Supplementary Information
for

Photoresponsive Peptoid Oligomers Bearing Azobenzene Side Chains

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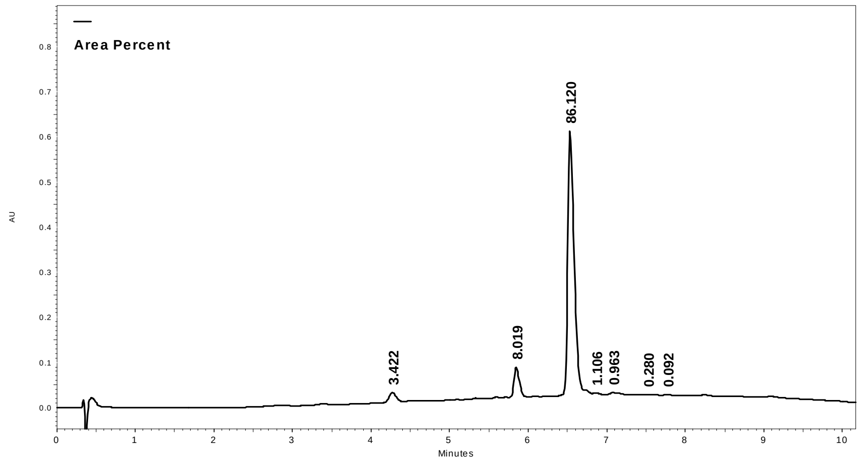
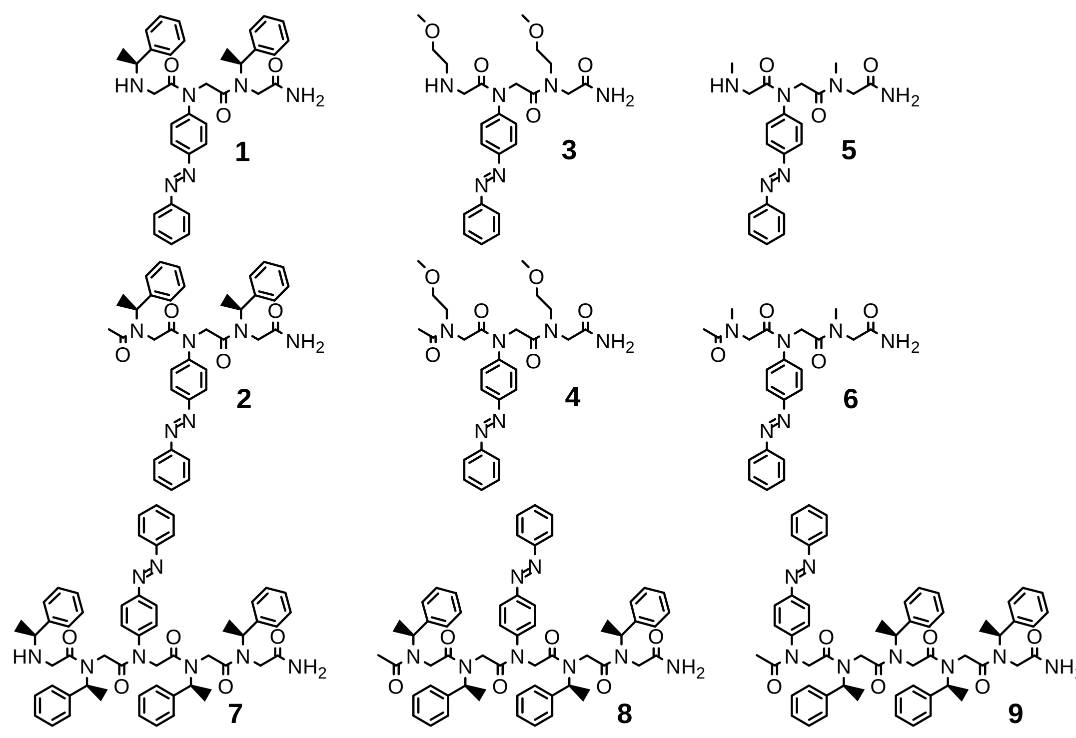
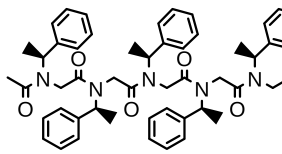
Synthesis of peptoid oligomers

A representative RP-HPLC analytical chromatograph of crude peptoid **1** is shown below. The dominant peak corresponds to the *trans*-azobenzene isomer, and the second-largest peak corresponds to the *cis*-azobenzene isomer.



