SUPPORTING INFORMATION FOR: EXPERIMENTAL EVIDENCE FOR WATER MEDIATED ELECTRON-TRANSFER THROUGH BIS-AMINO ACID DONOR-BRIDGE-ACCEPTOR OLIGOMERS

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Supporting Information Table of Contents

Supporting Figures

Supporting Tables

General Methods:

Pro4ss and Pro4rr (see supplemental figure 1) were synthesized according to literature procedure[i,ii,iii]. Anhydrous N-methylpyrrolidinone, Anhydrous Dimethylformamide, Anhydrous Dichloromethane, Redistilled Diisopropylethylamine, Tetrakis(triphenylphosphine)palladium0, Borane:dimethylamine complex, Diisopropylcarbodiimide, Pyrenecarboxylic acid, Allyl chloroformate, and 37% Formaldehyde solution were purchased from Aldrich. Methanol, Tetrahydrofuran, Triethylamine and Trifluoroacetic acid were purchased from Alfa Aesar. Palladium on Carbon and O-(7-Azabenzotriazole-1-yl)-N, N,N'N'-tetramethyluronium hexafluorophosphate (HATU) were purchased from Genscript, Fmoc-4-nitrophenylanaline was purchased from TCI organics. Fmoc-Lys(Boc)-OH was purchased from Novabiochem.

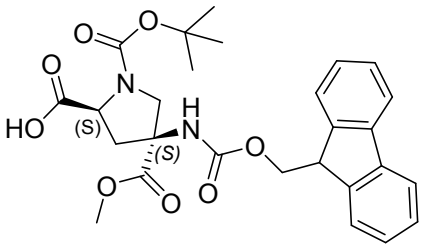
Flash Chromatography was perfored on an ISCO CombiFlash Companion with cartridges filled with Bodman 32-63 D (60Å) grade silica gel.

Analytical HPLC-MS analysis was performed on a Hewlett-Packard Series 1200 with a Waters Xterra MS C18 column (3.5um packing, 4.6 mm x 100mm) with a solvent system of water/acetonitrile with 0.1% formic acid at a flow rate of 0.8mL/min.

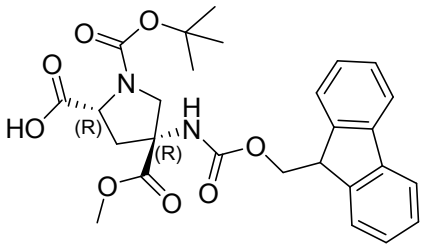
Preparatory Scale HPLC purification was performed on a Varian Prostar Prep HPLC with a Waters Xterra column (5um packing, 19mm x 100mm) with a solvent system of water/acetonitrile with 0.1% formic acid at a flow rate of 12mL/min.

NMR experiments were performed on a Bruker 500mHz NMR with a chemical shifts (δ) reported relative to DMSO-d6 or $CDCl_3$ residual solvent peaks.

HRESIQTOFMS analysis was performed by Ohio State University.



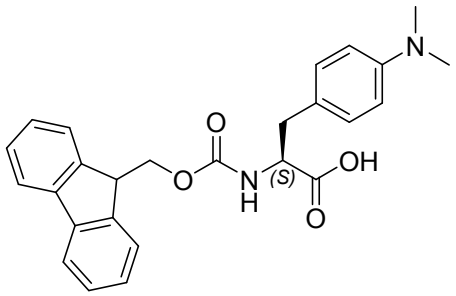
Pro4ss



Pro4rr

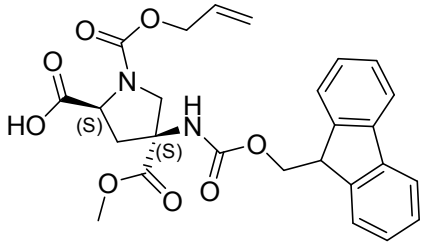
Supplemental Figure 1. Structures of Pro4ss and Pro4rr

Synthetic Methods:



(S)-2-(((9H-Fluoren-9-yl)methoxy)carbonylamino)-3-(4-(dimethylamino)phenyl)propanoic acid (sc1):

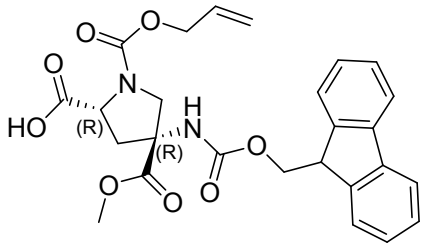
To a solution of Fmoc-4-nitrophenylanaline (1g, 2.3mmoles) in tetrahydrofuran/methanol (46mL, 1:1) was added 37% Formaldehyde (aq) (480uL, 4.6mmoles) followed by 69 mg of Palladium on Carbon. The reaction mixture was then degassed under vacuum, charged with H_2 (g), stirred overnight, concentrated under reduced pressure and purified by chromatography on silica (gradient elution over 16 column volumes from dichloromethane to 5% methanol in dichloromethane. Desired fractions were combined and concentrated under reduced pressure to yield (sc1) as a dark yellow solid (860 mg, 2.0mmoles, 87%). Purity was assessed by analytical HPLC-MS (See Supplementary Figure 1) ^{1}H NMR (500 MHz, rt, $CDCl_3$): δ 9.19 (br s, 1H), 7.77 (d, J = 7.55 Hz, 2H), 7.60 (t, J = 6.95 Hz, 2H), 7.41 (t, J = 7.40 Hz, 7.45 Hz, 2H), 7.32 (t, J = 7.40 Hz, 7.45 Hz, 2H), 7.10 (d, J = 8.20 Hz, 2H), 6.86 (d, J = 8.20 Hz, 2H), 5.53 (d, J = 7.65 Hz, 1H), 4.66 (q, J = 7.30 Hz, 3.00 Hz, 7.30 Hz, 1H), 4.35 (q, J = 7.30 Hz, 3.00 Hz, 7.30 Hz, 1H), 4.22 (t, J = 7.00 Hz, 7.00 Hz, 1H), 3.18 (m, 2H), 2.89 (s, 6H); HRESIQTOFMS calcd for $C_{26}H_{27}N_2O_4$ ($M + H^+$) 431.1971, measured 431.1967 (0.9ppm).



(2S,4S)-4-(((9H-fluoren-9-yl)methoxy)carbonylamino)-1-(allyloxycarbonyl)-4-(methoxy carbonyl) pyrrolidine-2-carboxylic acid (sc2):

To a solution of Pro4ss (1g, 1.96mmoles) in dichloromethane (14mL) was added trifluoroacetic acid (6mL). The reaction mixture was stirred for 4 hours then concentrated under reduced pressure. The residue was dissolved in tetrahydrofuran (10mL). Triethylamine (820uL, 5.88mmoles) was added followed by Allyl chloroformate (230uL, 2.15mmoles). The reaction mixture was stirred overnight, cooled to 0^{o}C, and acidified with 6M hydrochloric acid. The product was extracted with ethyl acetate. The organic portions were combined, washed with brine, dried over sodium sulfate, filtered, concentrated under reduced pressure and purified by chromatography on silica (gradient elution over 16 column volumes from dichloromethane to 5%

methanol in dichloromethane. Desired fractions were combined and concentrated under reduced pressure to yield (sc2) as a light yellow solid (914mg, 1.85mmoles, 94%). ^{1}H NMR (500 MHz, rt, DMSO-d6): δ 8.49 (bs, 1H), 8.11 (d, J = 7.45 Hz, 2H), 7.92 (d, J = 7.05 Hz, 2H), 7.64 (t, J = 7.30 Hz, 7.4 Hz, 2H), 7.56 (t, J = 7.30 Hz, 7.20 Hz, 2H), 6.17 (m, 1H), 5.52 (t, J = 16.7 Hz, 16.7 Hz, 1H), 5.43 (dd, J = 10.5 Hz, 17.9 Hz, 10.5 Hz, 1H), 4.77 (m, 2H), 4.54 (m, 4H), 4.29 (dd, J = 11.2 Hz, 24.2 Hz, 11.2 Hz, 1H), 3.82 (s, 3H), 3.80 (m, 1H), 3.11 (m, 1H).



