Supplementary Information for

Long, Self-Assembled Molecular Ladders by Cooperative Dynamic Covalent Reactions

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General Experimental Procedures

All chemicals and reagents, unless specified, were purchased from commercial sources and used as received without any further purification. Matrix-assisted laser desorption/ionization (MALDI) mass spectra were recorded using a Bruker Autoflex mass spectrometer, whereas electrospray ionization (ESI) mass spectra were recorded using an Agilent Q-TOF 1200 series spectrometer. All MALDI analyses, excluding Im_{16}, were performed in reflectron positive ion mode using 2-(4-hydroxyphenylazo)benzoic acid (HABA) as the matrix, where 3 μL of a solution of the sample in chloroform (1.5 mM) was mixed with 10 μL of a mixture of 6 mg matrix in 300 μL acetonitrile, spotted on a MALDI sample plate (Bruker), and allowed to air dry. MALDI analysis for Im_{16} was performed in linear positive ion mode. Reverse phase high performance liquid chromatography (RP-HPLC) was performed using a Shimadzu LC-6AD HPLC pump, equipped with a Shimadzu FRC 70A fraction collector, using analytical and preparative reversed phase Phenomenex Luna C18(2) columns with a linear gradient of water and acetonitrile as the eluent at 30°C, and monitored with a Shimadzu Prominence UV/vis detector at 214 nm. Analytical gel permeation chromatography (GPC) was similarly performed using a Shimadzu LC-6AD HPLC pump, equipped with a series of three Phenogel GPC/SEC columns (length 300 mm × diameter 7.8 mm, pore sizes of 500, 100, and 50 Å) with 94:4:2 (v/v/v) CHCl₃:MeOH:Et₃N as the eluent at 30°C, and monitored with a Shimadzu Prominence UV/vis detector at 313 nm. The analytical GPC was calibrated utilizing low dispersity polystyrene standards (low molecular weight Readycal Set, Fluka). UV-vis measurements were recorded on an Agilent Cary 60 spectrophotometer in anhydrous chloroform in quartz cuvettes with a 1 cm path length. Scans were taken over the range of 300 to 650 nm, and a background spectrum of pure solvent was subtracted from each scan. Sample concentrations were on the order of 100 μM for each of the peptoids studied. Spectra were then normalized for comparison.
Abbreviations
DABCYL-NHS: 4-(4-dimethylaminophenylazo)benzoic acid, succinimidyl ester
DABCYL-EN: DABCYL ethylene diamine
DCM: dichloromethane
DIC: N,N'-diisopropylcarbodiimide
DMF: N,N-dimethylformamide
EDANS: (5-(2-aminoethyl)amino)naphthalene-1-sulfonic acid
Et₃N: triethylamine
MeCN: acetonitrile
NMP: N-methyl-2-pyrroldione
TFA: trifluoroacetic acid
THF: tetrahydrofuran

Section 1: Dynamic Covalent Assembly of Molecular Ladders with n Rungs

Solid-Phase Synthesis of Oligopeptoids

Oligopeptoid synthesis was carried out on 133 mg of Rink Amide Resin SS (0.1 mmol scale, 100-200 mesh, 1% DVB, Advanced ChemTech) using an automated microwave peptide synthesizer (Liberty Blue, CEM Corporation). Three primary amine monomers, 4-(2-aminoethyl)-N-(tert-butoxycarbonyl)phenylamine (Am), 4-(1,3-dioxacyclopent-2-yl)benzylamine (Al), and 2-(2-ethoxyethoxy)ethylamine (E₃A) were synthesized as reported from a published approach. All other monomers, reagents, and solvents were purchased from commercial sources and directly used without further purification. Aldehyde and amine-functionalized oligopeptoids were synthesized according to a published submonomer approach to solid-phase peptoid synthesis. The resin was swelled for 5 min at room temperature and subsequently deprotected with 20% 4-methylpiperidine in DMF (v/v) for 30 s at 75°C and 90 s at 90°C, followed by bromoacetylation for 5 min at 75°C with simultaneous addition of 1.5 mL of 1.0 M bromoacetic acid in DMF and 1.5 mL of 1.0 M DIC in DMF. Halide displacement was then carried out by adding 2.5 mL of 0.5 M primary amine monomer in NMP followed by an incubation of 5 min at 75°C. These bromoacetylation and displacement reactions were alternated until the desired peptoid sequence was achieved. All synthesized peptoids were acetylated by treatment with acetic anhydride to cap the secondary amine end groups.
Cleavage and Side-chain Deprotection

