Cationic Azobenzenes as Light-Responsive Crosslinkers for Alginate-Based Supramolecular Hydrogels

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Supplementary Materials

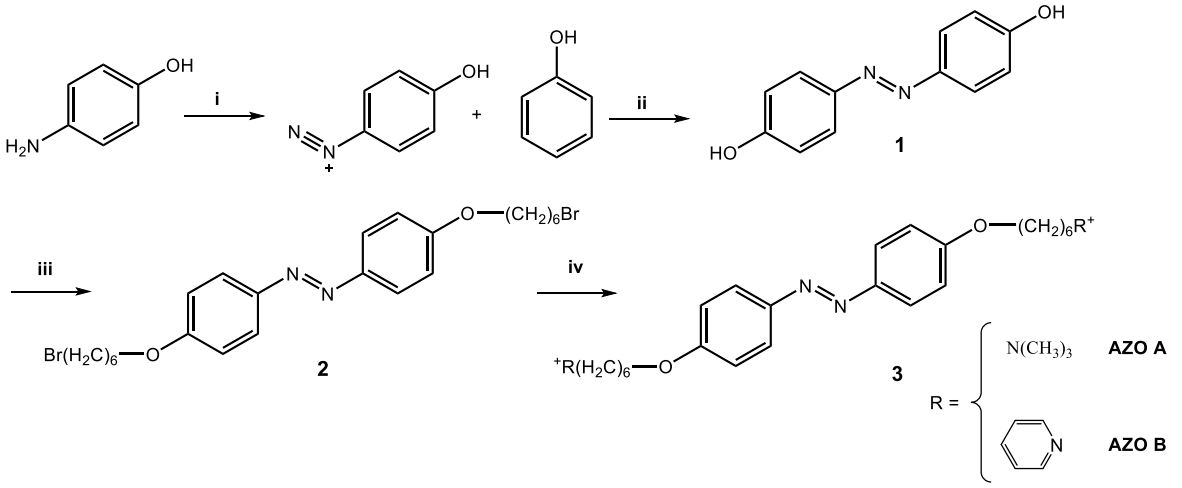

Figure S1. Synthetic scheme of AZO A and AZO B.

i) $NaNO_2$, H_2O/HCl, 0-5°C, 30 min; ii) NaOH pH=11, 10-15°C, 3h; iii) 1,6- dibromohexane, K_2CO_3, CH_3CN dry, reflux, 48h; iv) $N(CH_3)_3$ in ethanol solution, 50°C, 48h for AZO A and Py in acetonitrile, 70°C, 48h for AZO B.

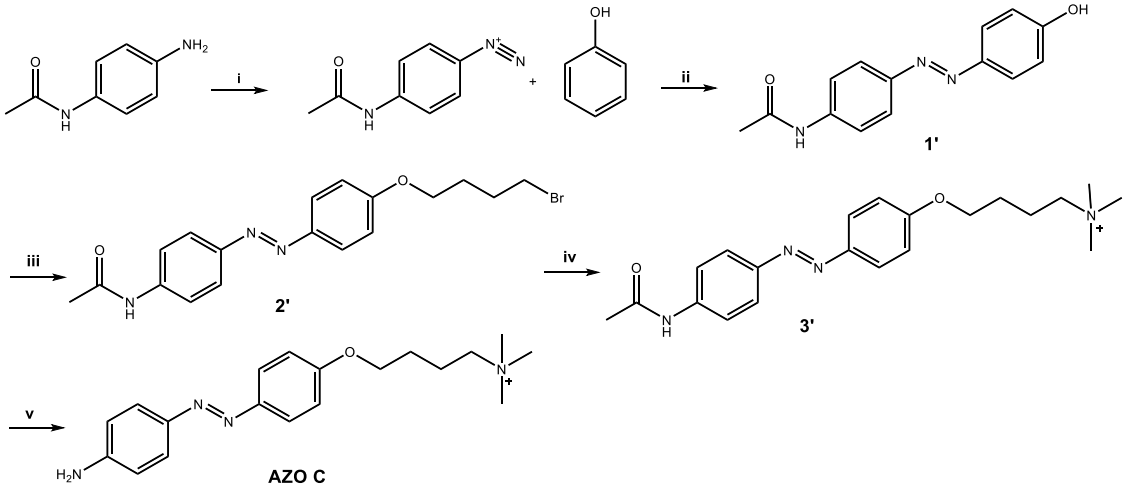

Figure S2. Synthetic scheme of AZO C.

i) $NaNO_2$, H_2O/HCl, 0-5°C, 30 min; ii) NaOH pH=11, 10-15°C, 3h; iii) 1,4-dibromobutane, K_2CO_3, KI, acetone, reflux, 4h; iv) $N(CH_3)_3$ in ethanol solution, 50°C, 48h; v) HCl conc, 40°C, overnight.