Structures of peptoid oligomers





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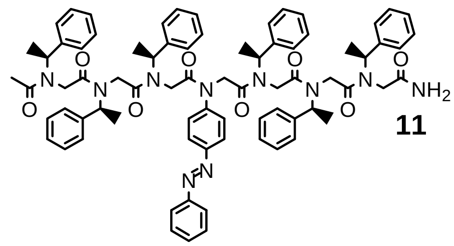

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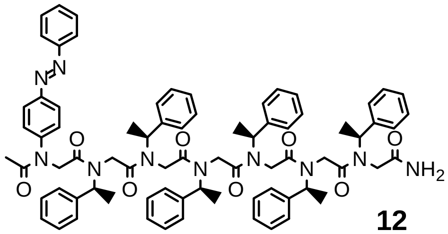

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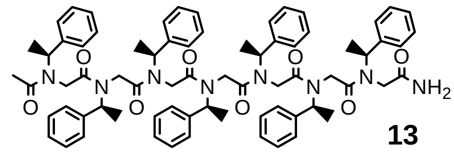

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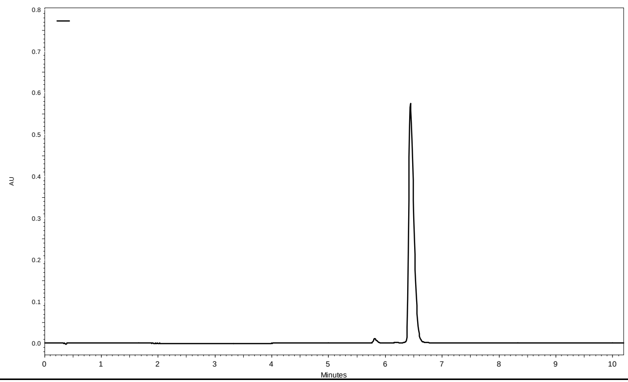