(2R,4R)-4-(((9H-fluoren-9-yl)methoxy)carbonylamino)-1-(allyloxycarbonyl)-4-(methoxy carbonyl) pyrrolidine-2-carboxylic acid (sc3):

To a solution of Pro4rr (1g, 1.96mmoles) in dichloromethane (14mL) was added trifluoroacetic acid (6mL). The reaction mixture was stirred for 4 hours then concentrated under reduced pressure. The residue was dissolved in tetrahydrofuran (10mL). Triethylamine (820uL, 5.88mmoles) was added followed by Allyl chloroformate (230uL, 2.15mmoles). The reaction mixture was stirred overnight, cooled to 0^{o}C, and acidified with 6M hydrochloric acid. The product was extracted with ethyl acetate. The organic portions were combined, washed with brine, dried over sodium sulfate, filtered, concentrated under reduced pressure and purified by chromatography on silica (gradient elution over 16 column volumes from dichloromethane to 5% methanol in dichloromethane. Desired fractions were combined and concentrated under reduced pressure to yield (sc3) as a light yellow solid (882mg, 1.78mmoles, 91%). ^{1}H NMR (500 MHz, rt, DMSO-d6): δ 8.49 (bs, 1H), 8.11 (d, J = 7.45 Hz, 2H), 7.92 (d, J = 7.05 Hz, 2H), 7.64 (t, J = 7.30 Hz, 7.4 Hz, 2H), 7.56 (t, J = 7.30 Hz, 7.20 Hz, 2H), 6.17 (m, 1H), 5.52 (t, J = 16.7 Hz, 16.7 Hz, 1H), 5.43 (dd, J = 10.5 Hz, 17.9 Hz, 10.5 Hz, 1H), 4.77 (m, 2H), 4.54 (m, 4H), 4.29 (dd, J = 11.2 Hz, 24.2 Hz, 11.2 Hz, 1H), 3.82 (s, 3H), 3.80 (m, 1H), 3.11 (m, 1H).

Solid Phase Oligomer Assembly

General procedure (A): Attachment to Wang resin

To a solution of the amino acid (10 equivalents based on resin loading) in dichloromethane (3mL/mmole of amino acid) was added diisopropylcarbodiimide (5 equivalents based on resin loading). The reaction mixture was allowed to stir for 30 minutes, concentrated under reduced pressure, reconstituted in dimethylformamide (5mL/mmole of amino acid) and added to a pre-swelled (in dimethylformamide) portion of resin in a solid phase reactor. To this solution was added dimethylaminopyridine (0.1 equivalents based on amino acid). The reaction mixture was stirred for 1 hour. The resin was filtered and washed with dimethylformamide, isopropanol, and dimethylformamide.

General procedure (B): HATU coupling

To a solution of amino acid (3 equivalents based on resin loading) and HATU (3 equivalents based on resin loading in N-methylpyrrolidine (5mL/mmole of amino acid) was added diisopropylethylamine (6 equivalents based on resin loading). The reaction mixture was added to a pre-swelled (in dimethylformamide) portion of resin in a solid phase reactor and stirred for 45 minutes. The resin was filtered and washed with dimethylformamide, isopropanol, and dimethylformamide.

General procedure (C): Fmoc deprotection

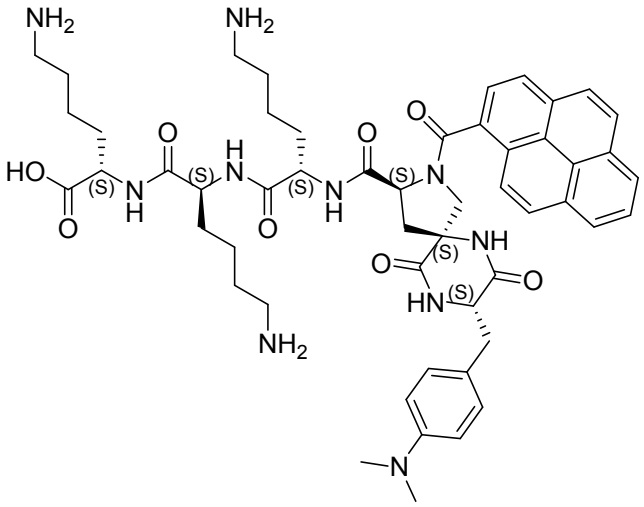
A solution of 20% of piperidine in dimethylformamide (15mL/mmole based on resin loading) was added to a pre-swelled (in dimethylformamide) portion of resin in a solid phase reactor and stirred for 15 minutes. The resin was filtered and washed with dimethylformamide, isopropanol, and dimethylformamide.

General procedure (D): Alloc deprotection

A solution of borane:dimethylamine complex (6 equivalents based on resin loading) in dichloromethane (10mL/mmole based on resin loading) was added to a pre-swelled (in dimethylformamide) portion of resin in a solid phase reactor and stirred for 5 minutes. To this solution was added a solution of tetrakis(triphenylphosphine)palladium0 (0.1 equivalents based on resin loading) in dichloromethane (10mL/mmole based on resin loading). The reaction mixture was stirred for 1 hour. The resin was filtered and washed with dimethylformamide, isopropanol, and dimethylformamide.

General procedure (E): Liberation from Wang resin

A solution of 5% triisopropylsilane and 5% water in trifluoroacetic acid (25 mL/mmole based on resin loading was added to a portion of resin (successively washed with dichloromethane and methanol, and thoroughly dried under vacuum) and stirred for 4 hours. The resin was filtered and washed with trifluoroacetic acid. The filtrate was concentrated, reconstituted in 75% acetonitrile in water (0.05% formic acid) and freeze-dried.



D-SSS-A (sc4):

Wang resin (200mg, 150umoles loading) was placed in a 15mL solid phase reactor. Fmoc-Lys(Boc)-OH (703mg, 1.5mmoles) was attached according to general procedure (A) using dichloromethane (4.5mL), diisopropylcarbodiimide (116uL, 750umoles), dimethylformamide (4.5mL), and dimethylaminopyridine (18.3mg, 150umoles). The terminal Fmoc group was removed according to general procedure (C) using 20% piperidine in dimethylformamide (2.25mL).

Fmoc-Lys(Boc)-OH (211mg, 450umoles) was coupled according to general procedure (B) using HATU (171mg, 450umoles), N-methylpyrrolidinone (2.25mL), and diisopropylethylamine (156uL, 900umoles). The terminal Fmoc group was removed according to general procedure (C) using 20% piperidine in dimethylformamide (2.25mL).