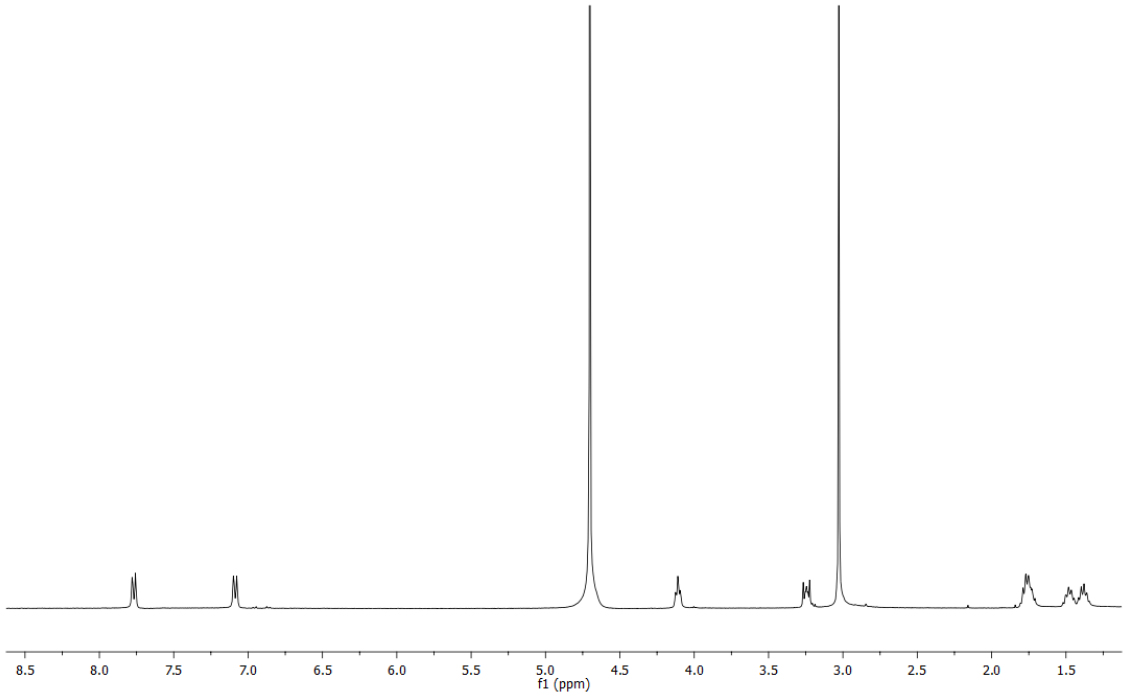

Figure S3. ^1H NMR of AZO A (D_2O; 400 MHz)

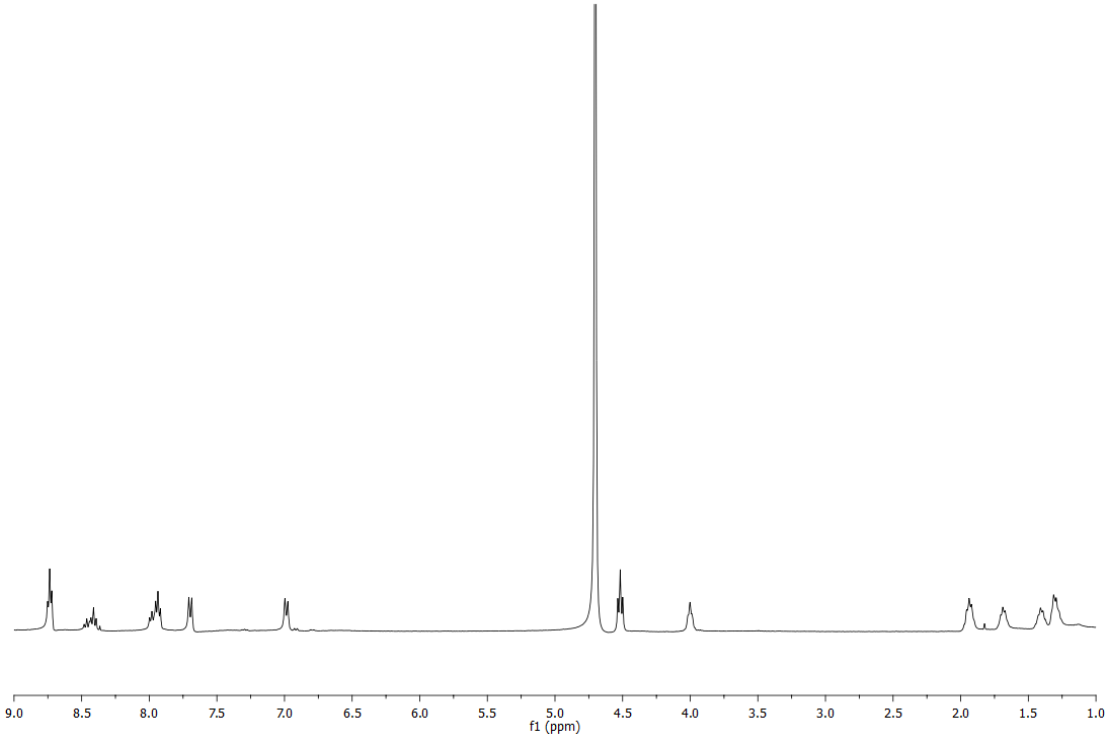

Figure S4. ^1H NMR of AZO B (D_2O; 400 MHz)