After solid-phase synthesis, the resultant dried Rink-amide resin was transferred to a 25 mL solid-phase peptide synthesis vessel (CG-1866, Chemglass) and treated with 4 mL of TFA cleavage cocktail for 10 – 25 min while bubbling with nitrogen at room temperature. The TFA cleavage solution was collected by filtering through the fritted glass into a 25 mL round bottom flask. The remaining resin was further rinsed twice with 2mL of fresh TFA cleavage cocktail to collect any residual peptoid. The cleavage solution was combined and evaporated by blowing a gentle stream of nitrogen to yield crude peptoid, the structures of which are illustrated in Figure S1. The crude product was reconstituted in HPLC grade MeCN/water (v/v, the least amount of MeCN to dissolve the crude peptoid oil) and further purified by preparative HPLC.

To note, TFA cleavage cocktail and cleavage time are dependent on the number and variety of protecting groups used. 95% aq. TFA was used to deprotect acetal-protected aldehyde-functionalized peptoids, whereas 95% TFA in DCM was used to deprotect Boc-protected amine-functionalized peptoids. Additionally, the crude amine-functionalized peptoids were subjected to 1 M NaHCO₃ to adjust the pH to ~7.6 prior to HPLC purification.¹

![Chemical structures of aldehyde- and amine-functionalized oligopeptoids: Alₙ (left) and Amₙ (right).](image)

Figure S1. Chemical structures of aldehyde- and amine-functionalized oligopeptoids: Alₙ (left) and Amₙ (right).

Purification of Oligopeptoids by Preparative RP-HPLC

All deprotected peptoids were purified by preparative RP-HPLC using a linear gradient of H₂O (A) and MeCN (B) at a flow rate of 12 mL/min. The purified fractions were combined, concentrated, reconstituted in 50% MeCN/H₂O (v/v), frozen with liquid nitrogen, and lyophilized to afford fluffy white powder. The purity of the collected, aldehyde- and amine-functionalized peptoids was further examined by analytical RP-HPLC.

-S3-
Preparative HPLC method:
(1) Al_8: (1) 30% B, 0.1 – 4.1 min; (2) 30% – 80% B, 4.1 – 24.1 min; (3) 80% – 30% B, 24.1 – 27.1 min;
(2) Al_10: (1) 30% B, 0.1 – 4.1 min; (2) 30% – 85% B, 4.1 – 26.1 min; (3) 85% – 30% B, 26.1 – 29.1 min;
(3) Al_12: (1) 30% B, 0.1 – 4.1 min; (2) 30% – 85% B, 4.1 – 26.1 min; (3) 85% B, 26.1 – 27.1 min; (4)
85% – 30% B, 27.1 – 30.1 min;
(4) Al_16: (1) 30% B, 0.1 – 4.1 min; (2) 30% – 60% B, 4.1 – 12.1 min; (3) 60% – 80% B, 12.1 – 28.1 min; (4)
80% – 30% B, 28.1 – 29.1 min;
(5) Am_8 & Am_10: (1) 20% B, 0.1 – 4.1 min; (2) 20% – 65% B, 4.1 – 30.1 min; (3) 65% – 20% B, 30.1 –
32.1 min;
(6) Al_12: (1) 25% B, 0.1 – 4.1 min; (2) 25% – 65% B, 4.1 – 36.1 min; (3) 65% – 25% B, 36.1 – 38.1 min;
(7) Al_16: (1) 35% B, 0.1 – 4.1 min; (2) 35% – 55% B, 4.1 – 12.1 min; (3) 55% – 70% B, 12.1 – 25.1 min; (4)
70% – 35% B, 25.1 – 28.1 min;

Table S1. Structural information of aldehyde-functionalized oligopeptoid sequences subjected to MALDI mass
spectrometry, HPLC and GPC analysis.

