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Synthesis and optical properties of new isomeric azo-containing bis(2-hydroxybenzaldehydes) with tetrafluorobenzene units

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Experimental part

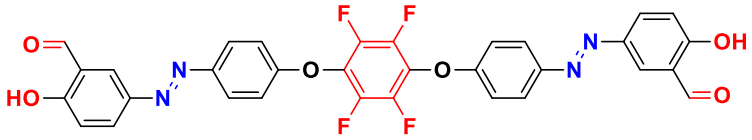
Materials. The initial diamines 4,4'-[(2,3,5,6-tetrafluoro-1,4-phenylene)bis(oxy)]dianiline (**DA-I**), 3,3'-[(2,3,5,6-tetrafluoro-1,4-phenylene)bis(oxy)]dianiline (**DA-II**) were prepared according to the previously described procedure [1]. 4,4'-[1,4-Phenylenebis(oxy)]dianiline (Arc Pharm, Inc, 98%), salicylaldehyde (Merck, 99%), $NaNO_2$ (Acros Organics, 99%), HCl (Acros Organics, 25%), NaOH (Acros Organics, 98%) have been used without additional purification. The other reagents and solvents were purified routinely.

Measurements. Fourier transform infrared (FTIR) spectra (4000−600 cm^{-1}) of the synthesized compounds were recorded on a TENSOR 37 spectrometer in KBr pellets. ^{1}H NMR spectra were recorded on a Varian VXR-300 (300 MHz) instrument or on a Bruker Avance 400 (400 MHz) instrument, ^{19}F NMR spectra – on a Varian Gemini 200 (188.14 MHz) instrument or on a Bruker Avance 400 (376.47 MHz) instrument, and ^{13}C NMR spectra – on a spectrometer Bruker Avance 400 (125.73 MHz) at room temperature in $(CD_3)_2SO$. Chemical shifts are given relative to dimethyl sulfoxide (δ = 2.50 ppm for ^{1}H NMR and δ = 40.00 ppm for ^{13}C NMR). For ^{19}F NMR fluorotrichloromethane was used as the internal standard. The UV-vis spectra were recorded on a Shimadzu UV-2450 spectrophotometer.

The investigation of the pH influence upon the UV-vis absorption maxima of **ABA-I** and **ABA-II** in DMAc has been conducted at a monomer concentration of 0.025 mg ml^{-1} by adding 1 drop of 1 N HCl solution to the **ABA-I** and **ABA-II** monomer solution in order to form an acid medium (pH ~ 2), and by adding 2 drops of 1*N* NaOH solution to the **ABA-I** and **ABA-II** monomer solution with a drop of 1*N* HCl in order to achieve acid neutralization and to form alkaline medium (pH ~ 12). By means of Du Pont Instruments, thermal gravimetric analyser 951TGA in the open air at a heating rate of 5 ^{o}C min^{-1} a thermostability has been studied.

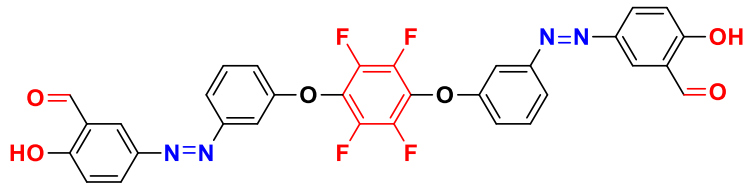
Synthesis of azo-containing monomers

*3,3'-{(2,3,5,6-Tetrafluoro-1,4-phenylene)bis[oxy-4,1-phenylene(E)diazene-2,1-diyl]}bis(6-hydroxybenzaldehyde) (**ABA-I**).*