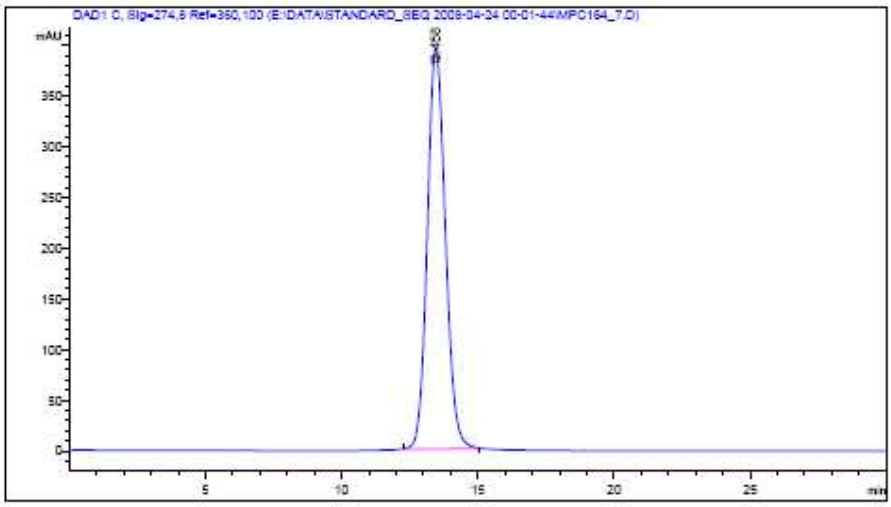
Fmoc-Lys(Boc)-OH (211mg, 450umoles) was coupled according to general procedure (B) using HATU (171mg, 450umoles), N-methylpyrrolidinone (2.25mL), and diisopropylethylamine (156uL, 900umoles). The terminal Fmoc group was removed according to general procedure (C) using 20% piperidine in dimethylformamide (2.25mL).

(sc2) (223mg, 450umoles) was coupled according to general procedure (B) using HATU (171mg, 450umoles), N-methylpyrrolidinone (2.25mL), and diisopropylethylamine (156uL, 900umoles). The terminal Fmoc group was removed according to general procedure (C) using 20% piperidine in dimethylformamide (2.25mL).

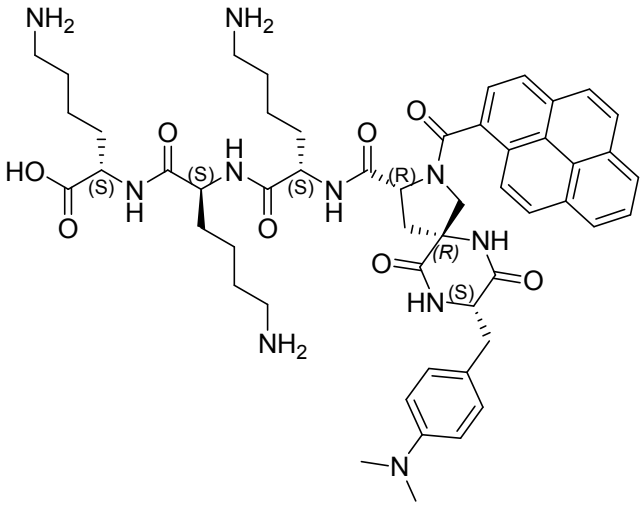
Fmoc-DMA-OH (sc1) (194mg, 450umoles) was coupled according to general procedure (B) using HATU (171mg, 450umoles), N-methylpyrrolidinone (2.25mL), and diisopropylethylamine (156uL, 900umoles). The terminal Fmoc group was removed according to general procedure (C) using 20% piperidine in dimethylformamide (2.25mL) and the reaction time was extended to 1 hour.

The Alloc group was removed according to general procedure (D) using borane:dimethylamine complex (53mg, 900umoles) in dichloromethane (2.5mL) and tetrakis(triphenylphosiphine)palladium0 (17mg, 15umoles) in dichloromethane (2mL). Pyrenecarboxylic acid (111mg, 450umoles) was coupled according to general procedure (B) using HATU (171mg, 450umoles), N-methylpyrrolidinone (2.25mL), and diisopropylethylamine (156uL, 900umoles).

(sc4) was liberated from the resin according to general procedure (E) using 3.75 mL of the cleavage cocktail. The residue was reconstituted in 75% acetonitrile in water (0.05% formic acid) and purified by reverse-phase chromatography (gradient elution over 30 minutes from water (0.1% formic acid) to 50% acetonitrile (0.05% formic acid) in water (0.1% formic acid). Desired fractions were combined and freeze-dried to yield (4) as a white powder. Purity was assessed with analytical HPLC-MS; mobile phase, (gradient elution over 30 minutes from water (0.1% formic acid) to 50% acetonitrile (0.05% formic acid) in water (0.1% formic acid), UV detection at 274nm, tR = 13.458 ESI-MS *m/z* (relative intensity): 229.10 (80.9%), 480.25 (100.0%), 959.30 (81.6%), 960.35 (51.0%), HRESIQTOFMS calculated for $C_{52}H_{67}N_{10}O_8$ ($M + H^+$) 959.5143 measured 959.5115 (2.9ppm).



Supplemental Figure 2. Reverse-Phase purified chromatogram of (sc4). UV detection at 274nm, tR = 13.458 ESI-MS *m/z* 959.30 (calculated for 958.51).



D-SRR-A (5):

Wang resin (200mg, 150umoles loading) was placed in a 15mL solid phase reactor. Fmoc-Lys(Boc)-OH (703mg, 1.5mmoles) was attached according to general procedure (A) using dichloromethane (4.5mL), diisopropylcarbodiimide (116uL, 750umoles), dimethylformamide (4.5mL), and dimethylaminopyridine (18.3mg, 150umoles). The terminal Fmoc group was removed according to general procedure (C) using 20% piperidine in dimethylformamide (2.25mL).

Fmoc-Lys(Boc)-OH (211mg, 450umoles) was coupled according to general procedure (B) using HATU (171mg, 450umoles), N-methylpyrrolidinone (2.25mL), and diisopropylethylamine (156uL, 900umoles). The terminal Fmoc group was removed according to general procedure (C) using 20% piperidine in dimethylformamide (2.25mL).

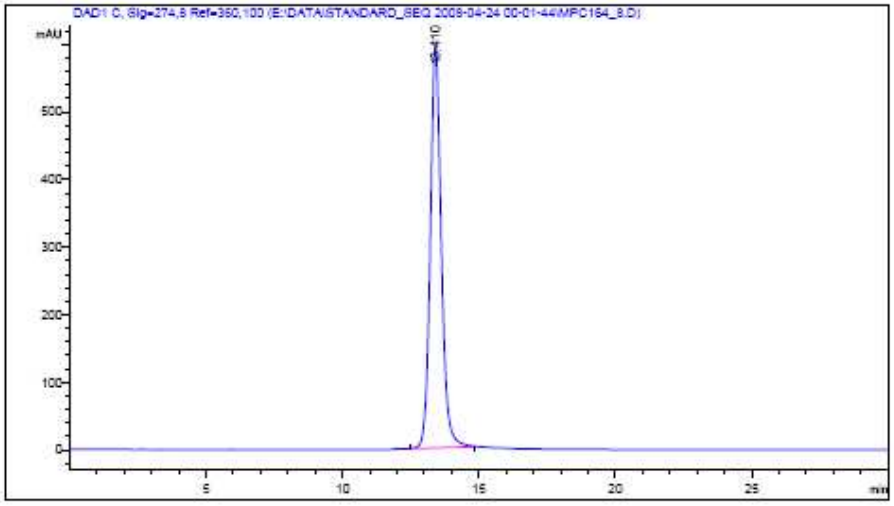
Fmoc-Lys(Boc)-OH (211mg, 450umoles) was coupled according to general procedure (B) using HATU (171mg, 450umoles), N-methylpyrrolidinone (2.25mL), and diisopropylethylamine (156uL, 900umoles). The terminal Fmoc group was removed according to general procedure (C) using 20% piperidine in dimethylformamide (2.25mL).

(sc3) (223mg, 450umoles) was coupled according to general procedure (B) using HATU (171mg, 450umoles), N-methylpyrrolidinone (2.25mL), and diisopropylethylamine (156uL, 900umoles). The terminal Fmoc group was removed according to general procedure (C) using 20% piperidine in dimethylformamide (2.25mL).

Fmoc-DMA-OH (sc1) (194mg, 450umoles) was coupled according to general procedure (B) using HATU (171mg, 450umoles), N-methylpyrrolidinone (2.25mL), and diisopropylethylamine (156uL, 900umoles). The terminal Fmoc group was removed according to general procedure (C) using 20% piperidine in dimethylformamide (2.25mL) and the reaction time was extended to 1 hour.

The Alloc group was removed according to general procedure (D) using borane:dimethylamine complex (53mg, 900umoles) in dichloromethane (2.5mL) and tetrakis(triphenylphosiphine)palladium0 (17mg, 15umoles) in dichloromethane (2mL). Pyrenecarboxylic acid (111mg, 450umoles) was coupled according to general procedure (B) using HATU (171mg, 450umoles), N-methylpyrrolidinone (2.25mL), and diisopropylethylamine (156uL, 900umoles).

(sc5) was liberated from the resin according to general procedure (E) using 3.75 mL of the cleavage cocktail. The residue was reconstituted in 75% acetonitrile in water (0.05% formic acid) and purified by reverse-phase chromatography (gradient elution over 30 minutes from water (0.1% formic acid) to 50% acetonitrile (0.05% formic acid) in water (0.1% formic acid)). Desired fractions were combined and freeze-dried to yield (5) as a white powder. Purity was assessed with analytical HPLC-MS; mobile phase, (gradient elution over 30 minutes from water (0.1% formic acid) to 50% acetonitrile (0.05% formic acid) in water (0.1% formic acid), UV detection at 274nm, tR = 13.410 ESI-MS *m/z* (relative intensity): 229.10 (80.9%), 480.25 (100.0%), 959.30 (81.6%), 960.30 (51.0%), HRESIQTOFMS calculated for $C_{52}H_{67}N_{10}O_8$ ($M + H^+$) 959.5143, measured 959.5102 (4.3ppm).



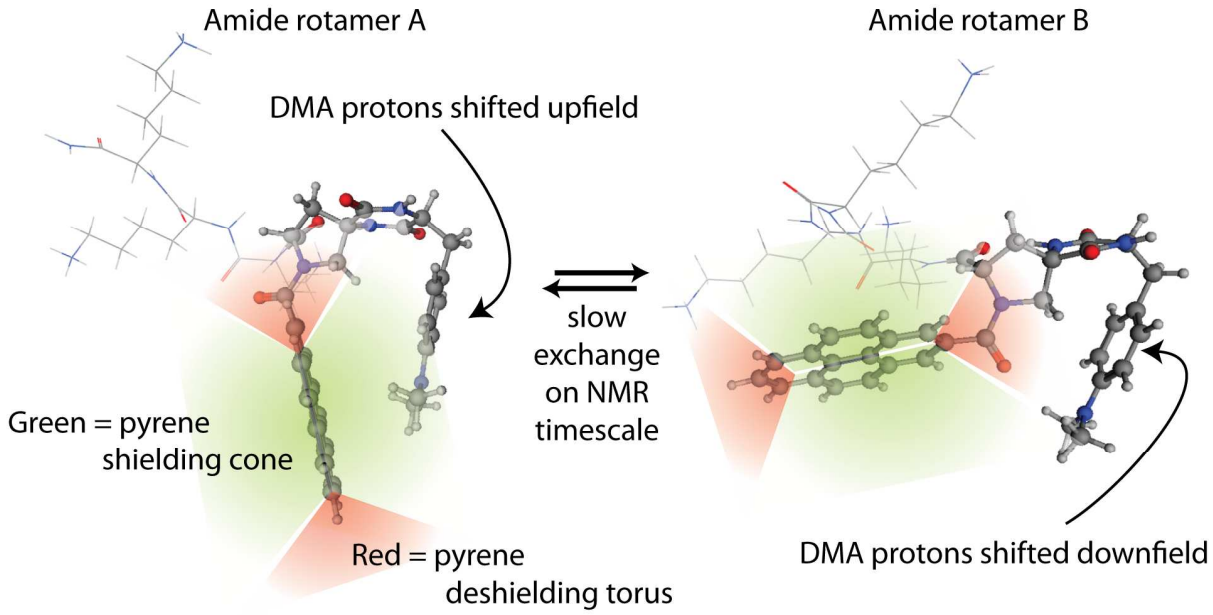
Supplemental Figure 3. Reverse-Phase purified chromatogram of (sc5). UV detection at 274nm, tR = 13.410 ESI-MS *m/z* 959.30 (calculated for 958.51).

Oligomer Characterization:

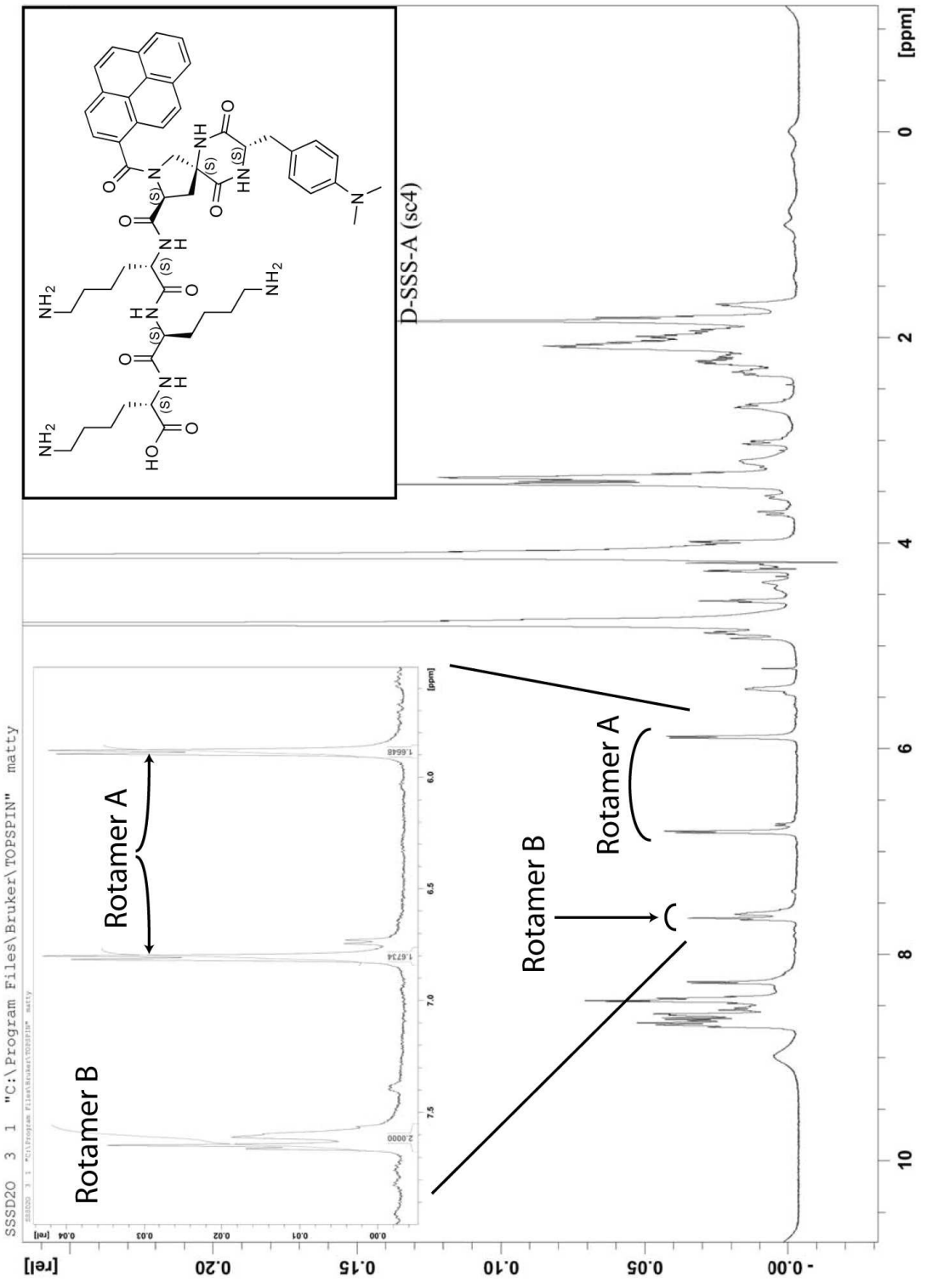
Oligomer NMR samples were prepared at 20 mM concentration in DMSO or D_2O. The NMR samples were treated with 10 uL of a 1M TFA-d to bring the final solution pH was 4.87-4.9 and were transferred to Shigemi Tubes. The NMR experiments were performed on a Bruker 500mHz instrument at elevated temperatures (330-333K). The pH and temperature settings were determined experimentally to provide optimized resolution of spectra. However all spectrum display a mixture of rotamers attributed to the slow rotation of the pyrene carboxamide.