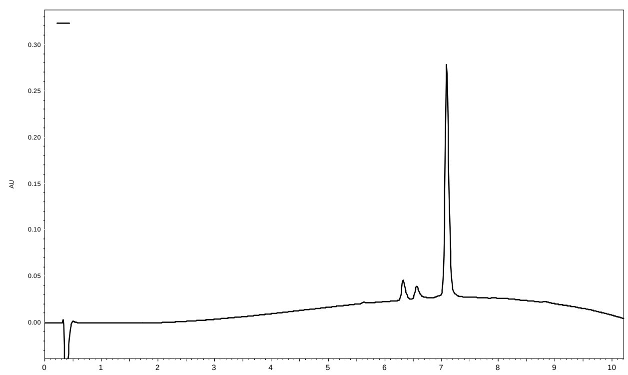
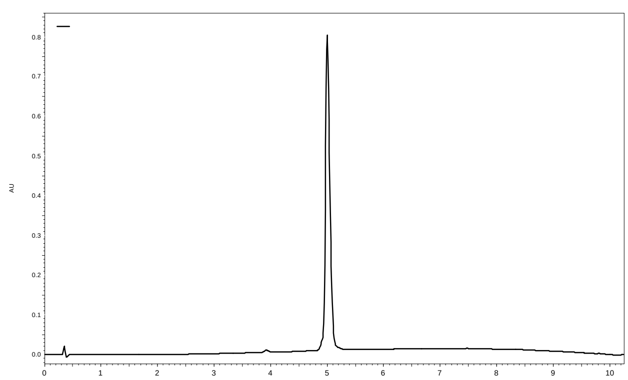
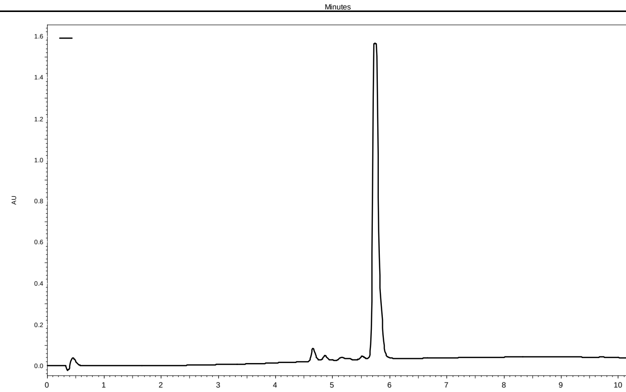
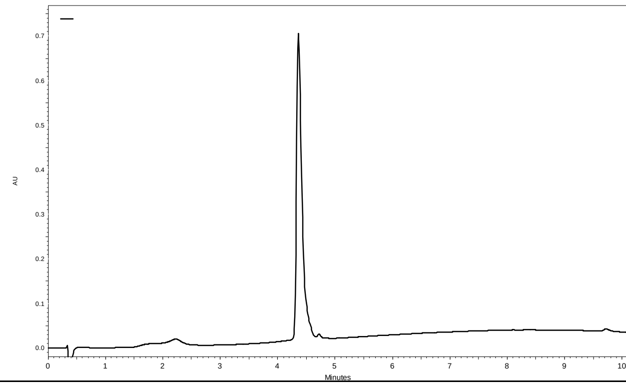
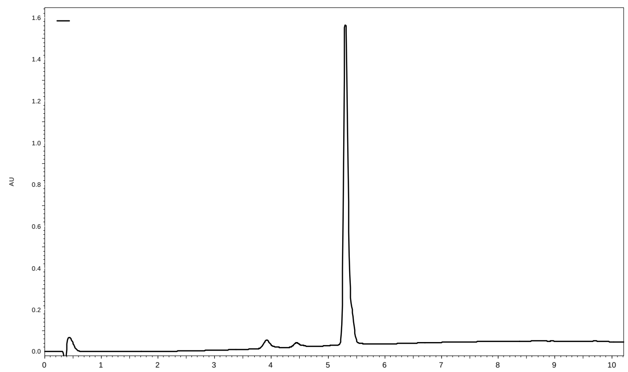
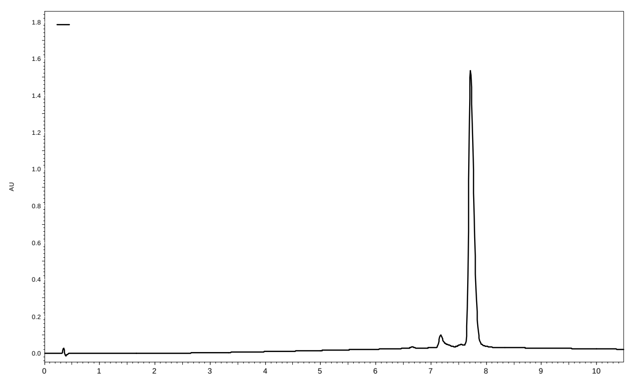
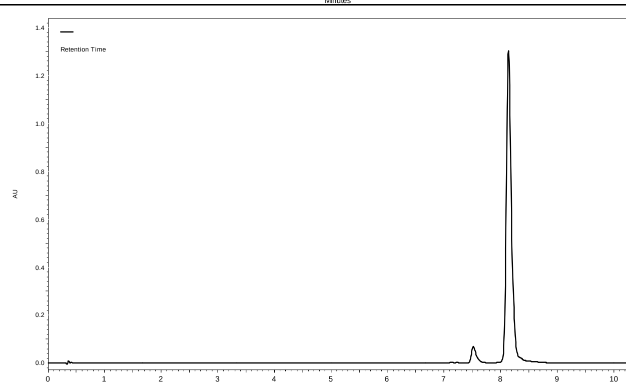
Characterization of peptoid oligomers