<table>
<thead>
<tr>
<th>Code</th>
<th>Formula</th>
<th>Exact mass M (g/mol)</th>
<th>Molecular weight (g/mol)</th>
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</thead>
<tbody>
<tr>
<td>Al_8</td>
<td>C_{138}H_{182}N_{16}O_{38}</td>
<td>2671.280</td>
<td>2673.048</td>
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<td>C_{174}H_{230}N_{20}O_{48}</td>
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<td>3369.846</td>
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<td>C_{210}H_{278}N_{24}O_{58}</td>
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<td>4066.644</td>
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<tr>
<td>Al_16</td>
<td>C_{282}H_{374}N_{32}O_{78}</td>
<td>5456.628</td>
<td>5460.240</td>
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Table S2. Structural information of aldehyde-functionalized oligopeptoid sequences subjected to MALDI mass
spectrometry, HPLC and GPC analysis.

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<th>Code</th>
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<th>Exact mass M (g/mol)</th>
<th>Molecular weight (g/mol)</th>
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</thead>
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<tr>
<td>Am_10</td>
<td>C_{174}H_{260}N_{30}O_{38}</td>
<td>3377.934</td>
<td>3380.166</td>
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<tr>
<td>Am_12</td>
<td>C_{210}H_{314}N_{36}O_{46}</td>
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<td>4079.028</td>
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<tr>
<td>Am_16</td>
<td>C_{282}H_{422}N_{48}O_{62}</td>
<td>5473.134</td>
<td>5476.142</td>
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</tbody>
</table>
MALDI Mass Spectra of Purified, Aldehyde- and Amine-Functionalized Oligopeptoids

Figure S2. MALDI mass spectra of aldehyde-functionalized oligopeptoids purified by preparative RP-HPLC. Expected molecular weights: \([M_{Al_8}+Na]^+ = 2694.269; [M_{Al_{10}}+Na]^+ = 3390.606; [M_{Al_{12}}+Na]^+ = 4086.943; [M_{Al_{16}}+Na]^+ = 5479.618.\)

Figure S3. MALDI mass spectra of amine-functionalized oligopeptoids purified by preparative RP-HPLC. Expected molecular weights: \([M_{Am_8}+Na]^+ = 2702.522; [M_{Am_{10}}+Na]^+ = 3400.923; [M_{Am_{12}}+Na]^+ = 4099.323; [M_{Am_{16}}+Na]^+ = 5496.124.\)
Analytical HPLC Traces of Purified, Aldehyde- and Amine-Functionalized Oligopeptoids

Figure S4. Analytical HPLC traces of aldehyde-functionalized oligopeptoids. Purity: Al$_8$, 97.5%; Al$_{10}$, 96.1%; Al$_{12}$, 95.4%; Al$_{16}$, 99.3%. Analytical HPLC method: flow rate at 1 mL/min; A: H$_2$O, B: MeCN; 20% – 90% B 0 – 20 min, 90% – 20% B 20 – 23 min.

Figure S5. Analytical HPLC traces of amine-functionalized oligopeptoids. Purity: Am$_8$, 99.8%; Am$_{10}$, 96.9%; Am$_{12}$, 98.8%; Am$_{16}$, 98.9%. Analytical HPLC method: flow rate at 1 mL/min; A: H$_2$O, B: MeCN; 20% – 80% B 0 – 20 min, 80% – 20% B 20 – 23 min.
Analytical GPC Traces of Purified, Aldehyde- and Amine-Functionalized Oligopeptoids

Figure S6. Analytical GPC of aldehyde-functionalized oligopeptoids. Analytical GPC method: isocratic flow rate at 1 mL/min; eluent: CHCl3/CH3OH/ET3N (94/4/2, v/v/v). Al_8, $V_r = 18.92$ mL, $M_n = 3667$ g/mol; Al_10, $V_r = 18.54$ mL, $M_n = 4571$ g/mol; Al_12, $V_r = 18.24$ mL, $M_n = 5502$ g/mol; Al_16, $V_r = 17.81$ mL, $M_n = 7245$ g/mol.