NMR Experiment	Supplemental Figure	Integration of Conformer A	Integration of Conformer B	Relative population A:B
(sc4) D_2O	3	1.6691	1.0000	63:37
(sc4) DMSO	4	1.8444	1.0000	65:35
(sc5) D_2O	5	1.7281	1.0000	63:37

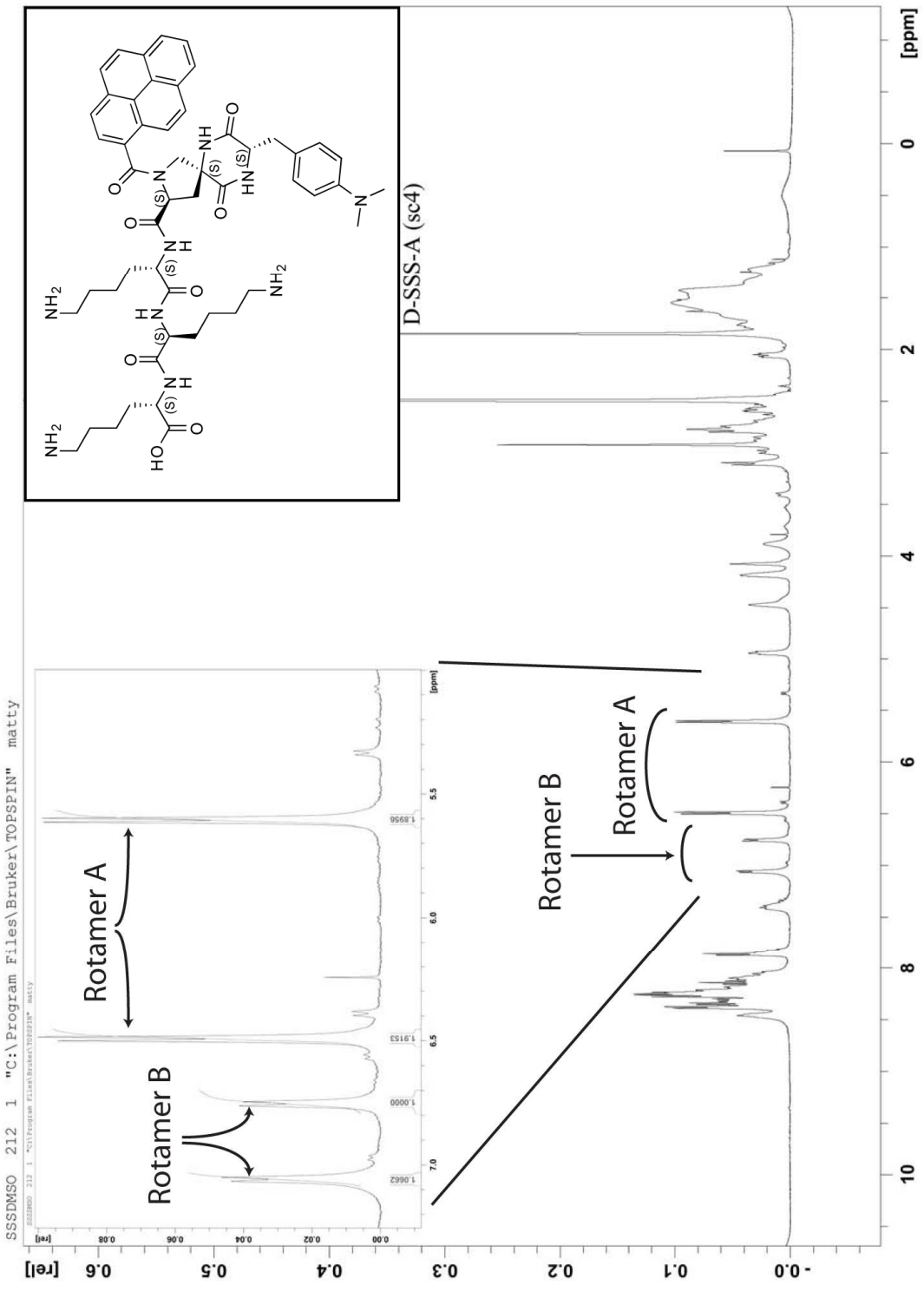
Supplemental Table 1. NMR analysis of conformer ratio. Integration of the Aromatic protons on the Dimethylanaline displayed as a ratio of the two slowly exchanging tertiary amide rotamers Rotamers A and B for (sc4) refer to the rotameric species of the pyrene carboxamide modeled in Supplemental Figure 4. Rotamer A is the more shielded (up-field) constituent and Rotamer B is the less shielded (down-field) constituent. Both rotamers A and B of sc5 have their dimethylaniline hydrogens shifted downfield because the relative stereochemistry of this molecule holds the dimethylaniline group out of the pyrene shielding cone permanently.