At the first stage, HCl solution (18% aq., 7.34 g) is added to diamine **DA-I** (2.20 g, 6.04 mmol). The obtained mixture is stirred and cooled to -5 °C. On intensive stirring, $NaNO_2$ solution (2.5*M*, 4.83 ml) is added for 1.5 – 2 h. The completion of diazotisation is determined by HNO_2 sampling on a potassium iodide starch paper. At the second stage, the obtained diazonium salt (**DS-I)** is added to a solution of salicylaldehyde (1.47 g, 12.08 mmol) in NaOH (2*N*, aq, 12.07 ml) on violent stirring, not allowing the temperature to exceed 5 ºC and maintaining the solution pH alkaline. On completion of the azo-coupling reaction, the solution pH was brought toneutral. The obtained yellow mixture is filtered, washed with water, dried, purified by boiling in $CHCl_3$ (to extract impurities) and dried under vacuum at 80°C. Yield 91 % (3.47 g). m.p. >160 ºC with decomposition, ^{1}H NMR (DMSO-d_6, 400 MHz, δ, ppm): 11.57 (s, 2H, OH), 10.36 (s, 2H, CHO), 8.17 (s, 2H, Ph), 8.09 (d, 2H, *J* 9.3 Hz, Ph), 7.93 (d, 4H, *J* 7.5 Hz, Ph), 7.45 (d, 4H, *J* 7.5 Hz, Ph), 7.22 (d, 2H, *J* 8.4 Hz, Ph). ^{13}C NMR (DMSO-d_6, 126 MHz, δ, ppm): 190.60 (CHO), 169.80 (C-OH), 157.78 (Ph-C(O)), 148.65, 142.03 (Ph-C(N)), 141.97 (Ph-CF, J_{CF} 266.29 Hz), 129.70 (Ph-C(O)), 128.45, 125.98, 123.85, 122.94, 121.25, 116.03 (Ph-C). ^{19}F NMR (DMSO-d_6, 376 MHz, δ, ppm): -154.89 (s, 4F, Ph). FTIR (ν/cm^{-1}): 3600-3100 (OH), 1662 (CHO), 1508-1492 (Ph), 1211 (Ph-O-Ph), 1006-993 (Ph-F). UV-vis spectra: λ_{1max} 356 nm, λ_{2max} 464 nm.

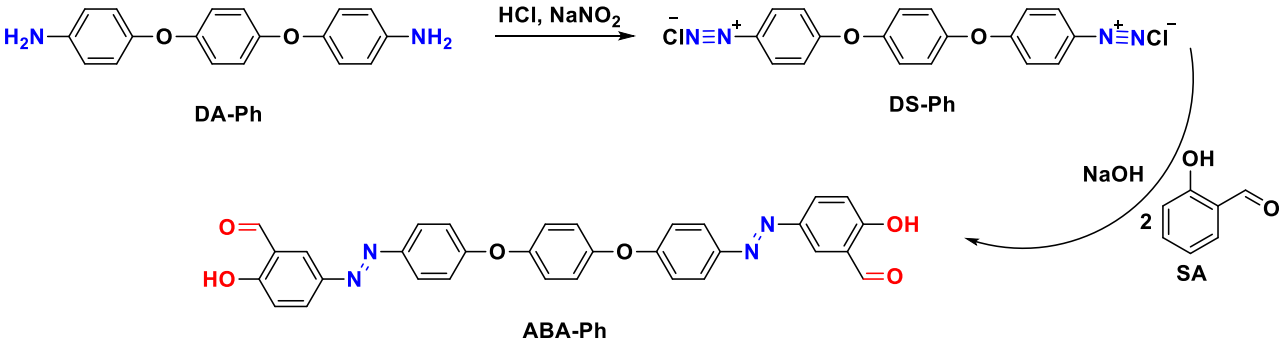
*3,3'-{(2,3,5,6-Tetrafluoro-1,4-phenylene)bis[oxy-3,1-phenylene(E)diazene-2,1-diyl]}bis(6-hydroxybenzaldehyde) (**ABA-II**)*