Figure S7. Analytical GPC of amine-functionalized oligopeptoids. Analytical GPC method: isocratic flow rate at 1 mL/min; eluent: CHCl3/CH3OH/ET3N (94/4/2, v/v/v). Am_8, $V_r = 19.10$ mL, $M_n = 3390$ g/mol; Am_10, $V_r = 18.68$ mL, $M_n = 4194$ g/mol; Am_12, $V_r = 18.42$ mL, $M_n = 4923$ g/mol; Am_16, $V_r = 17.92$ mL, $M_n = 6750$ g/mol.
General Procedure for Self-Assembly of Molecular Ladders of Length $n$

Scheme S1. Dimerization of peptoid-based molecular ladders via imine metathesis.

The approach used to dimerize aldehyde- and amine-functionalized peptoid oligomers to form molecular ladders followed a previously published method. Briefly, 1 μmol of the peptoid oligomer Al$_n$ was mixed with 1 μmol of its complementary strand Am$_n$, in anhydrous CHCl$_3$ with a total reaction volume of 1 mL. To the reaction mixture, Sc(OTf)$_3$ (0.04 eq. per imine bond, 10 mM stock solution dissolved in MeCN) was added to catalyze the transimination and imine metathesis reactions (see Figure S8) and the mixture allowed to stir for a week. The reaction mixture was then directly analyzed by MALDI mass spectrometry and analytical GPC.

Figure S8. Influence of Sc(OTf)$_3$ on the rate of molecular ladder formation. Here, peptoid sequences Al$_3$ and Am$_3$, mixed in 1:1 stoichiometric ratios (1 mM) in chloroform, were allowed to react for 1 hour either with or without the addition of 4 mol% Sc(OTf)$_3$, followed by reduction with sodium cyanoborohydride. (a) MALDI-TOF mass spectra of the crude reaction mixtures demonstrate the rapid and exclusive generation of the desired Im$_3$ molecular ladder in the presence of Sc(OTf)$_3$, whereas the assembly reaction performed in the absence of the Sc(III) catalyst did not proceed to completion, yielding additional, out-of-registry species composed of three and four peptoid strands. (b) GPC traces for the crude reaction mixtures confirm the presence of high molecular weight, out-of-registry species for the assembly reaction performed in the absence of Sc(III).
Table S3. Structural information of peptoid-based ladder oligomers subjected to MALDI mass spectrometry and GPC analysis.

<table>
<thead>
<tr>
<th>Code</th>
<th>Formula</th>
<th>Exact mass (g/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Im_8</td>
<td>C_{276}H_{372}N_{40}O_{60}</td>
<td>5206.729</td>
</tr>
<tr>
<td>Im_10</td>
<td>C_{348}H_{470}N_{50}O_{76}</td>
<td>6565.445</td>
</tr>
<tr>
<td>Im_12</td>
<td>C_{420}H_{568}N_{60}O_{92}</td>
<td>7924.161</td>
</tr>
<tr>
<td>Im_16</td>
<td>C_{564}H_{764}N_{80}O_{124}</td>
<td>10641.594</td>
</tr>
</tbody>
</table>

Figure S9. GPC traces for crude reaction mixtures. The traces are normalized to the height of the largest peak. Im_8, 
$V_r = 18.23$ mL, $M_n = 5494$ g/mol; Im_10, $V_r = 18.00$ mL, $M_n = 6332$ g/mol; Im_12, $V_r = 17.75$ mL, $M_n = 7503$ g/mol; Im_16, $V_r = 17.27$ mL, $M_n = 10570$ g/mol.

Deconvolution of GPC Traces

GPC traces of peptoid-based ladder oligomers were deconvoluted by fitting Gaussian functions to simulate the peaks using a script written in-house with Matlab R2012a (Mathworks Inc.). In each case, the baseline was subtracted and then 2-3 simulated peaks were utilized to fit the spectra.

Figure S10. Deconvoluted GPC traces of peptoid-based, dimerized molecular ladders (a) Im_8, (b) Im_10, and (c) Im_12 (straight reaction mixtures). The target product peak is labeled in red.
Table S4. GPC analysis of peptoid-based, dimerized molecular ladders.