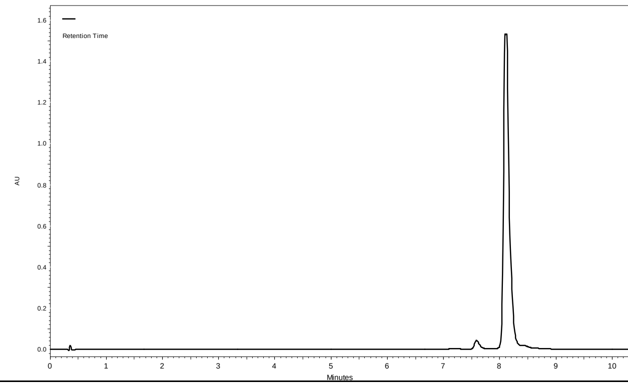
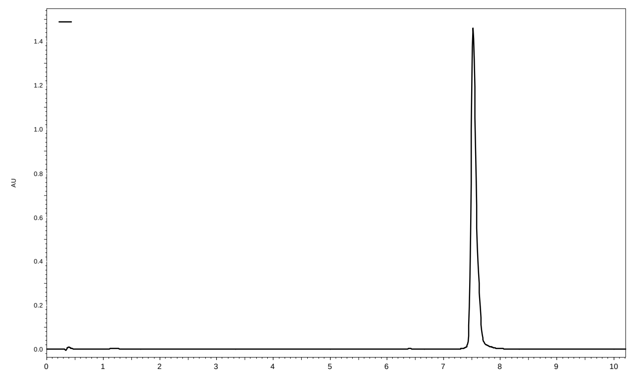
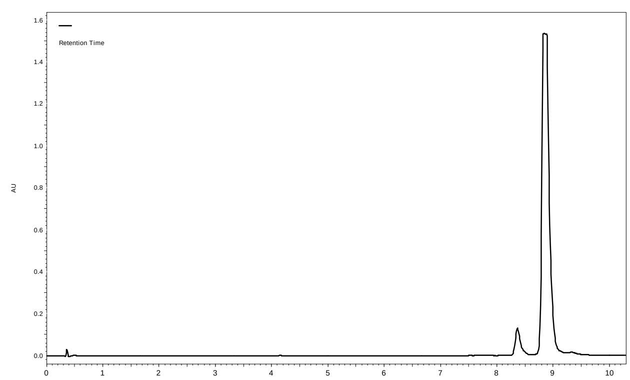
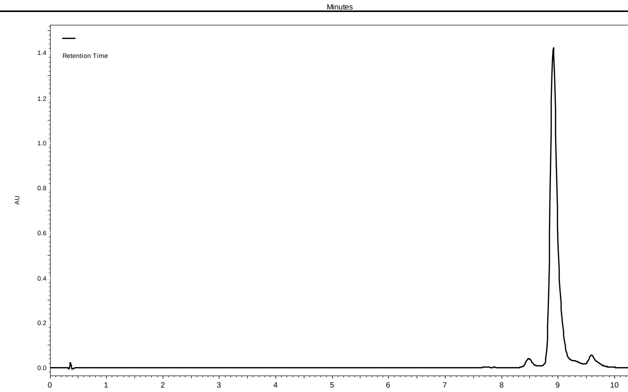
1. Liquid Chromatography/Mass Spectrometry of purified oligomers:
   *N*spe = (S)-*N*-(1-phenylethyl)glycine, *N*azb = *N*-(*p*-phenylazo-phenyl)glycine, *N*me = *N*-(2-methoxy-ethyl)glycine, *Sar* = *N*-(methyl)glycine or sarcosine