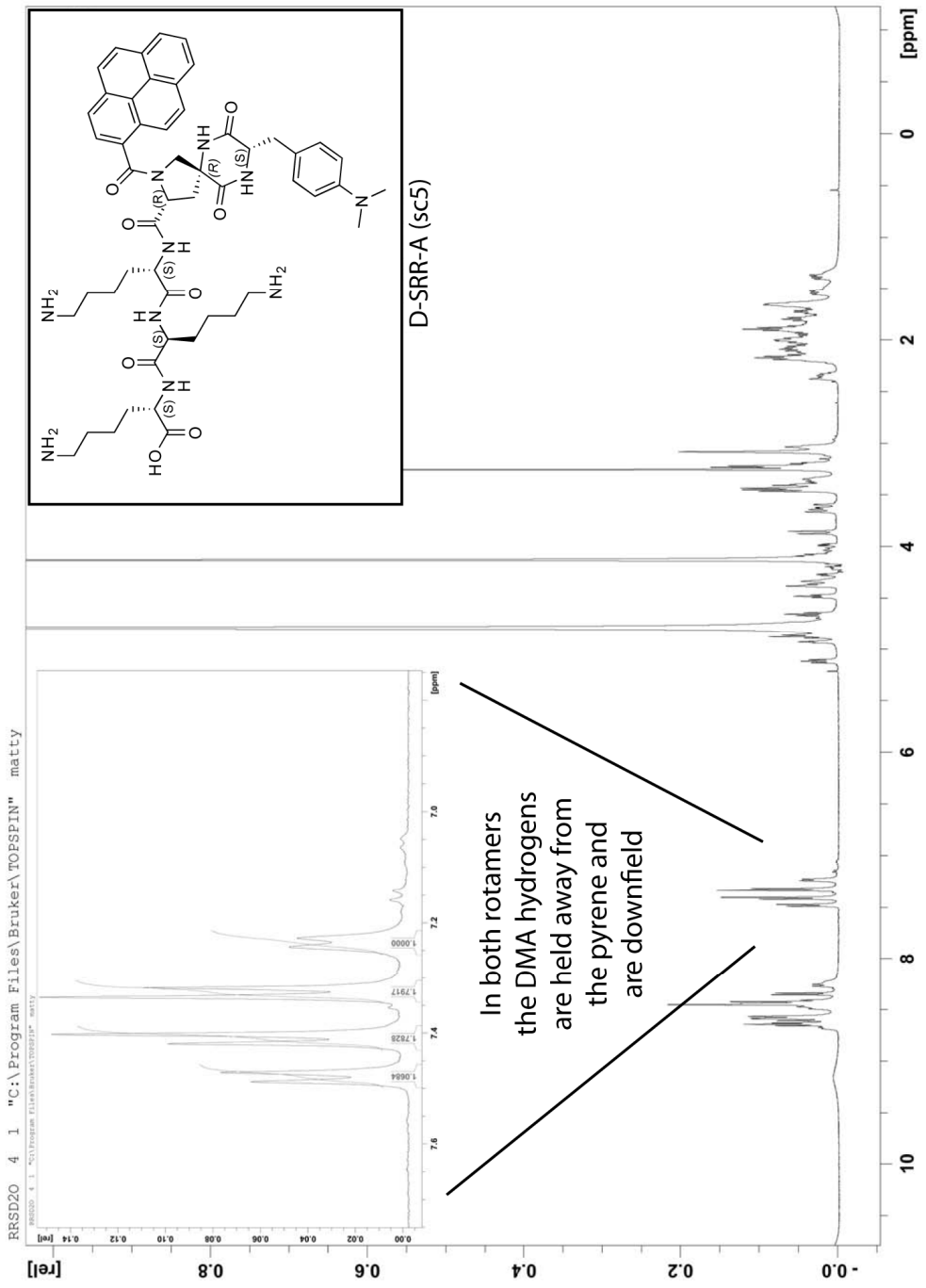
Supplemental Figure 4. Molecular models of pyrenecarboxamide rotamers in (sc4).



Supplemental Figure 5. ^{1}H NMR (500 MHz, D_2O, pH 4.90, 333K) of D-SSS-A (sc4)



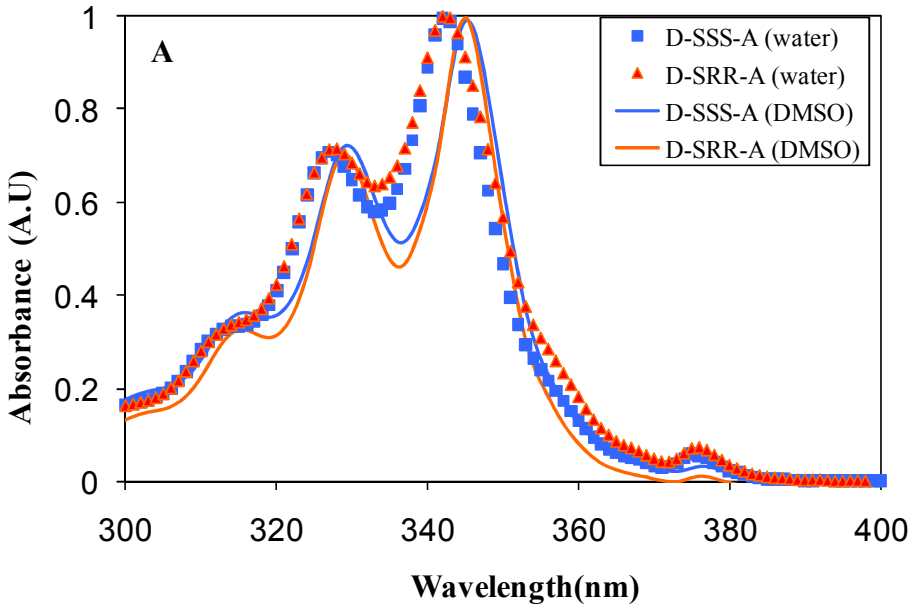
Supplemental Figure 6. ^{1}H NMR (500 MHz, DMSO, pH 4.90, 330K) of D-SSS-A (sc4)

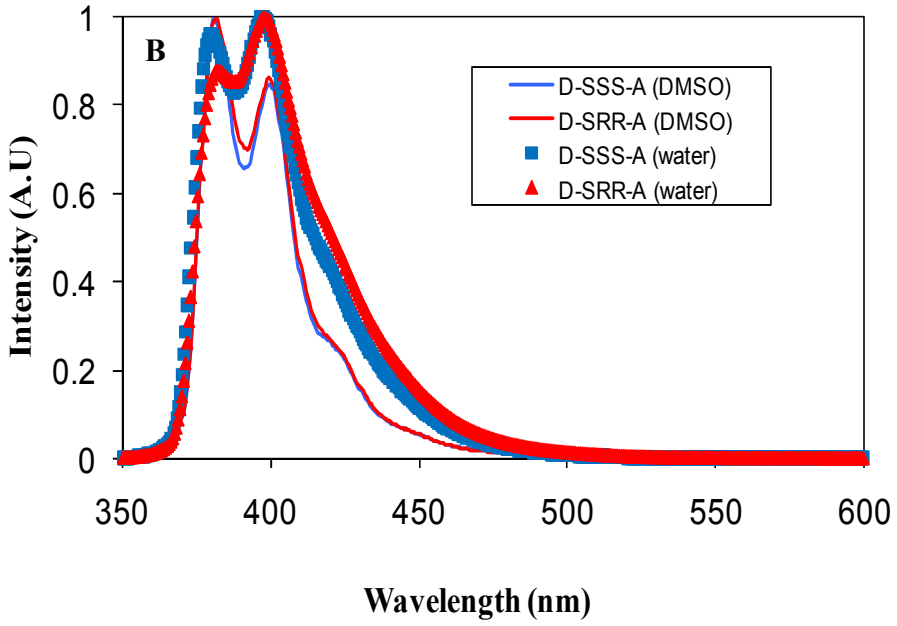


Supplemental Figure 7. ^{1}H NMR (500 MHz, D_2O, pH 4.87, 333K) of D-SRR-A (sc5)

Steady-State Absorption and Fluorescence Spectra of D-SSS-A and D-SRR-A

Steady-state absorption (A) and fluorescence (B) spectra for D-SSS-A and D-SRR-A in water and DMSO are shown below. The fluorescence spectra were obtained at an excitation wavelength of 330 nm.





Fitting of the experimental data to the semiclassical electron transfer equation:

The semiclassical model for electron transfer in the nonadiabatic limit begins with a Fermi's Golden Rule expression for the transition rate; namely

$$k_{ET} = (2\pi / \hbar)|V|^2 FCWDS$$

where $\hbar$ is Planck's constant divided by 2π, $|V|$ is the electronic coupling matrix element, and FCWDS is the Franck-Condon weighted density of states. Previous work has successfully applied the Golden Rule rate constant expression with a single effective quantum mode, and described k_{ET} by the semiclassical rate equation.

$$k_{ET} = \frac{4\pi^2}{h} |V|^2 \frac{1}{\sqrt{4\lambda_S \pi k_B T}} \sum_{n=0}^{\infty} \exp(-S)\left(\frac{S^n}{n!}\right) \exp\left[-\frac{(\Delta_r G + \lambda_S + nh\nu)^2}{4\lambda_S k_B T}\right] \qquad \mathbf{1}$$

where λ_S is the solvent reorganization energy; $\Delta_r G$ is the reaction free energy; $S = \frac{\lambda_v}{h\nu}$; and λ_v is the internal reorganization energy. The $h\nu$ term refers to the characteristic energy of a single effective quantized mode that is involved in the electron transfer reaction and is a characteristic of the solute. The sum is performed over the vibrational states of the effective quantum mode. The quantities $h\nu$ and λ_v are determined primarily by the donor and acceptor groups and are not sensitive to their separation. This analysis uses a value of 1400 cm^{-1} for the single effective quantized mode ν and 0.19 eV for the solute reorganization energy λ_v. This effective mode frequency is comparable to typical carbon-carbon stretching frequencies in aromatic ring systems and taken from our previous work carried out on C-shaped DBA molecules having the similar donor and acceptor groups (reference 15 mentioned in the reference section of the text).

Calculation of reorganization energy considering the elliptical cavity:

The reorganization energy λ_S for the compounds **D-SSS-A**, **D-SRR-A** in water and DMSO were calculated from a continuum model of solvation using the following equation where the solvent cavity is considered to be ellipsoidal.

$$\lambda_S = \frac{\Delta\mu^2}{2AB^2}\left(\frac{1}{D_{OP}} - \frac{1}{D_S}\right)\sum_{n=1}^{n=\infty} X_n \qquad \mathbf{2}$$

and

$$X_n = (1/2)(2n+1)\left[1-(-1)^n\right]k(k^2-1)Q_n(k)/P_n(k) \qquad \mathbf{3}$$

where $\Delta\mu$ is the dipole moment difference, $P_n(k)$ and $Q_n(k)$ are the Legendre polynomials of the first kind and second kind respectively. 2A and 2B are the lengths of the major axis and the minor axis of the ellipsoid. k is given by $k = \sqrt{\frac{A^2}{A^2 - B^2}}$.

The molecular diameters for **D-SRR-A** were taken to be 13.5 Å, 5 Å, and 8 Å, and for **D-SSS-A**, they were taken to be 8 Å, 5 Å, and 10 Å. This model is for a symmetric ellipsoid, so calculations were done using 13.5 Å and 6.5 Å (average of other two axis) for **D-SRR-A** and 8 Å and 7.5 Å (average of other two axis) for **D-SSS-R** . The computed values of $\sum_{n=1}^{n=\infty} X_n$ for **D-SSS-A** and **D-SRR-A** are 0.951645 and 0.702741 respectively.

If we assume that a full charge moves the center-to-center distance in **D-SSS-A**, it will produce a dipole moment of 22 D. If we carry out a similar calculation on **D-SRR-A** the dipole moment value we obtain is 46 D, which is quite large. If the dipole moment change from **D-SSS-A** to **D-**

SRR-A is assumed to scale as the effective radius increase from **D-SSS-A** and **D-SRR-A** (1.10 times assuming the constant volume approximation between the two ellipsoids) then a dipole moment of 24 D is found for **D-SRR-A**. Using the values of $(1/D_{op}-1/D_s)$ for water and DMSO, which are 0.55 and 0.437 respectively, we can use Equation 2 to obtain the reorganization energy of **D-SSS-A** in water of 1.42 eV, and the reorganization energy of **D-SRR-A** in water of 1.14 eV (for $\Delta\mu \sim 24$ D) [we find 3.67 eV for $\Delta\mu = 46$ D]. Similarly, the reorganization energy of **D-SSS-A** in DMSO is 1.12 eV, and the reorganization energy of **D-SRR-A** in DMSO is 0.91 eV (for $\Delta\mu \sim 24$ D) [we find 2.91 eV for $\Delta\mu = 46$ D]. In the current work, λ_S was calculated using Equation 2 and kept fixed for water and DMSO. The electronic coupling $|V|$ and the free energy change Δ_rG were used as adjustable parameters in Equation 1. Using all the parameters λ_S, λ_V, ν, ΔG (adjustable), $|V|$ (adjustable) in Equation 1, we can calculate the semiclassical electron transfer rate. The calculated k_{ET} values were fitted to the experimental electron transfer rate constant values using the "*Solver*" function in Excel 2007. The values of the Gibbs energy and electronic coupling that are reported in the text were found from this fit.

This analysis gives a solvent reorganization energy that is smaller for **D-SSR-A** than **D-SSS-A**, whereas one might expect a somewhat larger value given the larger charge displacement. We note that equation 2, shows that the larger ellipsoidal length acts for **D-SRR-A** causes this decrease even though the dipole is chosen to be somewhat larger. Because of the difficulties in assessing the dipole moment change and in lieu of a more detailed numerical calculation of the reorganization energy, we have analyzed how the fitting parameters |V| and Δ_rG change for the **D-SRR-A** data with different reorganization energies. We find that by keeping the internal reorganization parameters fixed at $\lambda_v = 0.19$ eV and $\nu = 1400$ cm^{-1}, and changing the solvent reorganization the electronic coupling parameters changes somewhat but does not impact our conclusion.

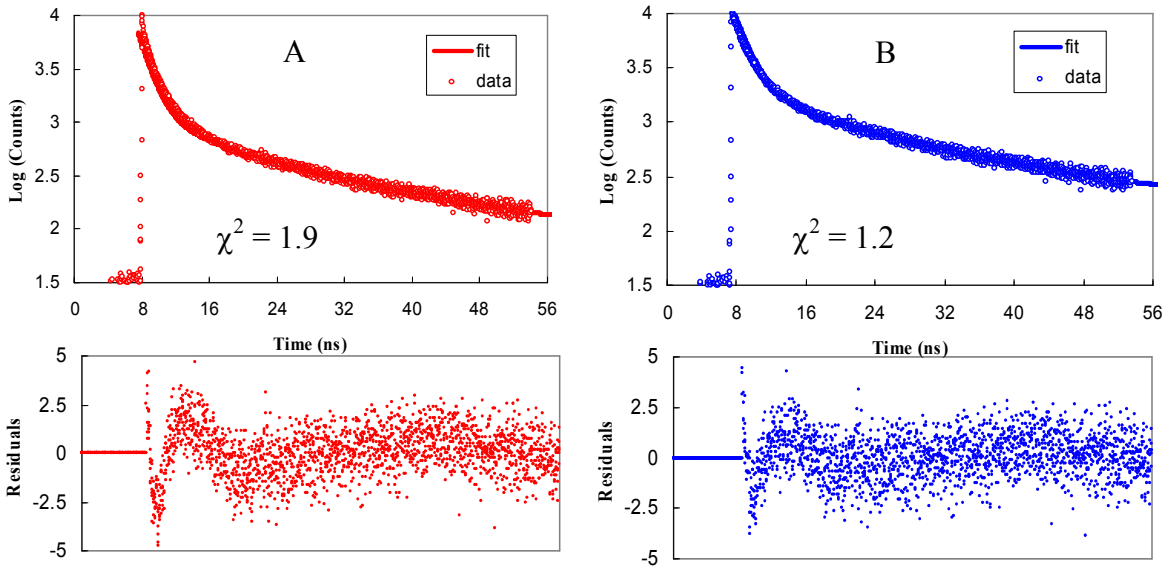
Solvent	**λ_s / eV**	**|V| / cm-1**	**Δ_rG / eV**
Water	1.12	12	-0.54
Water	1.42	12	-0.76
Water	1.72	12	-1.00
DMSO	0.91	13	-0.36
DMSO	1.12	14	-0.51
DMSO	1.33	14	-0.66

Experimental Rate Constant Data:

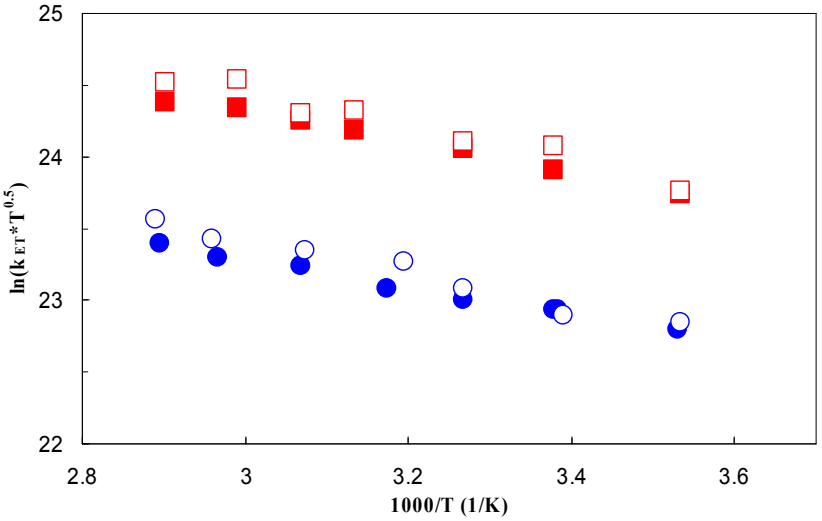
The fluorescence decay laws of the molecules **D-SSS-A** and **D-SRR-A** were found to be double exponential in both water and DMSO. The long lifetime component is of smaller amplitude, and it has a relaxation time that is close to that found for the acceptor only control molecule studied in solution (**SSS-A**). This most likely corresponds to **D-SSS-A** and **D-SRR-A** rotamers that have the pyrene moiety rotated away from the donor. The lifetimes suggest that the electron transfer rate constant for one of these rotamers is small or similar to the acceptor's intrinsic fluorescence decay (see Table 4). The short decay time components, which dominate

the decay law, are assigned to rotamers in which the pyrene and dimethylaniline moieties define a cleft. Given that the rate constant in **D-SRR-A** does not change between DMSO and water suggests that the electronic coupling is bridge mediated in this case, but differs between the rotamers. Conformational effects on the efficiency of bridge mediated charge transfer have been reported previously for other systems.

We have performed the fits to fluorescence decay data in DMSO by two different methods. In one case we kept the population of the two rotamers fixed at the same ratio as obtained from the NMR studies. In the other case we let the fit proceed with no restrictions on the population ratio. Although the lifetime and the fit quality changes somewhat between the two cases, the overall electron transfer rate constant does not change much. Figure 8 shows how the fit quality differs in the two cases for **D-SSS-A** in DMSO at 303K. The electron transfer rate constants obtained from such fits are plotted in Figure S9 as a function of temperature. The closed and open circles in Figure S9 represent the two types of fits. The variation in rate constant values with fitting method is much smaller than the difference in rate constant with solvent type.



Supplemental Figure 8. Representative fluorescence decay data. Panel A represents the fluorescence decay of **D-SRR-A** in DMSO keeping the population ratio of the two rotamers fixed to that obtained from NMR experiment. Panel B represents the fluorescence decay of **D-SRR-A** in DMSO when the population ratio is varied



Supplemental Figure 9. This figure plots the temperature dependent electron transfer rate constant kET that is obtained for **D-SSS-A** in water and DMSO by using the two different fit methods (optimal amplitudes and NMR constrained amplitudes). The plot shows the rate constants for water (red closed square) and DMSO (blue closed circle) with optimized amplitudes, and for water (red open square) and DMSO (blue open circle) for populations (amplitudes) fixed at the value obtained from the NMR experiment.

Decay law fitting parameters:

Solvent	Temperature (K)	Lifetime τ_1 (ps)	A_1 (%)	Lifetime τ_2 (ps)	A_2 (%)	k_{ET} (s^{-1})
Water	283	807	65	15600	35	1.24 E+09
Water	296	599	64	12766	36	1.67 E+09
Water	306	592	62	11103	38	1.69 E+09
Water	319	484	62	11236	38	2.07 E+09
Water	326	498	64	11767	36	2.01 E+09
Water	334.5	404	61	8034	39	2.48 E+09
Water	344.5	418	64	7497	36	2.39 E+09
DMSO	283	2000.00	69	17915.64	31	5.00 E+08
DMSO	296	1687.59	67	15538.10	33	5.93 E+08
DMSO	306	1587.91	65	14045.17	35	6.30 E+08
DMSO	319	1488.44	67	12860.16	33	6.72 E+08
DMSO	326	1293.93	67	11591.00	33	7.73 E+08
DMSO	334.5	1386.79	64	10523.04	36	7.21 E+08
DMSO	344.5	1277.60	66	9867.35	34	7.83 E+08

Supplemental Table 2. D-SSS-A (sc4) in Water and DMSO excited at 330nm

Solvent	Temperature (K)	Lifetime τ_1 (ps)	A_1 (%)	Lifetime τ_2 (ps)	A_2 (%)	k_{ET} (s^{-1})
Water	283	2177	66	12620	34	4.59 E+08
Water	296	1885	64	12419	36	5.31 E+08
Water	306	1598	63	11336	37	6.26 E+08
Water	319	1578	62	12194	38	6.34 E+08
Water	326	1456	66	11842	34	6.87 E+08
Water	334.5	1445	67	11673	33	6.92 E+08
Water	344.5	1365	65	11308	35	7.33 E+08
DMSO	283	2066	80	20661	20	4.84 E+08
DMSO	296	1744	82	15538	18	5.73 E+08
DMSO	306	1585	81	14045	19	6.31 E+08
DMSO	319	1470	79	12860	21	6.80 E+08
DMSO	326	1348	80	16154	20	7.42 E+08
DMSO	334.5	1305	82	10523	18	7.66 E+08
DMSO	344.5	1219	81	9867	19	8.20 E+08

Supplemental Table 3. D-SRR-A (sc5) in Water and DMSO excited at 330nm

Solvent	Temperature (K)	Lifetime τ (ps)
Water	296	12620
Water	306	12419
Water	315	11842
Water	326	11336
Water	345	11308
DMSO	296	15538
DMSO	306	14045
DMSO	315	12860
DMSO	326	12096
DMSO	345	9867

Supplemental Table 4. Acceptor Only (SSS-A) in Water and DMSO excited at 330**nm**

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