<table>
<thead>
<tr>
<th>Code</th>
<th>$M_n$ by GPC (g/mol)</th>
<th>Expected $M_n$ (g/mol)</th>
<th>Area (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Im$_8$</td>
<td>5494</td>
<td>5210</td>
<td>61%</td>
</tr>
<tr>
<td>Im$_{10}$</td>
<td>6332</td>
<td>6570</td>
<td>79%</td>
</tr>
<tr>
<td>Im$_{12}$</td>
<td>7503</td>
<td>7930</td>
<td>79%</td>
</tr>
<tr>
<td>Im$_{16}$</td>
<td>10570</td>
<td>10649</td>
<td>-*</td>
</tr>
</tbody>
</table>

* unable to be determined due to the low signal-to-noise ratio of GPC trace for Im$_{16}$
Section 2: Kinetics Study of Molecular Ladder Formation

Hybridization kinetics experiments were performed for peptoid-based molecular ladders with 4, 8, 10, and 12 rungs. An inert peptoid sequence comprised of E³A spacer, denoted as E³A-21, was used at a known concentration as an internal standard for this kinetics study. E³A-21 was synthesized by a submonomer approach to solid-phase synthesis as reported previously using an automated synthesizer, further purified by preparative RP-HPLC, and characterized by MALDI mass spectrometry and analytical RP-HPLC (see Figure S11). Samples were prepared by adding Sc(OTf)₃ (0.04 eq. per imine bond, 10 mM stock solution dissolved in MeCN) and between 4 and 20 nmol E³A_21 into anhydrous chloroform, followed by the addition of 1 µmol of the peptoid oligomer Al_n and 1 µmol of Am_n into the mixture, making a total reaction volume of 1 mL. Aliquots of the reaction mixture were taken at increasing time intervals, and examined by MALDI mass spectrometry with a Bruker Autoflex mass spectrometer. Multiple regions of interest were ionized in each sample to obtain an average ratio of target peak areas, and concentrations of target molecular ladders and out of registry molecular ladders were calculated by comparing to the peak area of the internal standard.

Figure S11. Characterizations of the E³A_21 internal standard employed in kinetics experiments: (a) MALDI mass spectrum of E³A_21 purified by preparative RP-HPLC. Expected molecular weights: [M+Na]^+ = 3717.235; (b) analytical HPLC trace of E³A_21. Purity: 98.8%. Analytical HPLC method: flow rate at 1 mL/min; A: H₂O, B: MeCN; 20% B 0 – 4 min, 20% – 80% B 4 – 28 min, 80% – 20% B 28 – 32 min.
Figure S12. Kinetics of the formation of molecular ladder with $n = 4$ rungs over the course of 2 days. (a) MALDI-TOF mass spectra of the crude reaction mixture at increasing time intervals; (b) Concentration of the desired molecular ladder $\text{Im}_4$ and its out of registry molecular ladders versus time during the molecular ladder assembly process.

Table S5. Molecular weight of the desired molecular ladder with $n = 4$ rungs and its out of registry ladders subjected to MALDI analysis.

<table>
<thead>
<tr>
<th>$\text{Im}_4$</th>
<th>Expected Exact Mass M (g/mol)</th>
<th>Expected [M+Na]$^+$</th>
<th>Observed [M+Na]$^+$ by MALDI</th>
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<tbody>
<tr>
<td>$n = 4$</td>
<td>2489.296</td>
<td>2512.285</td>
<td>2512.661</td>
</tr>
<tr>
<td>$n-1$</td>
<td>2507.307</td>
<td>2530.296</td>
<td>2530.625</td>
</tr>
<tr>
<td>$n-2$</td>
<td>2525.317</td>
<td>2548.306</td>
<td>2548.609</td>
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<tr>
<td>$n-3$</td>
<td>2543.328</td>
<td>2566.317</td>
<td>2566.586</td>
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Figure S13. Kinetics of the formation of molecular ladder with $n = 8$ rungs over the course of 7 days. (a) MALDI-TOF mass spectra of the crude reaction mixture at increasing time intervals; (b) Concentration of the desired molecular ladder $\text{Im}_8$ and its out of registry molecular ladders versus time during the molecular ladder assembly process.
Table S6. Molecular weight of the desired molecular ladder with \( n = 8 \) rungs and its out of registry ladders subjected to MALDI analysis.