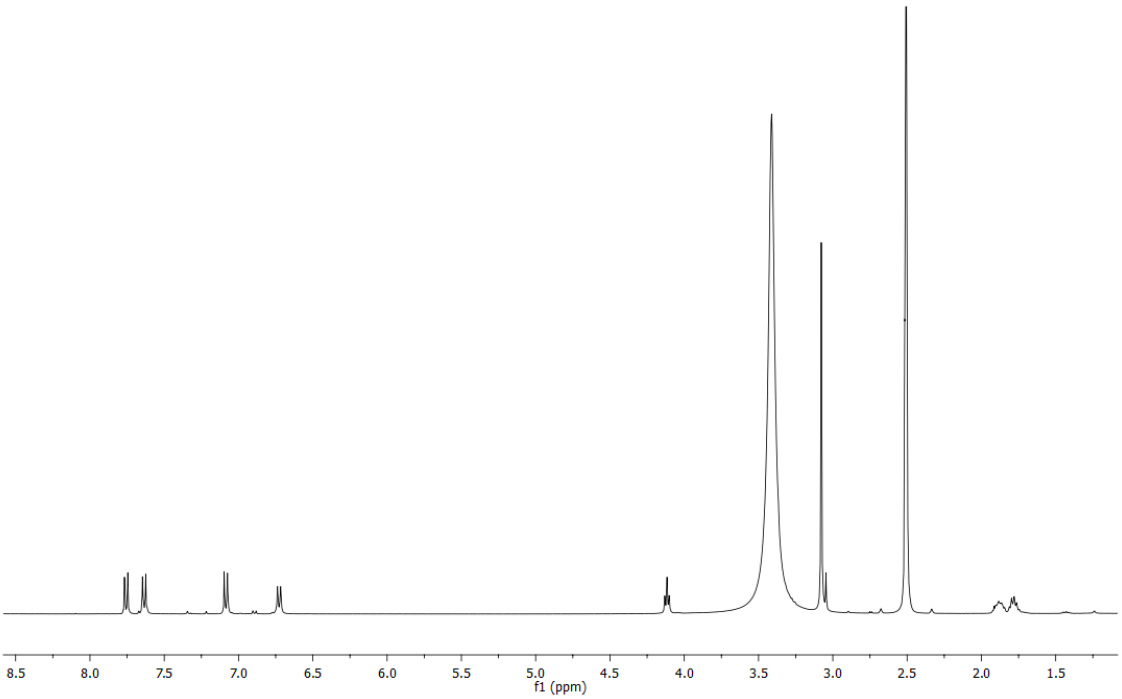

Figure S5. ^{1}H NMR of AZO C (DMSO-d_6; 400 MHz)

Table S1. Scheme of molecular behavior of the hydrogels under the action of pHs and lights

	Composition (wt%)	**Hydrogel pH 7**	**Hydrogel pH 4**	**Gel-sol (365nm irradiation)**	**Sol-gel (day light)**
SA_AZO A	8/0.5	×	✓	✓	✓
	8/1	×	✓	✓	✓
	5/0.5	×	×		
	5/1	×	✓	✓	✓
	2/0.5	×			
	2/1	×			
SA_AZO B	8/0.5	×			
	8/1	×			
	5/0.5	×	✓	✓	✓
	5/1	×	✓	✓	✓
	2/0.5	×	×		
	2/1	×	×		
SA_AZO C	8/0.5	×			
	8/1	×			
	5/0.5	×	✓	✓	✓
	5/1	×	✓	✓	✓
	2/0.5	×	×		
	2/1	×	×		

Table S2. IR absorption peaks of main functional groups of azobenzenes and corresponding hydrogels

Functional group	AZO A (cm^{-1})	AZO B (cm^{-1})	AZO C (cm^{-1})	SA_AZO A Hydrogel (cm^{-1})	SA_AZO B Hydrogel (cm^{-1})	SA_AZO C Hydrogel (cm^{-1})
-CH sp^2	3450-3380	3450-3380	3450-3380	3450-3380	3450-3380	3450-3380
-OH				3200 (of SA)	3200 (of SA)	
-NH_2			3500 1650 830			
-NH_3^+						3300-3190 1620
-CH sp^3	2940-2865	2940-2865	2940-2865	2940-2865	2940-2865	2940-2865
-COO^-				1600 1400 (of SA)	1600 1400 (of SA)	1600 1400 (of SA)
-C=C- aromatic	1598-1578	1600-1400	1504-1480			
-N=N-	1492	1492	1547			
-CH_3-(N^+)	1475					
-C-N- (C aromatic)	1238	1242	1379			
-C-N- (C aliphatic)	1140	1147	1253	1246 (of AZO A)	1250 (of AZO B)	