The compound **ABA-II** was synthesized analogously to **ABA-I** from DA-II. The resulting product was purified by boiling in $CHCl_3$ and dried under vacuum at 80 °C. Yield 89% (3.41 g). m.p. = 242-245 ºC, ^{1}H NMR (DMSO-d_6, 300 MHz, δ, ppm):11.58 (s, 2H, OH), 10.35 (s, 2H, CHO), 8.19 (s, 2H, Ph), 8.10 (d, 2H, *J* 9.3 Hz, Ph), 7.70-7.61 (m, 6H, Ph), 7.43 (d, 2H, *J* 7.5 Hz, Ph), 7.19 (d, 2H, *J* 8.4 Hz, Ph). ^{13}C NMR (DMSO-d_6, 126 MHz, δ, ppm): 190.39 (CHO), 163.65 (C-OH), 157.48 (Ph-C(O)), 153.36, 144.60 (Ph-C(N)), 142.08 (Ph-CF, J_{CF} 253.32 Hz), 130.96, 129.87 (Ph-C), 129.58 (Ph-C(O)), 124.04, 122.63, 118.39, 118.14, 117.61, 108.86 (Ph-C). ^{19}F NMR

(DMSO-d_6, 188 MHz, δ, ppm): -155.14 (s, 4F, Ph). FTIR (ν/cm^{-1}): 3600-3100 (OH), 1668 (CHO), 1508 (Ph), 1224 (Ph-O-Ph), 1024-989 (C-F). UV-vis spectra: λ_{1max} = 347 nm, λ_{2max} = 467 nm.

3,3'-{1,4-Phenylenebis[oxy-4,1-phenylene(E)diazene-2,1-diyl]}bis(6-hydroxybenzaldehyde)



The title compound was synthesized analogously to **ABA-I** using 4,4'-[1,4-phenylenebis(oxy)]dianiline as the starting material. The product was purified by boiling in $CHCl_3$ and dried under vacuum at 80 °C. Yield 89% (3.75 g), m.p. >210 °C with decomposition, FTIR (ν/cm^{-1}): 3700-3000 (OH), 1666 (CHO), 1488 (Ph), 1226 (Ph-O-Ph).