<table>
<thead>
<tr>
<th>( \text{Im}_8 )</th>
<th>Expected Exact Mass M (g/mol)</th>
<th>Expected ([\text{M}+\text{Na}]^+)</th>
<th>Observed ([\text{M}+\text{Na}]^+) by MALDI</th>
</tr>
</thead>
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<tr>
<td>( n = 8 )</td>
<td>5206.729</td>
<td>5229.718</td>
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<td>( n-1 )</td>
<td>5224.739</td>
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<td>( n-2 )</td>
<td>5242.75</td>
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<td>( n-3 )</td>
<td>5260.76</td>
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<td>5284.495</td>
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<td>( n-4 )</td>
<td>5278.771</td>
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<td>( n-5 )</td>
<td>5296.782</td>
<td>5319.771</td>
<td>5320.580</td>
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<td>( n-6 )</td>
<td>5314.792</td>
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<td>( n-7 )</td>
<td>5332.803</td>
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Figure S14. Kinetics of the formation of molecular ladder with \( n = 10 \) rungs over the course of 13 days. (a) MALDI-TOF mass spectra of the crude reaction mixture at increasing time intervals; (b) Concentration of the desired molecular ladder \( \text{Im}_{10} \) and its out of registry molecular ladders versus time during the molecular ladder assembly process.
Table S7. Molecular weight of the desired molecular ladder with $n = 10$ rungs and its out of registry ladders subjected to MALDI analysis.

<table>
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<tr>
<th>Im$_{10}$</th>
<th>Expected Exact Mass M (g/mol)</th>
<th>Expected [M+Na]$^+$</th>
<th>Observed [M+Na]$^+$ by MALDI</th>
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Table S8. Molecular weight of the desired molecular ladder with $n = 12$ rungs and its out of registry ladders subjected to MALDI analysis.

<table>
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<tr>
<th>Im$_{12}$</th>
<th>Expected Exact Mass M (g/mol)</th>
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<th>Observed [M+Na]$^+$ by MALDI</th>
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<tr>
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<td>8000.485</td>
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<td>8108.447</td>
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<td>$n-10$</td>
<td>8104.267</td>
<td>8127.256</td>
<td>8126.153</td>
</tr>
<tr>
<td>$n-11$</td>
<td>8122.277</td>
<td>8145.266</td>
<td>8143.880</td>
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</table>
Section 3: Forster Resonance Energy Transfer (FRET) for Registry Mechanism of Ladder Formation

Synthesis of DABCYL-EN for Solid-Phase Peptoid Synthesis

Scheme S2. Synthesis of DABCYL-EN for subsequent use as a primary amine-bearing submonomer in solid-phase peptoid synthesis.

To a 20 mL vial equipped with magnetic stirrer, 500 mg (1.36 mmol) of DABCYL succinimide ester and 10 mL (excess) of distilled ethylene diamine were added. The reaction was allowed to stir for 12 h and then excess ethylene diamine was removed by rotary evaporation. DCM (3 × 15 mL) was then added to the vial to extract the product and combined. The combined DCM solution was then washed with distilled water (2 × 10 mL) to remove excess amine and succinimide. The organic layer was dried over Na₂SO₄, filtered and solvent removed by rotary evaporation. The resulting red/orange solid was then dried for 3 h under high vacuum (398 mg, 91% yield).