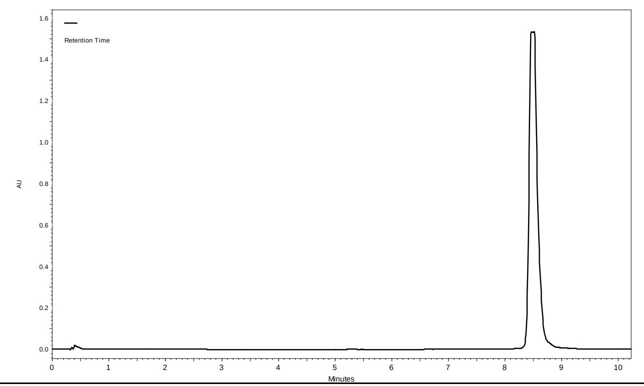
Compound	Sequence	Formula	Calc. m/z	Obs. m/z	Ion
1	*N*spe-*N*azb-*N*spe	$C_{34}H_{36}N_6O_3$	576.28	577.3	$M+H^+$
				599.3	$M+Na^+$
2	Ac-*N*spe-*N*azb-*N*spe	$C_{36}H_{38}N_6O_4$	618.30	619.1	$M+H^+$
				641.1	$M+Na^+$
3	*N*me-*N*azb-*N*me	$C_{24}H_{32}N_6O_5$	484.24	485.2	$M+H^+$
				507.2	$M+Na^+$
4	Ac-*N*me-*N*azb-*N*me	$C_{26}H_{34}N_6O_6$	526.25	427.0	$M+H^+$
				549.0	$M+Na^+$
5	Sar-*N*azb-Sar	$C_{20}H_{24}N_6O_3$	396.19	397.0	$M+H^+$
				399.0	$M+Na^+$
6	Ac-Sar-*N*azb-Sar	$C_{22}H_{26}N_6O_4$	438.20	439.0	$M+H^+$
				461.0	$M+Na^+$
7	(*N*spe)$_2$-*N*azb-(*N*spe)$_2$	$C_{54}H_{58}N_8O_5$	898.45	899.4	$M+H^+$
				921.4	$M+Na^+$
8	Ac-(*N*spe)$_2$-*N*azb-(*N*spe)$_2$	$C_{56}H_{60}N_8O_6$	940.46	941.4	$M+H^+$
				963.4	$M+Na^+$
9	Ac-*N*azb-(*N*spe)$_4$	$C_{56}H_{60}N_8O_6$	940.46	941.4	$M+H^+$
				963.4	$M+Na^+$
10	Ac-(*N*spe)$_5$	$C_{52}H_{60}N_6O_6$	864.46	865.4	$M+H^+$
				887.4	$M+Na^+$
11	Ac-(*N*spe)$_3$-*N*azb-(*N*spe)$_3$	$C_{76}H_{82}N_{10}O_8$	1262.63	1263.7	$M+H^+$
				1285.8	$M+Na^+$
12	Ac-*N*azb-(*N*spe)$_6$	$C_{76}H_{82}N_{10}O_8$	1262.63	1263.7	$M+H^+$
				1285.7	$M+Na^+$
13	Ac-(*N*spe)$_7$	$C_{72}H_{82}N_8O_8$	1186.63	1187.6	$M+H^+$
				1209.7	$M+Na^+$

2. Analytical Reverse Phase High Performace Liquid Chromatography of purified oligomers (5-95% acetonitrile in water, 10 minutes, 214 nm):

Compound	RP-HPLC Chromatograph	Retention Time
1		6.442 min
2		7.092 min
3		5.000 min
4		5.742 min

