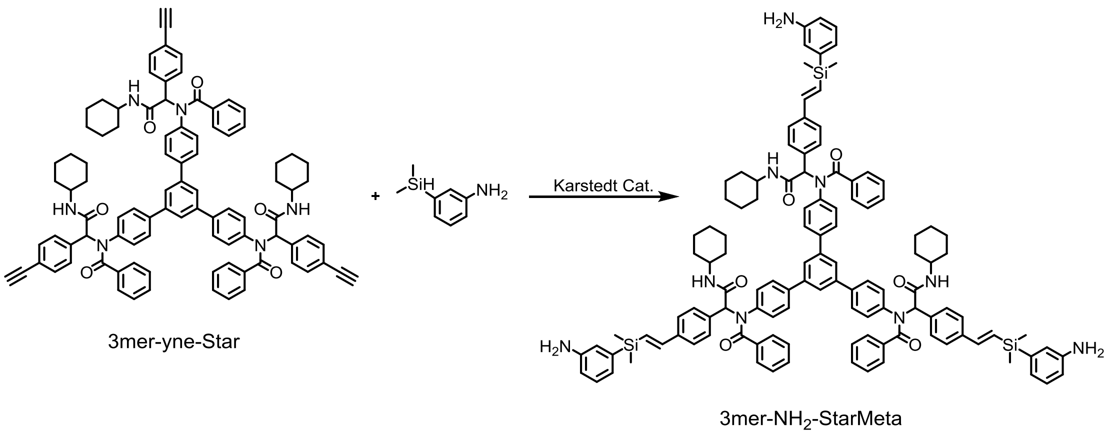


Figure S30. ^{1}H NMR spectrum of compound **3mer-yne-Star** in $CDCl_3$

3mer-NH$_2$-StarMeta



Scheme S25. Synthesis of **3mer-NH$_2$-StarMeta**

To a round-bottomed flask filled with argon were added 3mer-yne-Star (0.600g, 0.434mmol) and 3-(dimethylsilyl) aniline (0.591g, 3.91mmol) then the mixture was dissolved with anhydrous THF. After a drop of Karstedt catalyst was added, the solution was stirred at 25°C for 3d. After that the solution was poured into n-hexane so that the crude product crash out. The crude product was precipitated using excess n-hexane and subsequently dissolved in THF, this process was repeated twice, and then the product was dried to a constant weight in a vacuum oven to afford 3mer-NH$_2$-StarMeta as white powder (0.613g, yield77.0%).

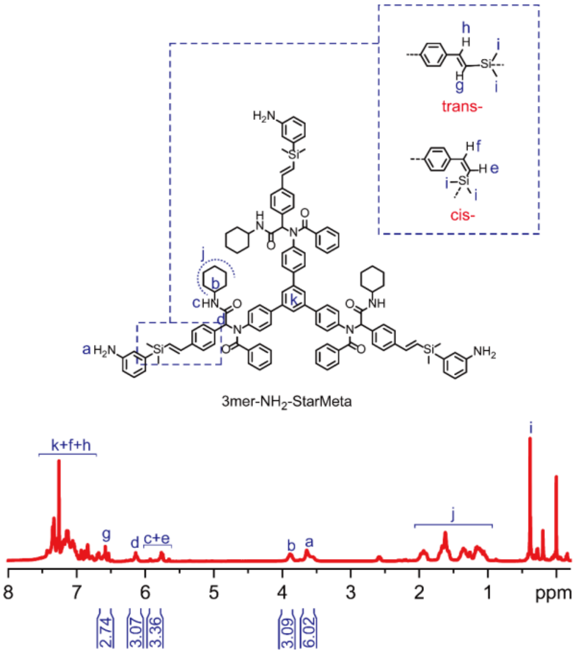
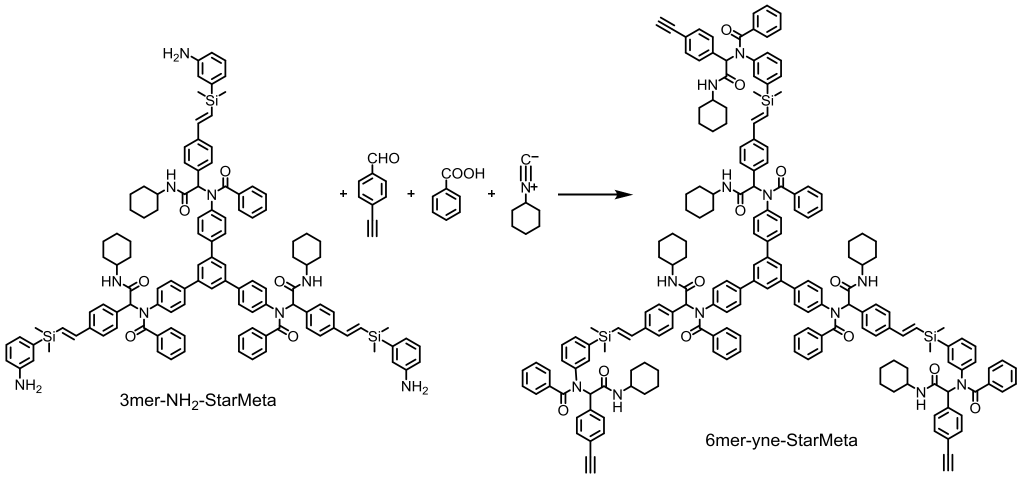


Figure S31. ^{1}H NMR spectrum of compound **3mer-NH$_2$-StarMeta** in CDCl$_3$

6mer-yne-StarMeta



Scheme S26. Synthesis of **6mer-yne-StarMeta**

To a round-bottomed flask were added 3mer-NH$_2$-StarMeta (0.393g,0.214mmol) dissolved with methanol and DMF. Then 4-ethynylbenzaldehyde (0.167g,1.28mmol) was added to the flask and stirred for 0.5h. After that benzoic acid (0.157g,1.28mmol) was added to the flask and isocyanocyclohexane (0.210g, 1.93mmol) was added to the flask lastly. The mixture was stirred at 25°C for 3d. The methanol was evaporated and DMF was evacuated by vacuum pump. After that the crude product was dissolved with

THF and the solution was poured into n-hexane so that the crude product crash out. The crude product was precipitated using excess n-hexane and subsequently dissolved in THF, this process was repeated twice, and then the product was dried to a constant weight in a vacuum oven to afford 6mer-yne-StarMeta as white powder (0.332g, yield54.2%).

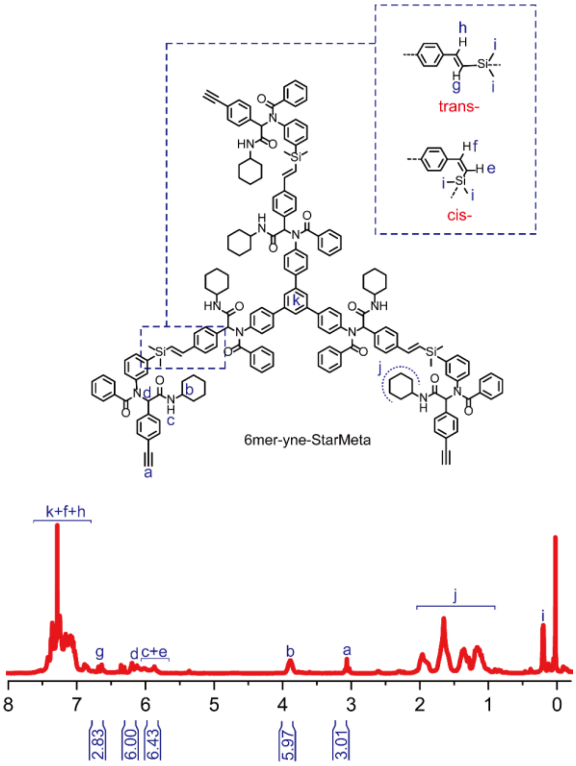
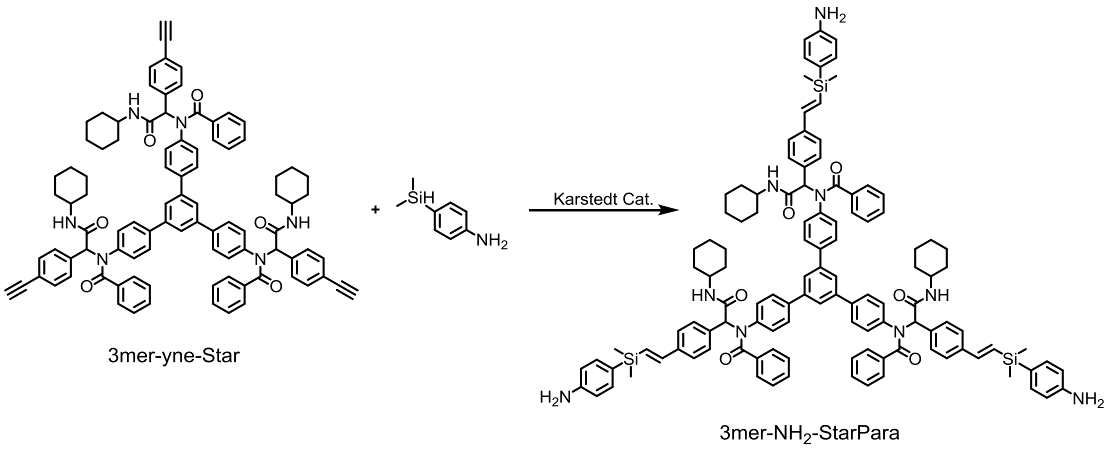


Figure S32. ^{1}H NMR spectrum of compound **6mer-yne-StarMeta** in $CDCl_3$

3.5 Star-shaped Para-oligomers

3mer-NH_2-StarPara



Scheme S27. Synthesis of **3mer-NH$_2$-StarPara**

To a round-bottomed flask filled with argon were added 3mer-yne-Star (0.600g, 0.434mmol) and 4-(dimethylsilyl) aniline (0.591g, 3.91mmol) then the mixture was dissolved with anhydrous THF. After a drop of Karstedt catalyst was added, the solution was stirred at 25^{o}C for 3d. After that the solution was poured into n-hexane so that the crude product crash out. The crude product was precipitated using excess n-hexane and subsequently dissolved in THF, this process was repeated twice, and then the product was dried to a constant weight in a vacuum oven to afford 3mer-NH$_2$-StarPara as white powder (0.662g, yield83.2%).

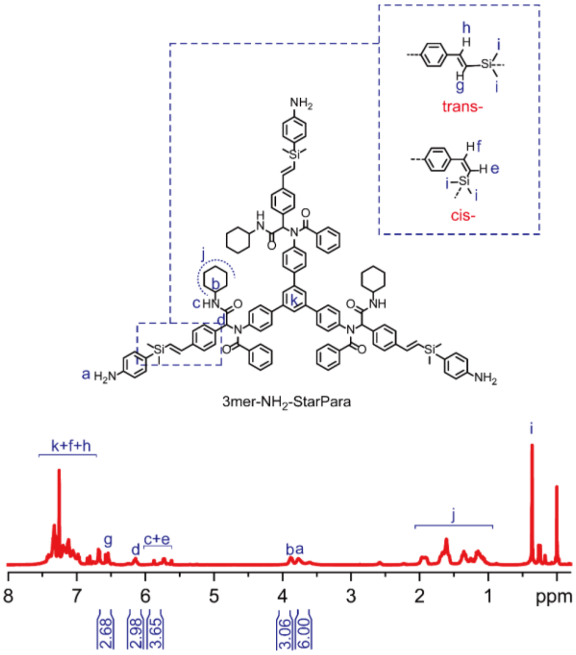
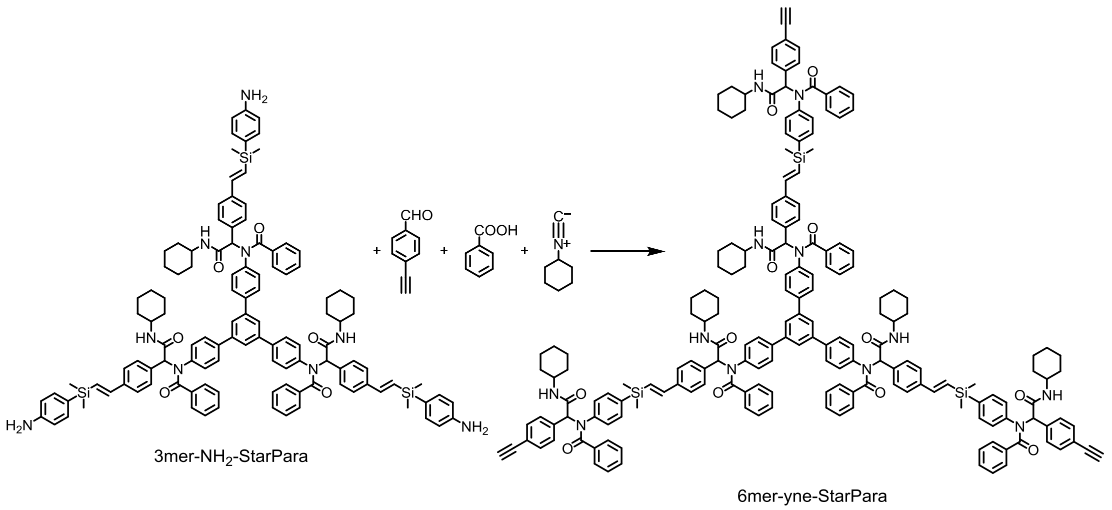


Figure S33. ^{1}H NMR spectrum of compound **3mer-NH$_2$-StarPara** in CDCl$_3$

6mer-yne-StarPara



Scheme S28. Synthesis of **6mer-yne-StarPara**

To a round-bottomed flask were added 3mer-NH_2-StarPara (0.380g,0.207mmol) dissolved with methanol and DMF. Then 4-ethynylbenzaldehyde (0.167g,1.24mmol) was added to the flask and stirred for 0.5h. After that benzoic acid (0.157g,1.24mmol) was added to the flask and isocyanocyclohexane (0.203g, 1.86mmol) was added to the flask lastly. The mixture was stirred at 25^{o}C for 3d. The methanol was evaporated and DMF was evacuated by vacuum pump. After that the crude product was dissolved with THF and the solution was poured into n-hexane so that the crude product crash out. The crude product was precipitated using excess n-hexane and subsequently dissolved in THF, this process was repeated twice, and then the product was dried to a constant weight in a vacuum oven to afford 6mer-yne-StarPara as white powder (0.311g, yield52.5%).

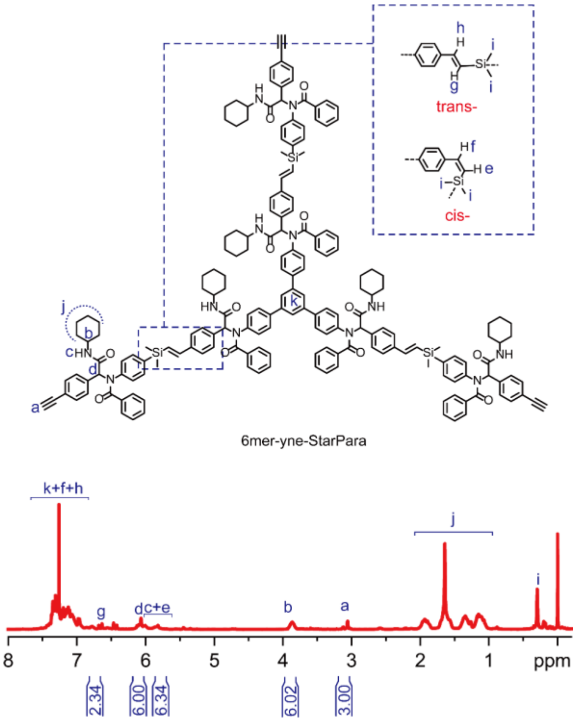


Figure S34. ^{1}H NMR spectrum of compound **6mer-yne-StarPara** in $CDCl_3$

4. The explanation of extra peak of MALDI-TOF-MS

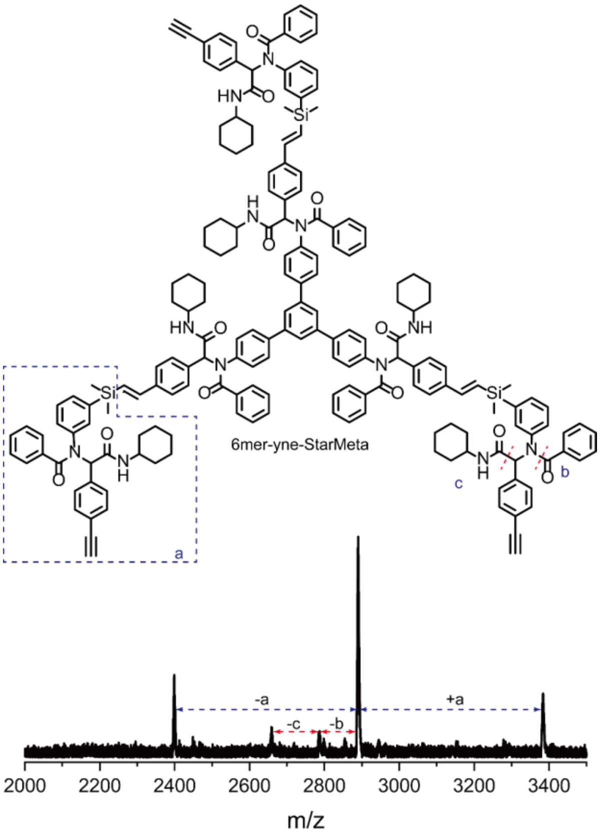


Figure S35. Detail cleavage piece explanation of MADLI-TOF-MS

The peak at 2655.8 and 2782.2 were referred to during the measurement procedure, the bond was broken and cut the b and c cleavage down. While the peak at 2393.1 and 3381.6 were referred to one repeat unit (a) is one more and one less because that in the last step of Hydrosilylation, there was one more or one less dimethylsilyl aniline addition.

5. Isolate yield of each step

Table S1 Isolated yield of Meta oligomers

Compound	MW(Da)	Purity	Scale(g)	Isolated yield
1mer-yne	436.22	>99%		
1mer-NH_2-Meta	587.30	>90%	0.95	88.2%
2mer-yne-Meta	930.45	>90%	0.89	59.1%
2mer-NH_2-Meta	1081.54	>90%	0.69	66.7%
3mer-yne-Meta	1424.69	>90%	0.64	70.4%
3mer-NH_2-Meta	1575.77	>90%	0.52	73.5%
4mer-yne-Meta	1918.93	>90%	0.49	77.4%
4mer-NH_2-Meta	2070.01	>90%	0.40	75.7%
5mer-yne-Meta	2413.17	>90%	0.32	68.6%
5mer-NH_2-Meta	2564.25	>90%	0.22	64.7%
6mer-yne-Meta	2907.41	>90%	0.18	72.2%

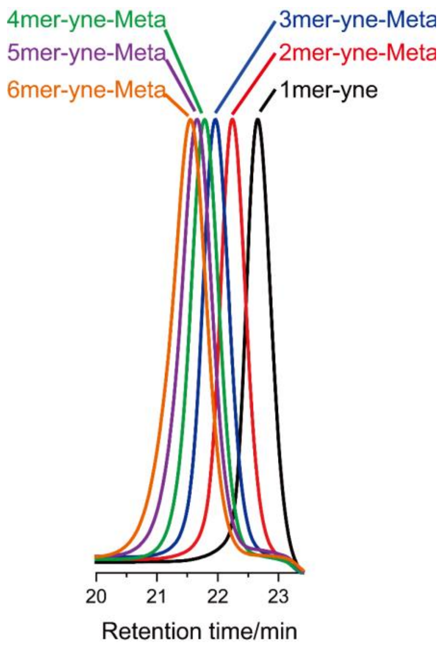


Figure S36 GPC traces of Meta oligomers

Table S2 Isolated yield of Para oligomers

Compound	MW(Da)	Purity	Scale(g)	Isolated yield
1mer-yne	436.22	>99%	0.80	
1mer-NH_2-Para	587.30	>90%	0.74	68.7%
2mer-yne-Para	930.45	>90%	0.72	61.4%
2mer-NH_2-Para	1081.54	>90%	0.46	55.0%
3mer-yne-Para	1424.69	>90%	0.43	71.0%
3mer-NH_2-Para	1575.77	>90%	0.32	67.3%
4mer-yne-Para	1918.93	>90%	0.27	69.3%
4mer-NH_2-Para	2070.01	>90%	0.20	68.7%
5mer-yne-Para	2413.17	>90%	0.14	60.0%
5mer-NH_2-Para	2564.25	>90%	0.10	67.2%
6mer-yne-Para	2907.41	>90%	0.063	72.2%

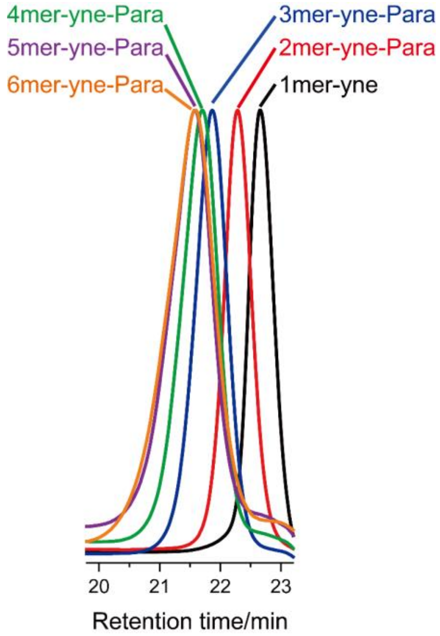


Figure S37 GPC traces of Para oligomers

Table S3 Isolated yield of StarMeta oligomers

Compound	MW(Da)	Purity	Scale(g)	Isolated yield
3mer-yne-Star	1380.65	>90%	0.60	
3mer-NH2-StarMeta	1833.89	>90%	0.61	77.0%
6mer-yne-StarMeta	2863.36	>90%	0.33	54.2%

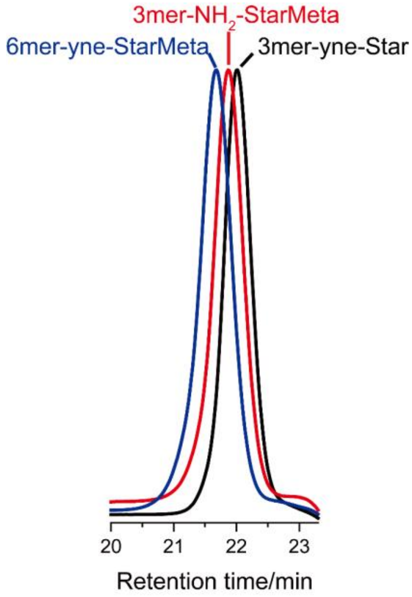


Figure S38 GPC traces of StarMeta oligomers

Table S4 Isolated yield of StarPara oligomers

Compound	MW(Da)	Purity	Scale(g)	Isolated yield
3mer-yne-Star	1380.65	>90%	0.60	
3mer-NH2-StarPara	1833.89	>90%	0.66	83.2%
6mer-yne-StarPara	2863.36	>90%	0.31	52.5%

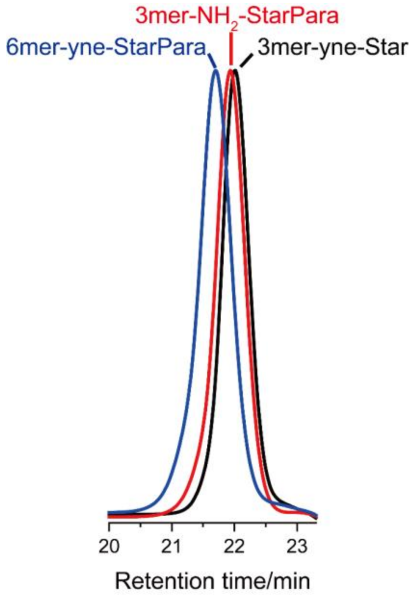


Figure S39 GPC traces of StarPara oligomers

6. MADLI-TOF-MS and ^{1}HNMR spectra of star-shaped oligomers

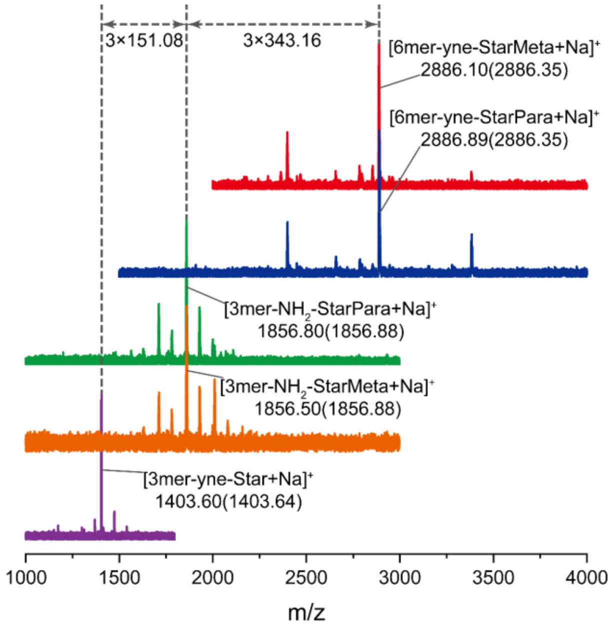


Figure S40. MALDI-TOF-MS of star-shaped oligomers

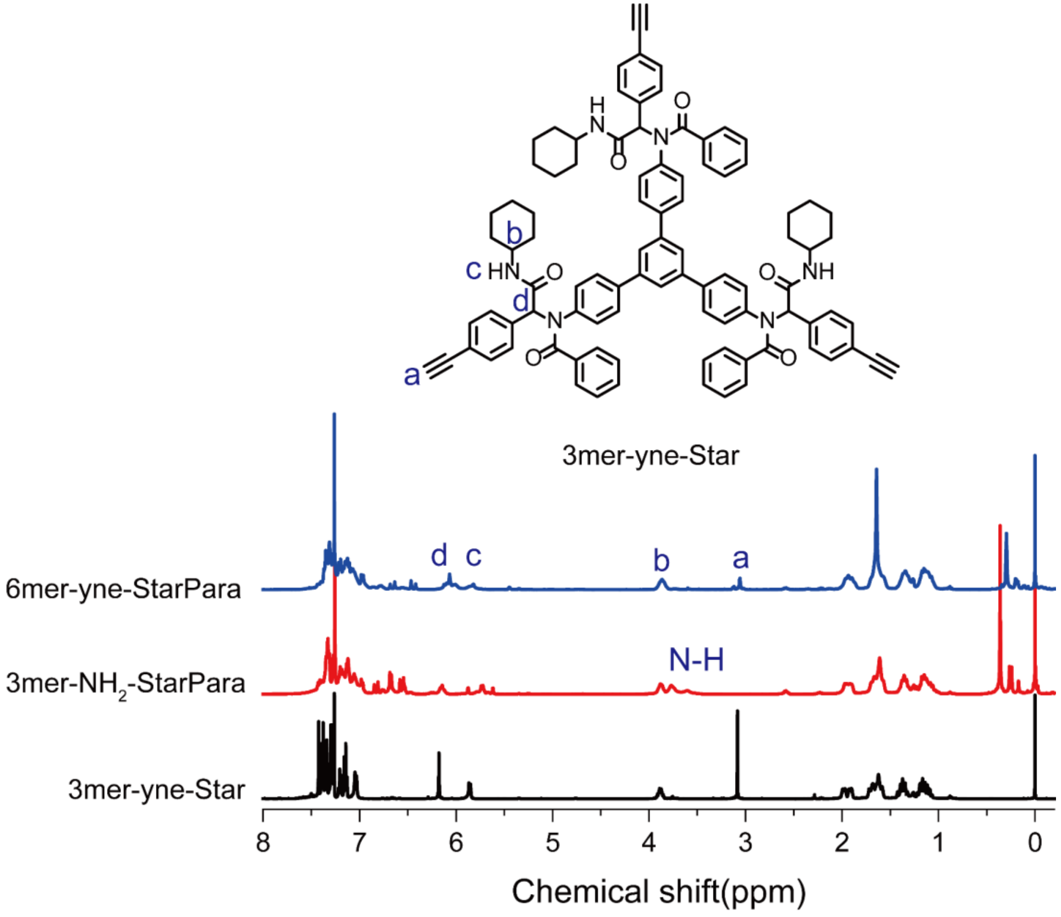


Figure S41.^{1}H NMR of star-shaped Para-oligomers

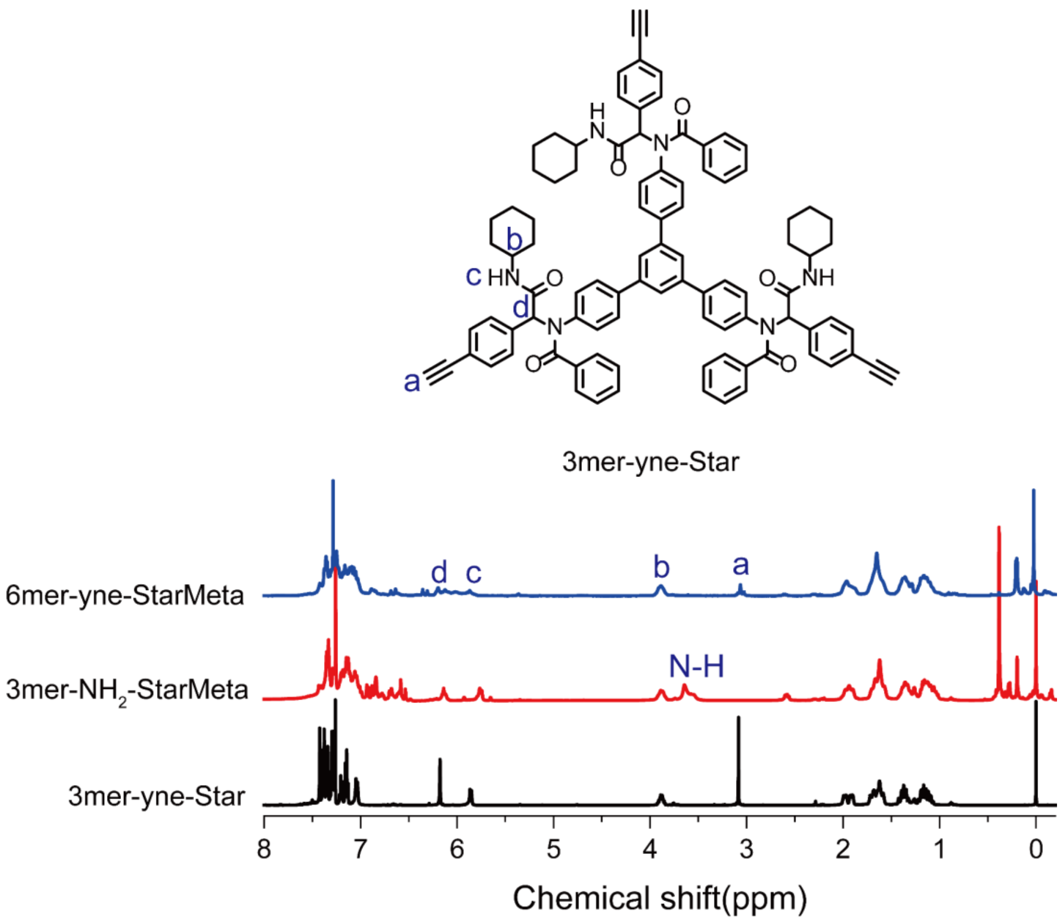


Figure S42.^{1}H NMR of star-shaped Meta-oligomers

7.Trans-/cis- linkage of discrete oligomers

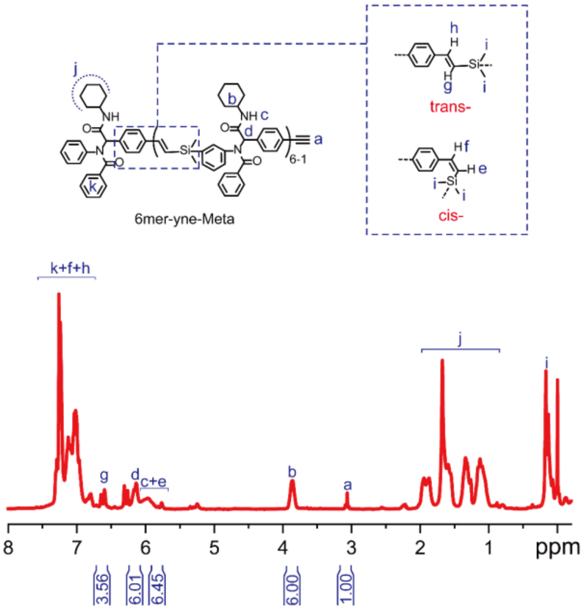


Figure S43.^{1}H NMR of 6mer-yne-Meta

During hydrosilylation of alkyne group in each step, there will be trans- or cis- linkage in the discrete oligomers, ^{1}H NMR was used to test the proportion of trans-/cis- structure. ^{1}H NMR of 6mer-yne-Meta was used as an example to explain the method to calculate the proportion of trans- and cis- linkage. The trans- proton signal g was at δ=6.6ppm, while cis- proton e was at 6.0ppm which was overlaid by proton c, the integral of proton c is equal to proton b and d because they are both characteristic proton of Ugi-4CR structure. The integral of proton c and e at δ=5.7-6.0ppm minus integral of proton d was calculated as the integral of cis- proton e. The proportion of trans- and cis- linkage was calculated as equation below.

$$cis\% = \frac{area(c+e) - area(d)}{area(c+e) - area(d) + area(g)} \times 100\%$$

$$trans\% = \frac{area(g)}{area(c+e) - area(d) + area(g)} \times 100\%$$

Table S5. Trans-/cis- linkage proportion of isomeric monodisperse oligomers

Compound	Cis%	Trans%
6mer-yne-Meta	11.2	88.8
6mer-yne-Para	23.0	77.0
6mer-yne-StarMeta	13.2	86.8
6mer-yne-StarPara	12.7	87.3