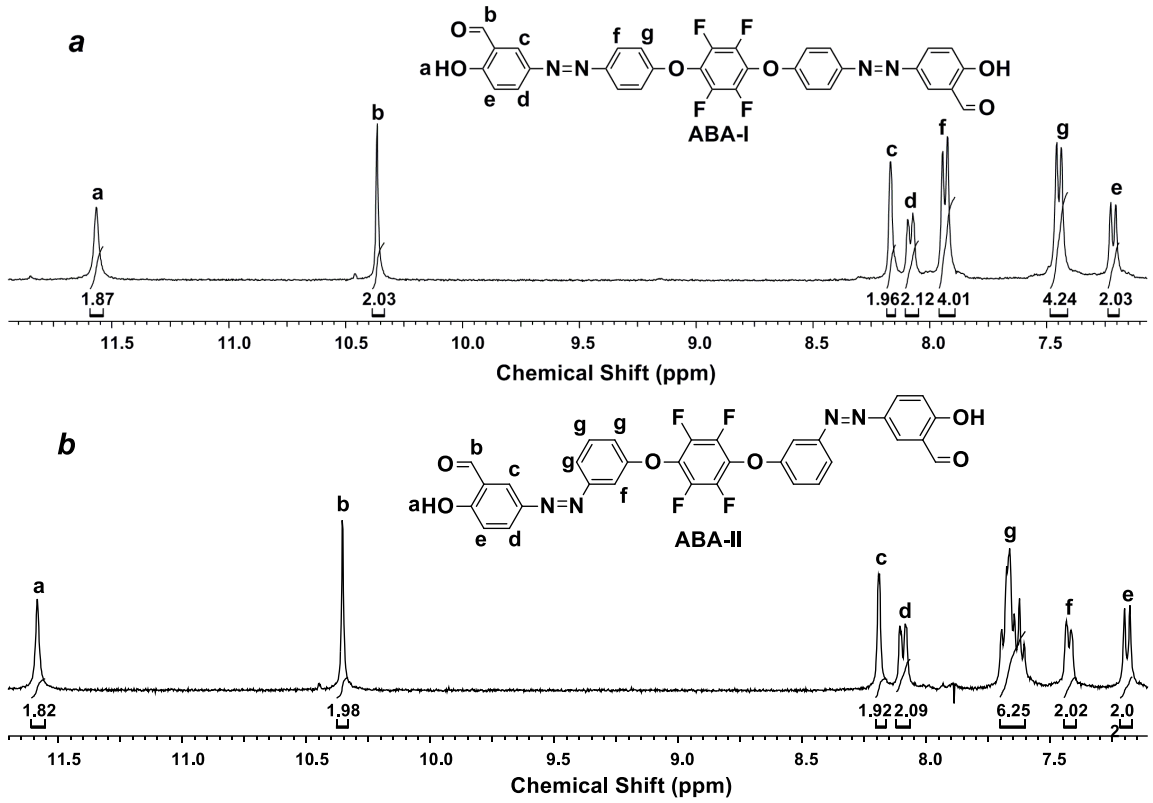


Figure S1 ^{1}H NMR spectra of the **ABA-I** (a) and **ABA-II** (b) monomers.