**1H NMR** (700 MHz, DMSO-d6) δ: 8.52 (s, 1H, -NH-), 7.99 (d, 2H, Ar), 7.82 (m, 4H, Ar), 6.84 (d, 2H, Ar), 3.29 (t, 2H, -NH-CH₂-), 2.70 (t, 2H, -CH₂-NH₂), 2.08 (s, 6H, -N(CH₃)₂)

**13C NMR** (175 MHz, DMSO-d6) δ: 165.73, 153.88, 152.81, 142.62, 134.94, 128.32, 125.07, 111.57, 43.11, 41.30, 30.70

**ESI+:** 312.1 m/z [M+H]+

Preparation of oligopeptoids for FRET study

Six primary amine monomers, 4-(2-aminoethyl)-N-(tert-butyloxycarbonyl) phenylamine (Am), 4-(1,3-dioxacyclopent-2-yl)benzylamine (Al), 2-(2-ethoxyethoxy)ethylamine (E³A), benzylamine (Bz), EDANS and DABCYL-EN were utilized for the synthesis of peptoids for FRET study. Peptoids containing EDANS and DABCYL were prepared according to the aforementioned submonomer approach to solid-phase synthesis. However, 0.2 M EDANS in DMF/DBU (4:1, v/v) and 0.2 M DABCYL-EN in NMP were used for halide displacement instead. Additionally, halide displacement with EDANS was proceeded twice to ensure the reaction completion. Subsequently, the resultant peptoids were cleaved from the resin beads by treatment with a TFA cleavage cocktail and purified by preparative HPLC. Peptoids containing DABCYL were purified by preparative RP-HPLC using a linear gradient of H₂O (A) and MeCN (B) at a
flow rate of 12 mL/min. The purified fractions were combined, concentrated, reconstituted in 50% MeCN/H$_2$O (v/v), frozen with liquid nitrogen and lyophilized to afford fluffy white powders. The purity of the collected peptoids with DABCYL was further examined by analytical RP-HPLC. Peptoids containing EDANS were purified using 0.1%TFA in both water (A) and MeCN (B) as eluent. The purified fractions were combined and evaporated to dryness. The resultant peptoids were dissolved in methanol and evaporated to dryness several times to remove the trace amount of TFA.

Table S9. Structural information of oligopeptoid sequences subjected to FRET study.

<table>
<thead>
<tr>
<th>Code</th>
<th>Structure</th>
<th>Formula</th>
<th>Exact mass M (g/mol)</th>
<th>Molecular weight (g/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al$_{12}$-EDANS</td>
<td><img src="image" alt="Structure" /></td>
<td>C$<em>{232}$H$</em>{307}$N$<em>{27}$O$</em>{65}$S</td>
<td>4543.127</td>
<td>4546.192</td>
</tr>
<tr>
<td>Am$_{12}$-DABCYL</td>
<td><img src="image" alt="Structure" /></td>
<td>C$<em>{237}$H$</em>{350}$N$<em>{42}$O$</em>{51}$</td>
<td>4600.6085</td>
<td>4603.650</td>
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<tr>
<td>Bz$_{12}$-EDANS</td>
<td><img src="image" alt="Structure" /></td>
<td>C$<em>{220}$H$</em>{307}$N$<em>{27}$O$</em>{53}$S</td>
<td>4207.188</td>
<td>4210.072</td>
</tr>
<tr>
<td>Al-Bz$_{11}$-EDANS</td>
<td><img src="image" alt="Structure" /></td>
<td>C$<em>{221}$H$</em>{307}$N$<em>{27}$O$</em>{54}$S</td>
<td>4235.183</td>
<td>4238.082</td>
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</table>
**Preparative HPLC method:**

1. **Al$_{12}$-EDANS:** (1) 40% B, 0.1 – 4.1 min; (2) 40% – 70% B, 4.1 – 31.7 min; (3) 70% – 40% B, 31.7 – 33.7 min;
2. **Am$_{12}$-DABCYL:** (1) 30% B, 0.1 – 4.1 min; (2) 30% – 75% B, 4.1 – 34.1 min; (3) 75% – 30% B, 34.1 – 36.1 min;
3. **Bz$_{12}$-EDANS:** (1) 50% B, 0.1 – 4.1 min; (2) 50% – 85% B, 4.1 – 32.9 min; (3) 85% – 50% B, 32.9 – 34.9 min;
4. **Al-Bz$_{11}$-EDANS:** (1) 50% B, 0.1 – 4.1 min; (2) 50% – 85% B, 4.1 – 36.1 min; (3) 85% – 50% B, 36.1 – 38.1 min;
5. **Am-Bz$_{11}$-DABCYL & Bz$_{11}$-Am-DABCYL** (1) 55% B, 0.1 – 4.1 min; (2) 55% – 95% B, 4.1 – 32.7 min; (3) 95% – 55% B, 32.7 – 4.7 min.
ESI-MS spectra were acquired and deconvoluted by the Agilent Qualitative Analysis Program.