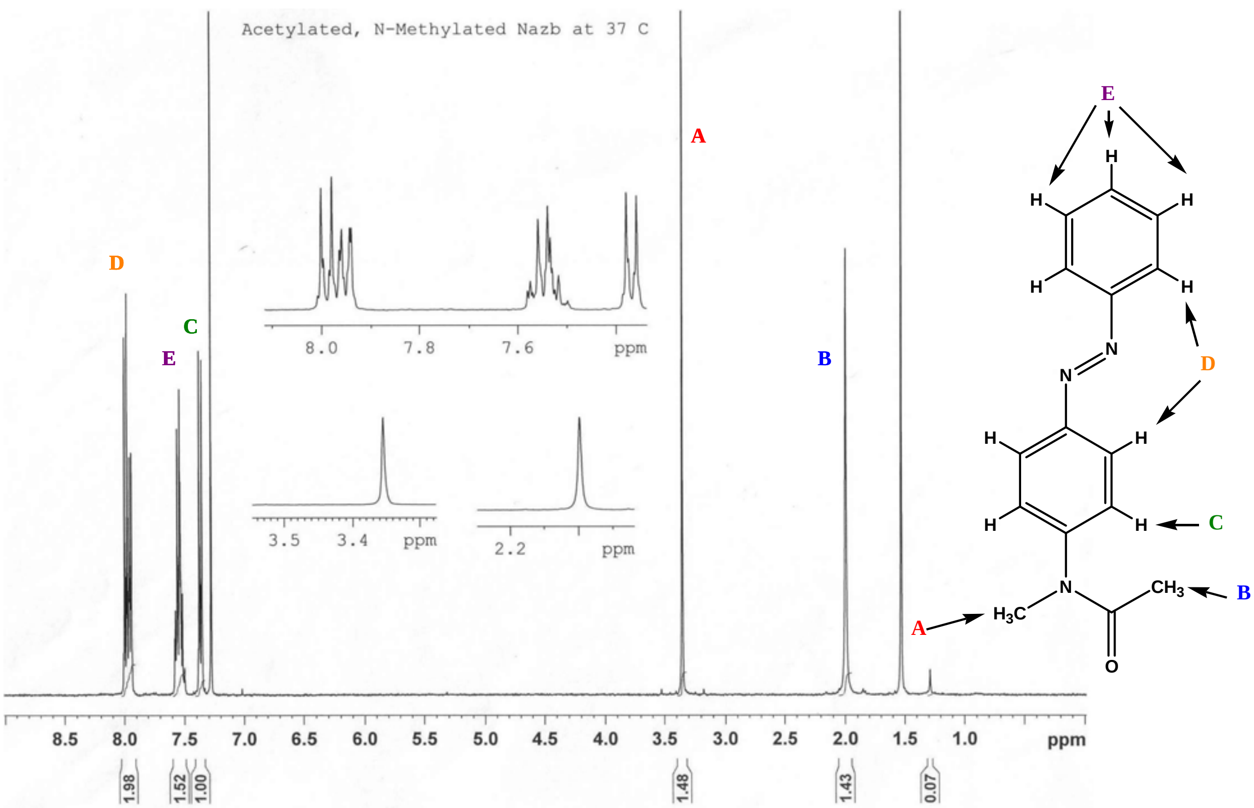
5		4.358 min
6		5.308 min
7		7.717 min
8		8.142 min

9		8.092 min
10		7.525 min
11		8.842 min
12		8.917 min

13		8.525 min

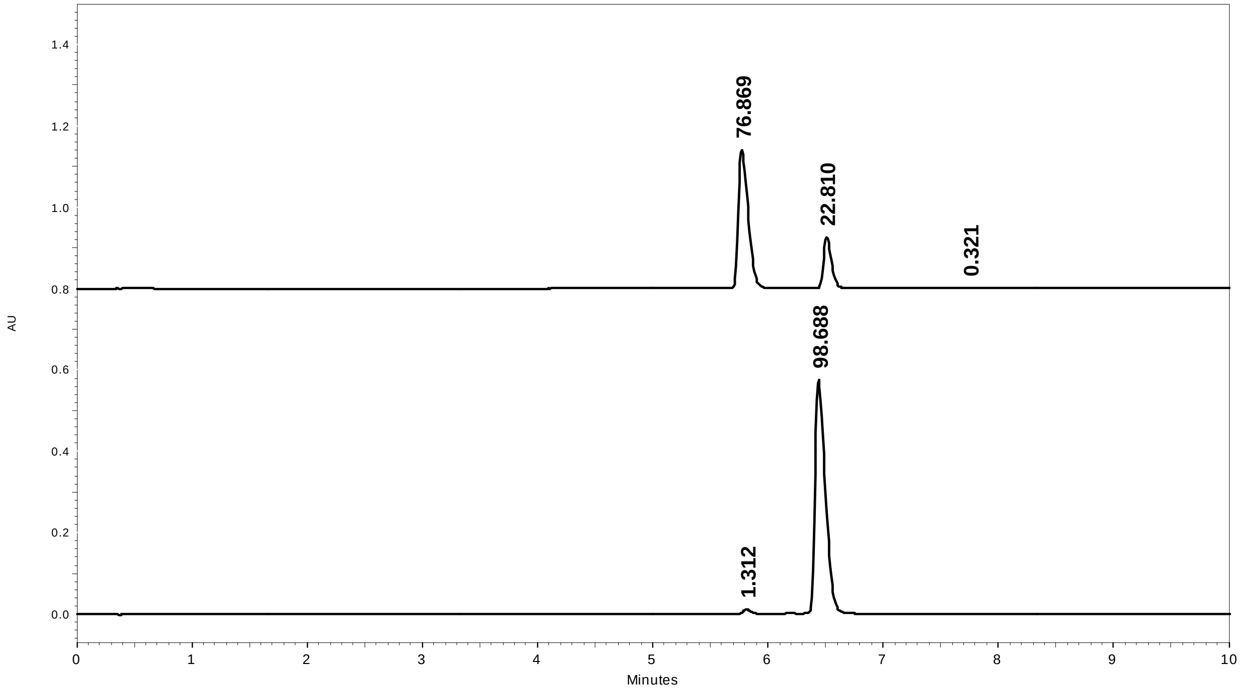
Based on LC/MS data, RP-HPLC chromatographs containing two dominant peaks are believed to be the *trans*- and *cis*-azobenzene isomers of the same oligomer.

Characterization of *N*-methyl-4-phenylazo-acetanilide (14)



Trans- to _cis_-azobenzene Photoisomerization of oligomer 1 monitored via HPLC at 273 nm

Before irradiation (below) after irradiation (above)



Calculation of rate constants for *cis*- to *trans*- thermal isomerization

The approximate rates of thermal back-isomerization for each compound were obtained using absorbance data collected at 325 nm as described above. First, it was assumed that since all samples were purified and stored in the dark, each compound existed exclusively in the *trans*-azobenzene form prior to any irradiation. Thus, before irradiation (at time *b*):

$$A_b = \varepsilon_{trans}[trans](1cm) \rightarrow \varepsilon_{trans} = \frac{A_b}{[trans]_b(1cm)}$$

After irradiation the absorbance A_t at time t can be described as follows:

$$A_t = A_{cis} + A_{trans} = \varepsilon_{cis}[cis]_t(1cm) + \varepsilon_{trans}[trans]_t(1cm)$$

$$A_t = \varepsilon_{cis}[cis]_t(1cm) + \frac{A_b}{[trans]_b}[trans]_t$$

Since, at all times, $[total] = [trans]_b = [cis]_t + [trans]_t$

$$A_t = \varepsilon_{cis}[cis]_t(1cm) + \frac{A_b}{[trans]_b}\left([trans]_b - [cis]_t\right)$$

$$A_t = \varepsilon_{cis}[cis]_t(1cm) + A_b - \frac{A_b}{[trans]_b}[cis]_t$$

$$A_t = [cis]_t\left(\varepsilon_{cis}(1cm) - \frac{A_b}{[trans]_b}\right) + A_b$$

Thus, the following relationship can be found:

$$\frac{[cis]_t}{[cis]_0} = \frac{A_t - A_b}{A_0 - A_b}$$

This value was plotted for each compound as a function of time, and fitted to an exponential regression ($R^2 > 0.98$ in every case). From this regression, the rate constant and half-life were readily calculated using the first order rate-law.