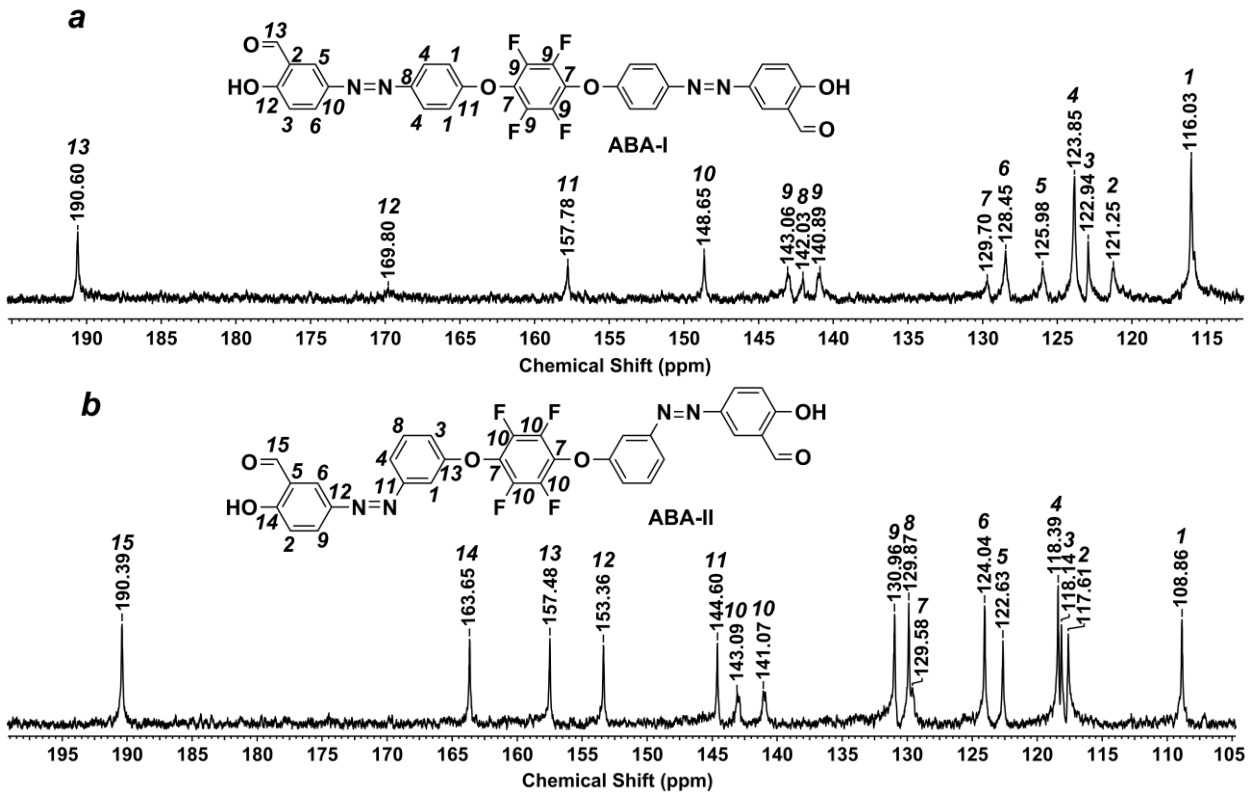


Figure S2 ^{13}C NMR spectra of the **ABA-I** (a) and **ABA-II** (b) monomers.

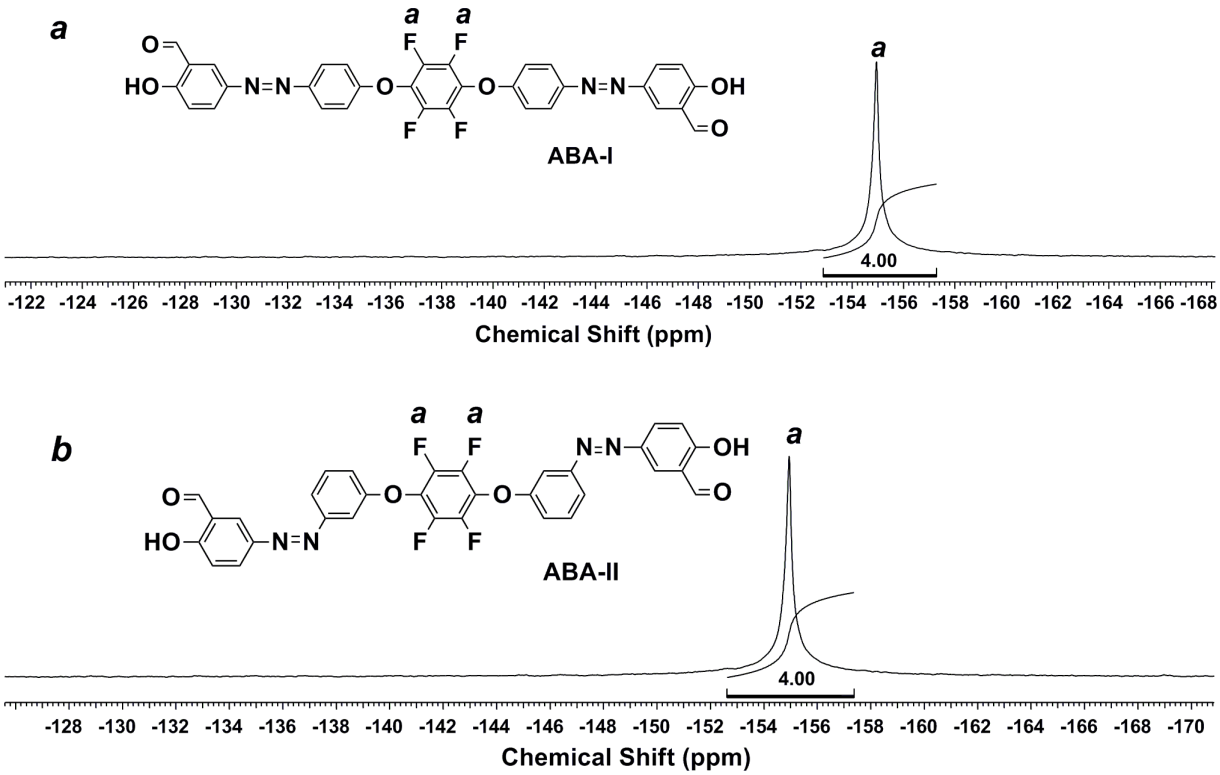


Figure S3 ^{19}F NMR spectra of the **ABA-I** (a) and **ABA-II** (b) monomers.

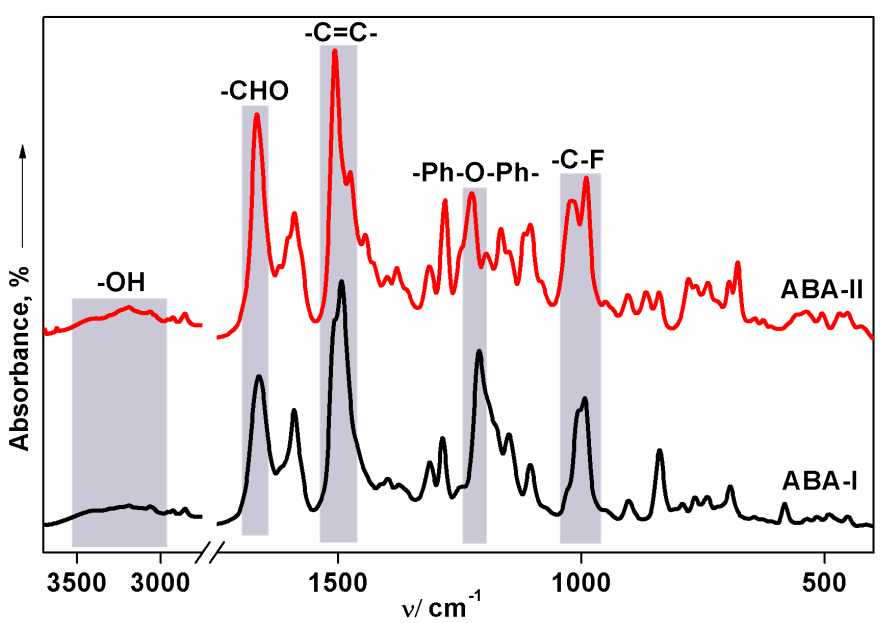


Figure S4 FTIR spectra of the **ABA-I** and **ABA-II** monomers.

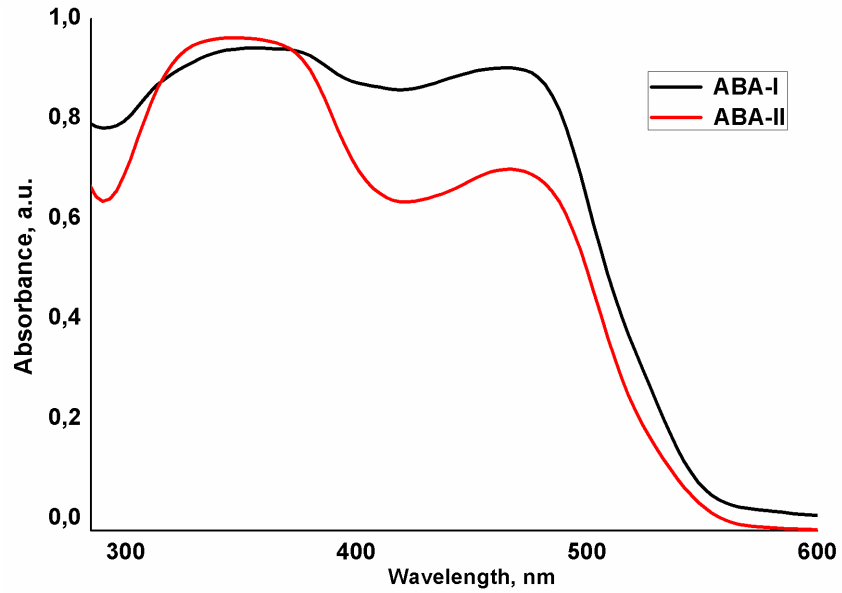


Figure S5 UV-vis spectra of the **ABA-I** and **ABA-II** monomers in DMA (c=0.025 mg/ml).

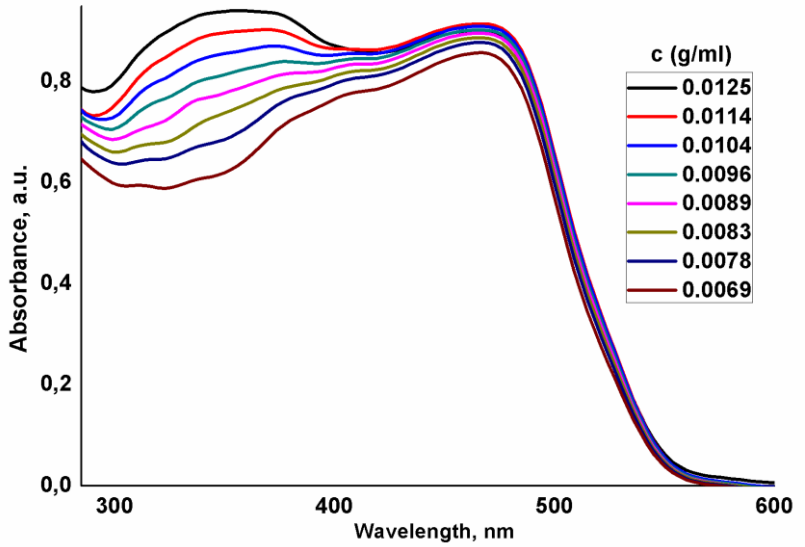


Figure S6 UV-vis spectra of **ABA-I** in DMA at various concentrations.

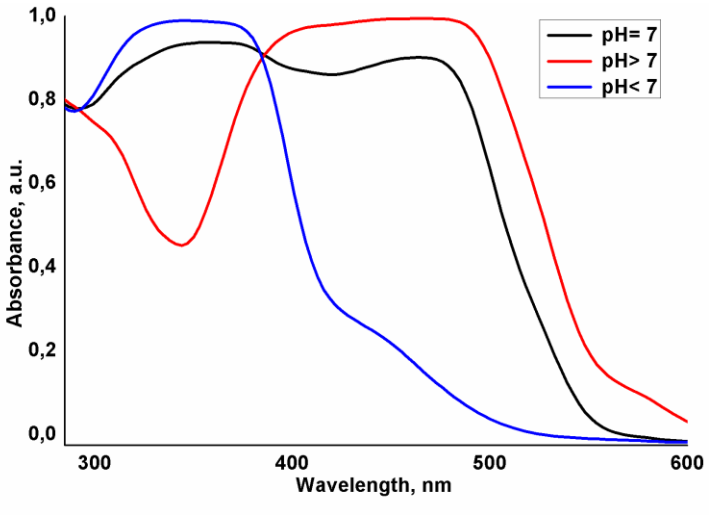


Figure S7 UV-vis spectra of **ABA-I** at different pH (c=0.025 mg/ml).

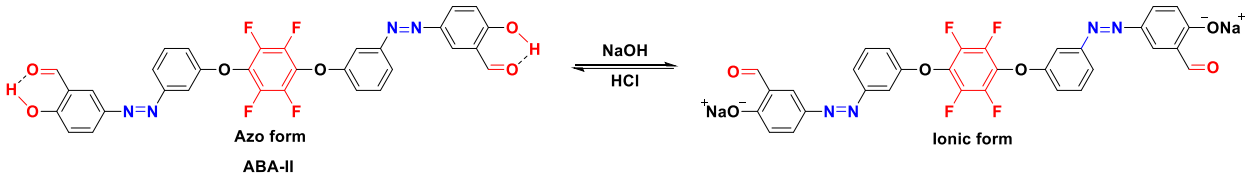


Figure S8 Azo and ionic forms of **ABA-II** in the DMA.

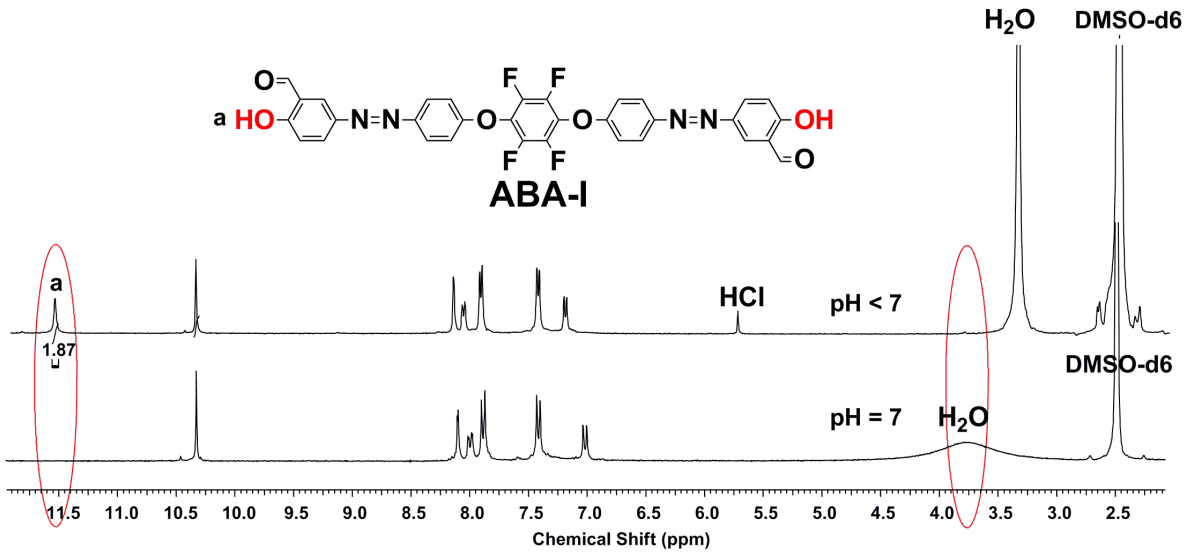


Figure S9 ^{1}H NMR spectra **ABA-I** in acidic and neutral media.

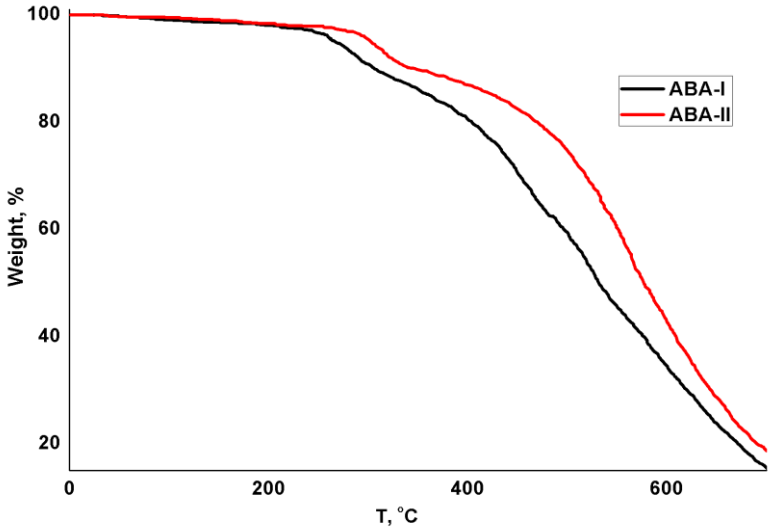


Figure S10 TGA curves of the **ABA-I** and **ABA-II** monomers.

References

1. A. E. Borodin and B. F. Malichenko, *Dopov. Akad. Nauk Ukr. RSR, Ser. Geol. Khim. Biol.*, 1978, **8**, 710.