Figure S15. Deconvoluted ESI-MS spectra of oligopeptoids containing FRET pairs purified by preparative RP-HPLC: (a) Al$_{12}$-EDANS; (b) Am$_{12}$-DABCYL; (c) Bz$_{12}$-EDANS; (d) Al-Bz$_{11}$-EDANS; (e) Am-Bz$_{11}$-DABCYL; (f) Bz$_{11}$-Am-DABCYL.
Figure S16. Analytical HPLC traces of oligopeptoids comprised of FRET pairs. Purity: Al$_{12}$-EDANS, 99.3%; Am$_{12}$-DABCYL, 95.8%; Bz$_{12}$-EDANS, 98.4%; Al-Bz$_{11}$-EDANS, 97.9%; Am-Bz$_{11}$-DABCYL, 96.1%; Bz$_{11}$-Am-DABCYL, 97.2%.
Figure S17. UV absorption and emission of peptoids containing either EDANS or DABCYL subjected to FRET study: (a) Al$_{12}$-EDANS, 99.3%; (b) Bz$_{12}$-EDANS; (c) Al-Bz$_{11}$-EDANS; (d) Am$_{12}$-DABCYL; (e) Am-Bz$_{11}$-DABCYL; (f) Bz$_{11}$-Am-DABCYL.
Figure S18. Analytical GPC of Am\textsubscript{12}-DABCYL (a) and Al\textsubscript{12}-EDANS (b). Analytical GPC method: isocratic flow rate at 1 mL/min; eluent: CHCl\textsubscript{3}/CH\textsubscript{3}OH/Et\textsubscript{3}N (94/4/2, v/v/v). Am\textsubscript{12}-DABCYL, $V_r = 18.41$ mL, $M_n = 4932$ g/mol; Al\textsubscript{12}-EDANS, $V_r = 18.70$ mL, $M_n = 4155$ g/mol.

Table S10. Deconvoluted peak analysis of Im\textsubscript{12}-FRET.

<table>
<thead>
<tr>
<th>Code</th>
<th>$M_n$ by GPC (g/mol)</th>
<th>Expected $M_n$ (g/mol)</th>
<th>Area (%)</th>
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</thead>
<tbody>
<tr>
<td>Im\textsubscript{12}-FRET</td>
<td>8799</td>
<td>8934</td>
<td>46</td>
</tr>
</tbody>
</table>

Photoluminescence spectroscopy:

Photoluminescence measurements were obtained on a Horiba Fluoromax-2 spectrofluorometer. Samples were prepared by adding 50 nmol EDANS peptoid solution and 2.4 $\mu$L of 10 mM Sc(OTf)$_3$ into 2 mL of
solvent (chloroform) in a 4 mL quartz cuvette (1 cm path length) with magnetic stir bar. Basic fluorescence measurements were then taken, excited at 343 nm and collected over the range 355 – 650 nm with slits set at 2.5 nm, and temperature controlled at 25°C. Then 50 nmol DABCYL peptoid were then added to the system for FRET type kinetics measurements. Kinetics experiments were taken in single wavelength collection mode at 464 nm over a course of 16 hours at increasing intervals (i.e., every 30 sec for 5 min, every 15 min for 1 hours, every 30 min for 2 hours, and then hourly for the remaining time points).

Figure S20. Circular dichroism (CD) spectra of Al₁₂ and Am₁₂. CD spectra were collected on a Jasco-815 CD spectrometer. Peptoids were dissolved in acetonitrile at concentrations of 25 mM. Blank scans containing only acetonitrile were collected and subtracted as background. Al₁₂ and Am₁₂ both exhibit spectra typical of random coil conformations, confirming non-ordered secondary structures for achiral peptoids.³

References: