**Synthesis, Characterization, and Environmental Applications of Novel Per-Fluorinated Organic Polymers with Azo- and Azomethine-Based Linkers via Nucleophilic Aromatic Substitution**

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| **Title** |
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Scheme S1: Proposed mechanism of the nucleophilic aromatic substitution reaction (NAS).



Table S1: Reported values of the chemical shift of 19F-NMR and different sites. [1]

|  |  |
| --- | --- |
| Compound | Chemical Shift (ppm) |
| Benzene + Hexafluorobenzene | -163.2 |
| Mono-fluorobenezne | -112.9 |
| 1,2-Difluorobenezne | -138.4 |
| 1,3-Difluorobenezne | -109.9 |
| 1,4-Difluorobenezne | -119.6 |
| 1,2,4-Triflourobenzne | -143.5  -133.5  -115.7 |
| 1,2,4,5-Tetrafluorobenezne | -139.7 |
| Penta-fluorobenzene | -162.5  -154.2  -139.2 |

**List of 1H- and 13C-NMR Spectra of the monomers**

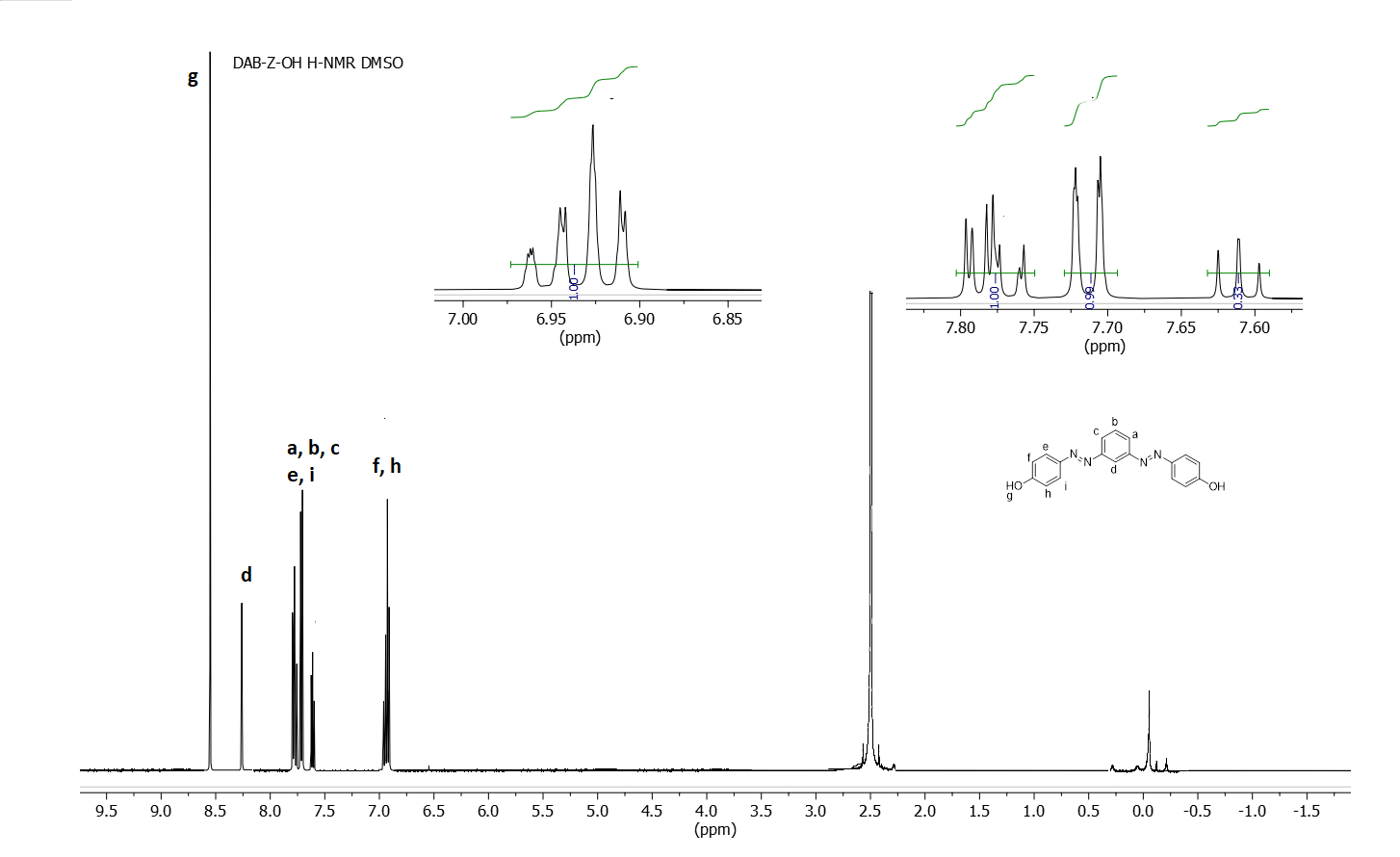
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Figure S1: 1H-NMR spectra of DAB-Z-OH

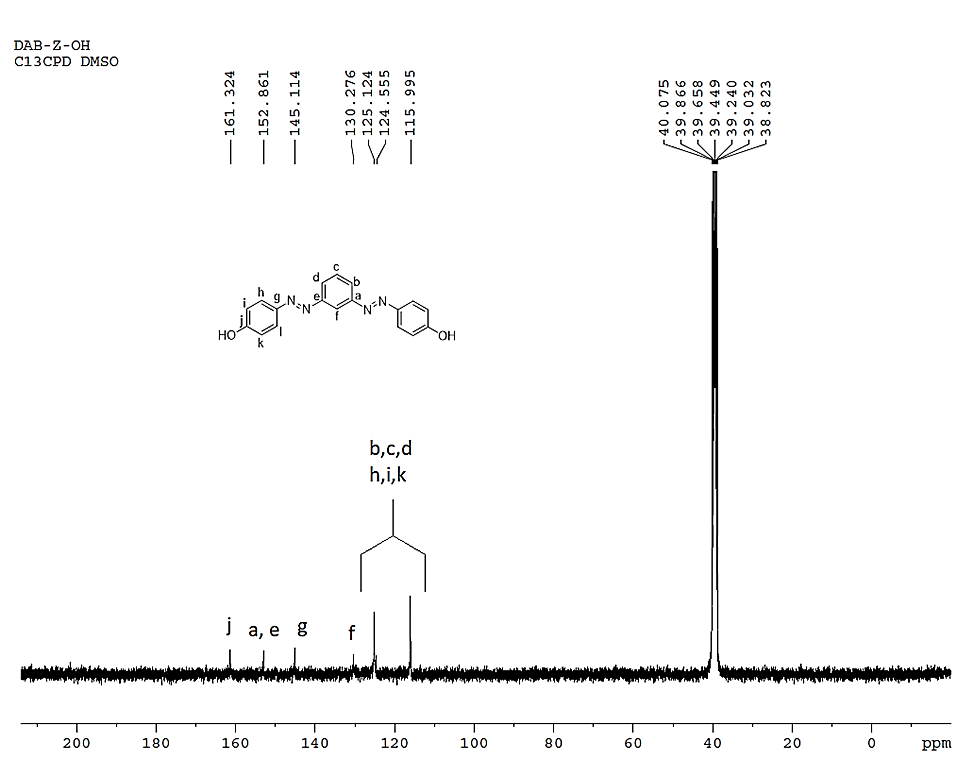


Figure S2: 13C-NMR spectra of DAB-Z-OH

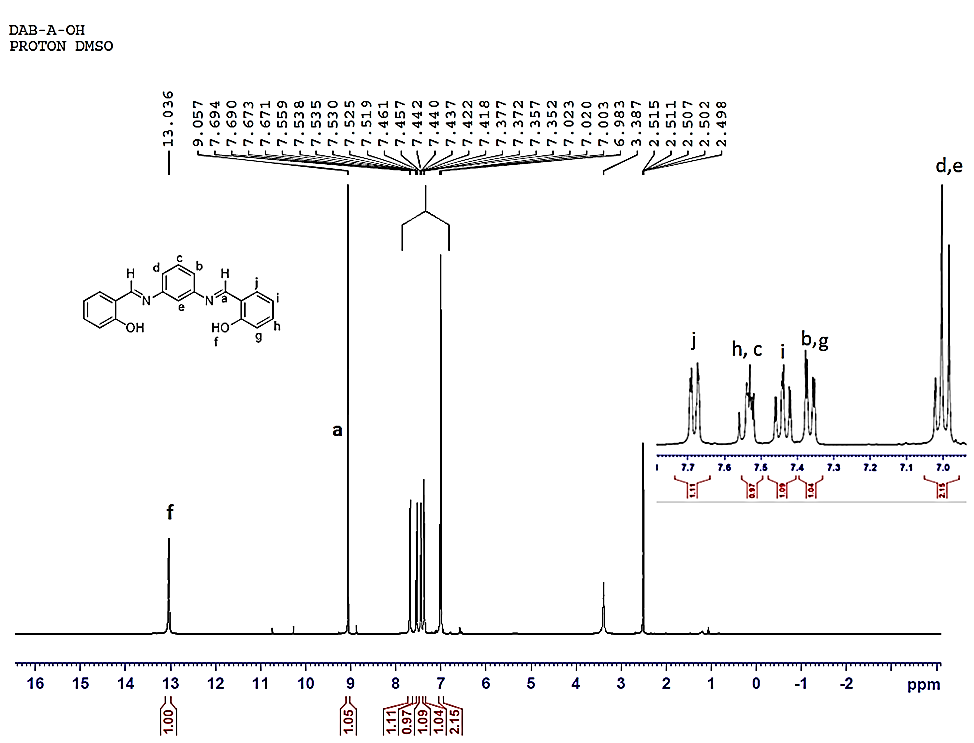


Figure S3: 1H-NMR spectra of DAB-A-OH

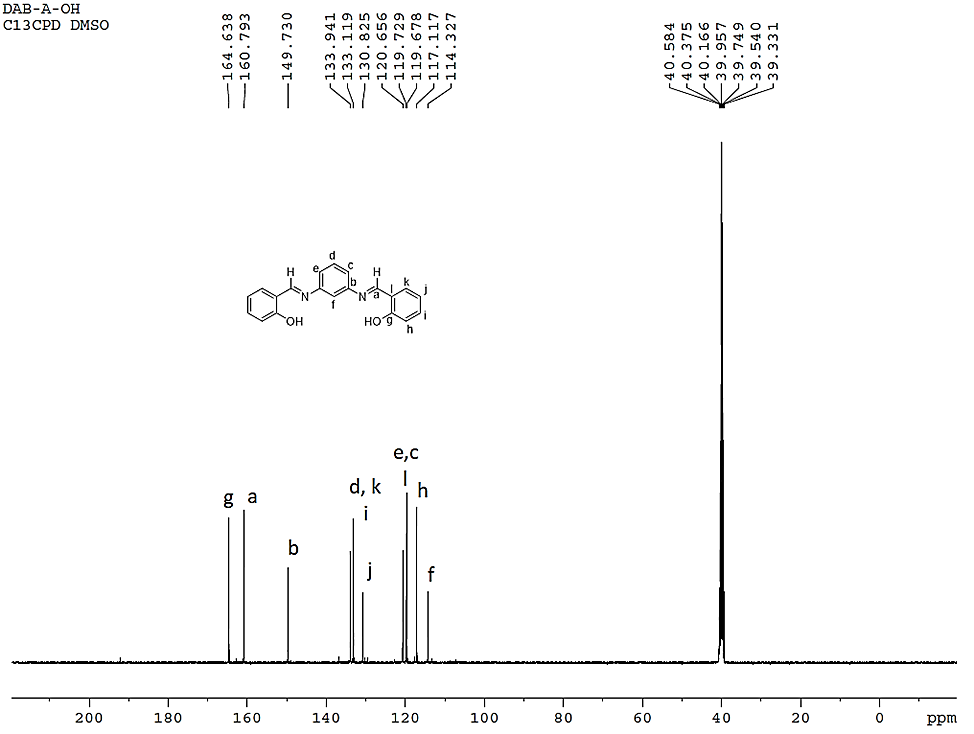
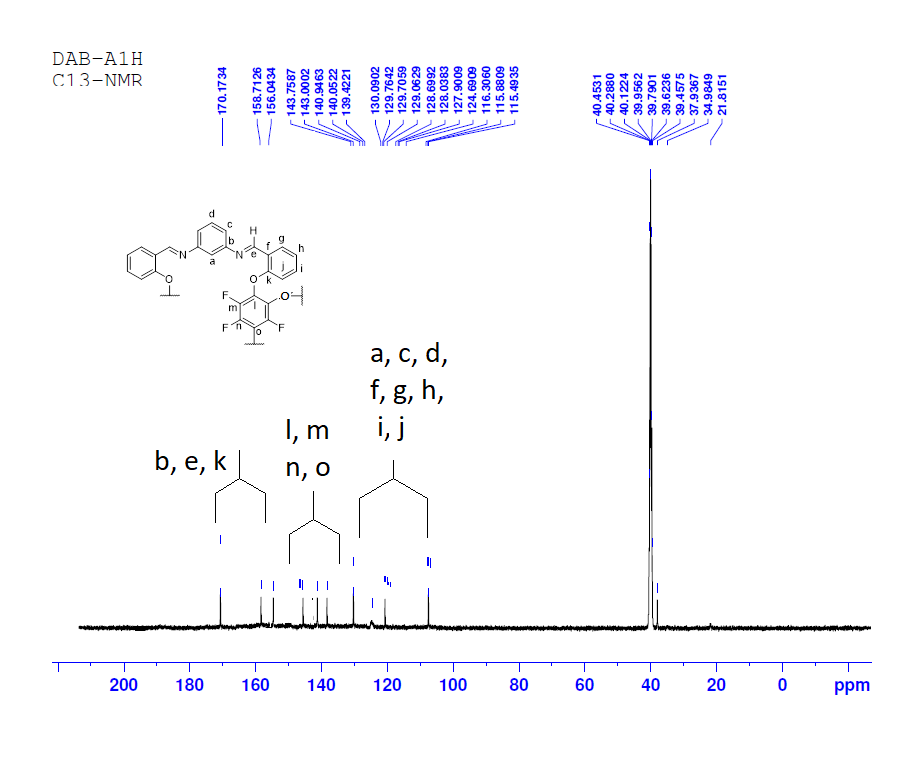


Figure S4 : 13C-NMR spectra of DAB-A-OH

**1H- and 13C-NMR Spectra of the Polymers**

Figure S5 : 1H-NMR spectra of DAB-A-1h

Figure S6 : 13C-NMR spectra of DAB-A-1h

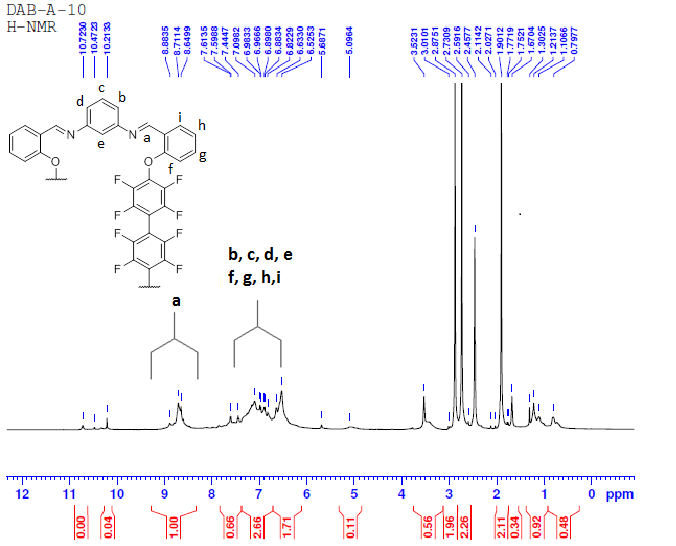
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Figure S7 : 1H-NMR spectra of DAB-A-1O

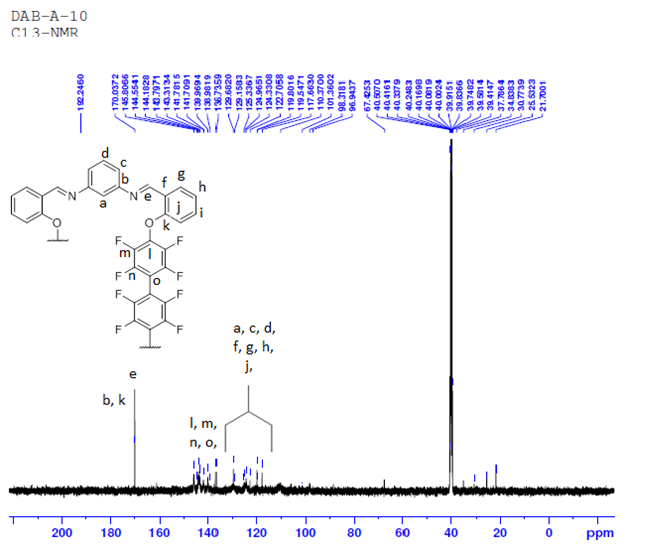
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Figure S8 : 13C-NMR spectra of DAB-A-1O

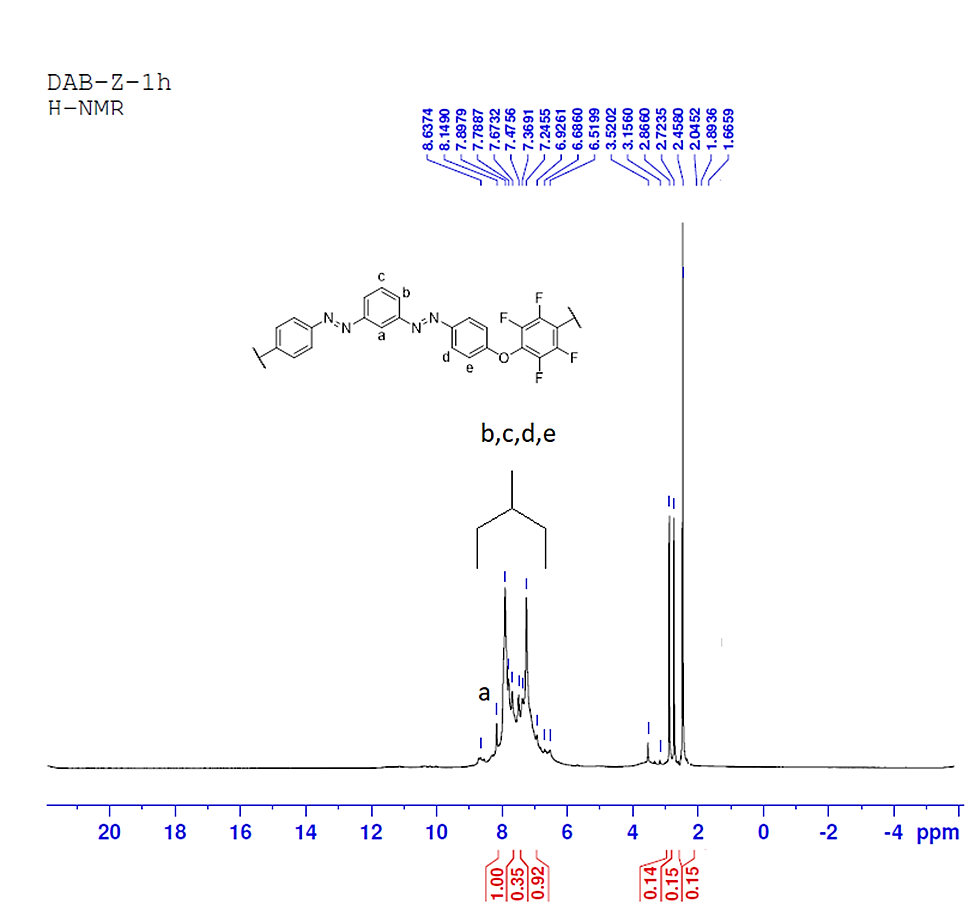


Figure S9 : 1H-NMR spectra of DAB-Z-1h

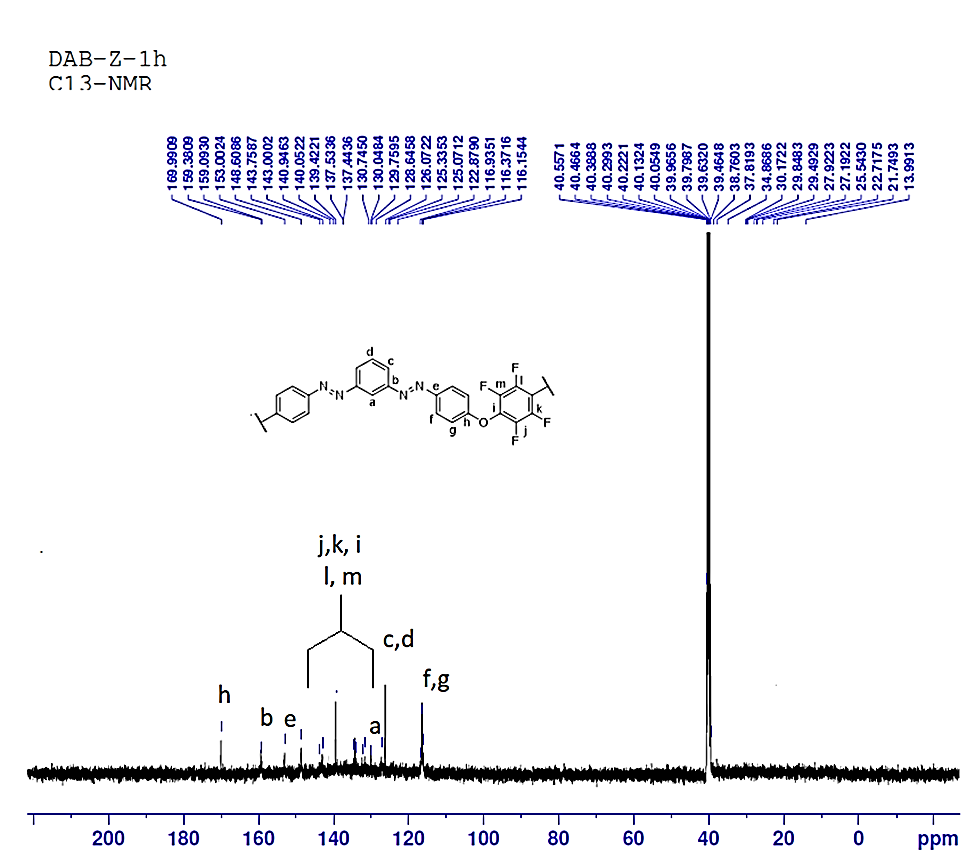


Figure S10 : 13C-NMR spectra of DAB-Z-1h

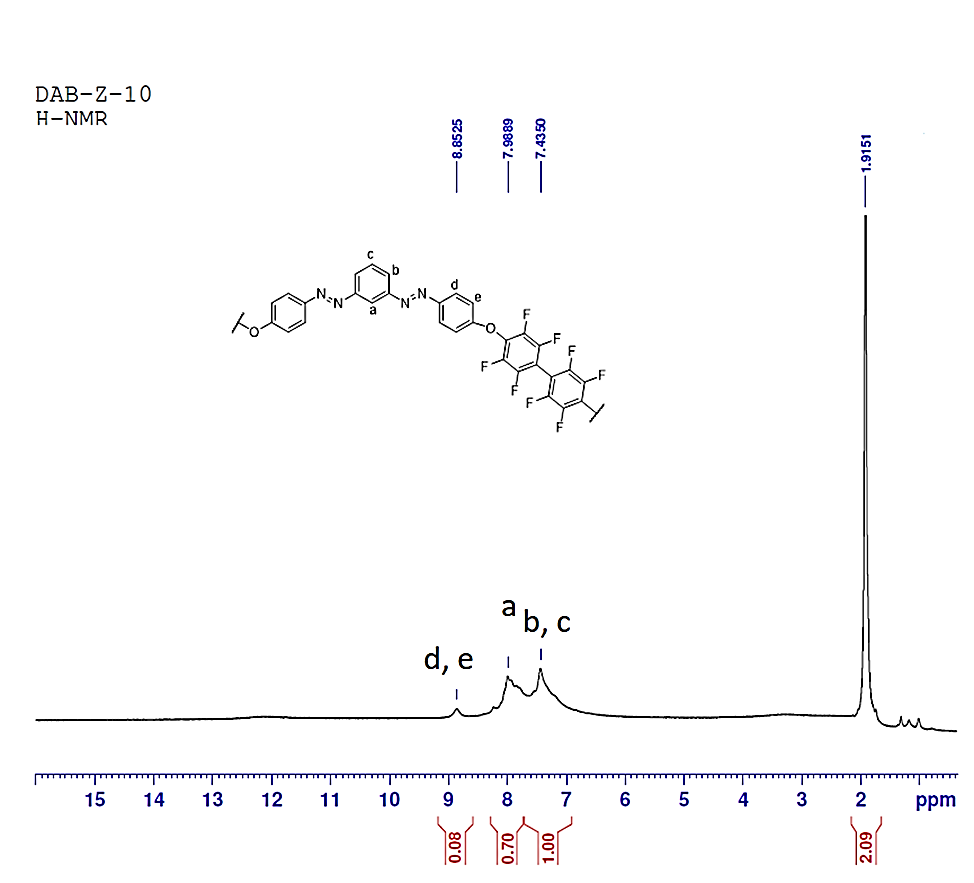


Figure S11 : 1H-NMR spectra of DAB-Z-1O

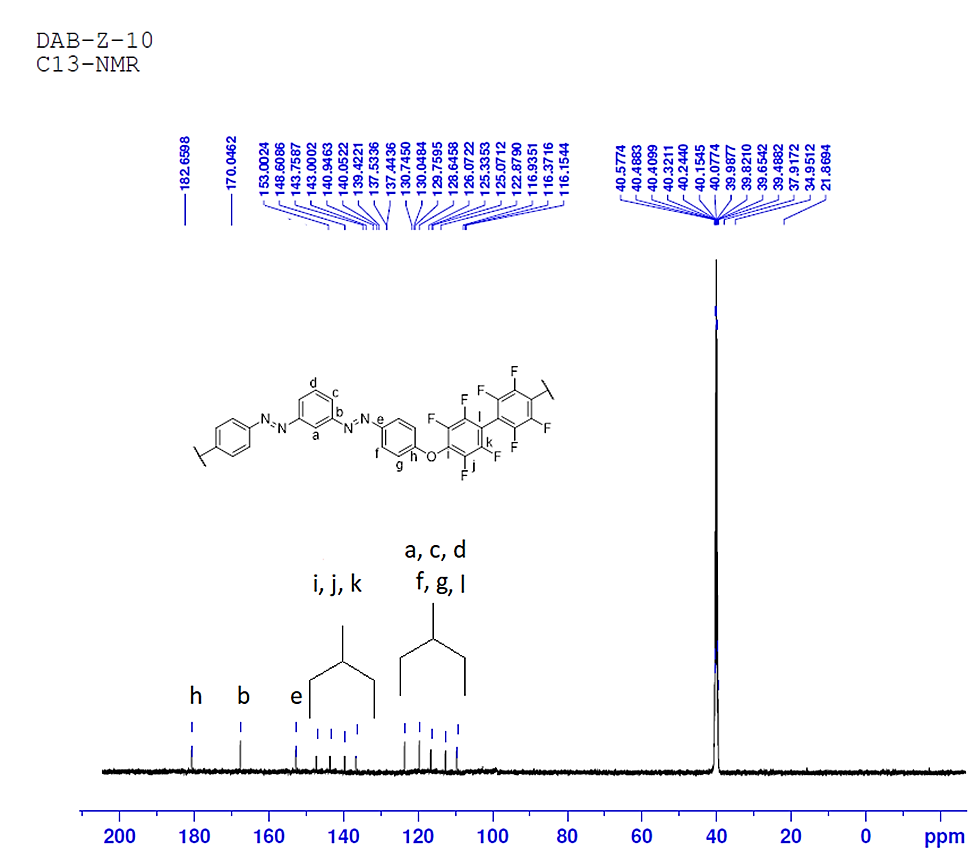
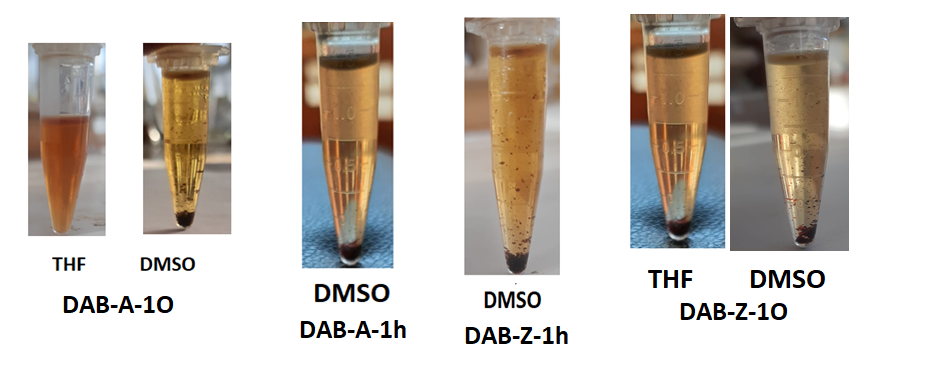


Figure S12 : 13C-NMR spectra of DAB-Z-1O

**Figure S13**: Proposed sites of zero and non-zero dipole moments of the polymers; (bold arrow create µ = 0, dashed arrow creates µ > 0).



**Figure S14:** Solubility behavior of the polymers in THF and DMSO. (Note: DAB-A-1h, DAB-Z-1h were completely insoluble in THF)



**Part 2: Optical properties of the polymers**

The degree of conjugation in the aromatic linkers (HFB and DFB) as well as in the resulting polymers (DAB-A-1h, DAB-A-1O, DAB-Z-1h, and DAB-Z-1O) was investigated by measuring their UV-Vis absorption spectra in DMSO. The maximum absorption wavelength (λmax) is directly related to the degree of π-orbital overlap in conjugated systems. Thus, a comparison of the UV-Vis spectra of the linkers and the polymers provides information about the extent of π-π\* transition in the extended conjugated systems.

Figure S15.A displays the absorption spectra of DAB-A-1h, DAB-A-1O, and DAB-A-OH. The absorption spectrum of DAB-A-OH exhibited two λmax values at 350 and 276 nm, corresponding to the absorption of the azomethine (C=N) and phenyl groups, respectively. After the polymerization of DAB-A-OH with HFB and DFB, the λmax shifted to 305 and 322 nm, respectively. This shift may be attributed to the incorporation of the fluorinated linkers and the modification of the chain planarity, leading to a hypsochromic effect [2].

Figure S15.B shows the UV-Vis spectra of DAB-Z-OH, DAB-Z-1h, and DAB-Z-1O. DAB-Z-OH exhibited two maxima at 366 and 440 nm in the absorption spectrum. The less intense maximum at 440 nm is indicative of the presence of azo-hydrazone-enamine tautomeric forms, which are formed due to interactions with DMSO [3]. Similarly, DAB-Z-1h and DAB-Z-1O, the azo-based polymers, exhibited hypsochromic shifts in their UV-Vis spectra to 334 and 342 nm, respectively. This shift was more significant than that observed in the azomethine-based polymers, possibly because of the presence of N=N and the higher fluorine content [4]. The hypsochromic shift observed in the absorption spectra could also be influenced by several other factors such as hydrogen bonding of the nitrogen sites, different chain conformations, and alterations in planarity.

**Figure S15** UV–Vis absorption spectra of (A) DAB-A-OH and (B) DAB-Z-OH and their fluorinated polymers.

To investigate the impact of structural variations on the optical properties of the polymers, the bandgap (Eg) was determined using the Tauc relation applied to solutions of known concentrations or from transmittance spectra [2]. The Eg values were calculated by extrapolating the linear region of the UV-Vis spectra to x = λ, y = 0, as shown in Figure S16.A-B. The linear region in the UV-Vis spectra indicates the first sharp increase in absorption or the absorption onset. The λ values obtained from this region were then used in the Equation 1240/λ to calculate Eg. As a consequence of the polymerization, Eg values were found to increase, which can be attributed to the inclusion of fluorine groups in the polymer chains of all polymers.



**Figure S16** Experimental determination of λ onset corresponding to the bandgap values of (A) DAB-A-OH and (B) DAB-Z-OH and their corresponding polymers.

**TableS2.** λ max of monomers and polymers.

|  |  |  |  |
| --- | --- | --- | --- |
| Monomers/Polymers | λ maxa (nm) | λonsetb | Bandgap Eg (eV) |
| DAB-A-OH | 391 | 391 | 3.17 |
| DAB-A-1O | 322 | 373 | 3.32 |
| DAB-A-1h | 305 | 362 | 3.42 |
| DAB-Z-OH | 366 | 588 | 2.10 |
| DAB-Z-1O | 342 | 414 | 2.99 |
| DAB-Z-1h | 334 | 421 | 2.94 |
| a λmax determined from the UV–Vis absorption spectra. b λ onset: wavelength at the first increase in absorbance. | | | |

**Part 3: BET surface area calculations**

The BET surface area of the polymers was determined by using Multi-point BET plot by using eq (1), where Xm is the monolayer capacity, P/P0 relative pressure, and C is constant. The plot of is performed by using, at minimum, three data points, in the P/P0 range 0.025 to 0.30, which should give a linear relation with a positive slope. It is well-known that at relative pressures higher than 0.5, there is the onset of capillary condensation, and at relatively low pressures only a monolayer gas adsorption occurs. gives liners plot with positive slope.

When the values of the slope and y-intercept is determined by using least squares regression, the monolayer capacity Xm can be calculated by applying eq (2).

Once **Xm** is determined, the total surface area **SA** can be calculated from eq (3), where **Av** is Avogadro's number (6.022 \*1023), **Am** is the cross sectional area of the adsorbate and equals 0.138 nm2 for an absorbed argon molecule, and **Mv** is the molar volume, which equals 22414 mL as STP conditions.

According to the above equations, the calculated Xm and SA values along with the slope, and intercepts of the plots are summarized in table S3.

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| Table S3. BET plots data of the polymers | | | | |
| Equation | y = a + b\*x |  |  |  |
| Plot | DAB-A-1O | DAB-A-1h | DAB-Z-1h | DAB-Z-1O |
| Weight | No Weighting |  |  |  |
| Intercept (i) | -4.58E-09 | -2.795E-09 | -2.677E-09 | -1.678E-09 |
| Slope (s) | 0.0129972 | 0.0091831 | 0.0075039 | 0.0048092 |
| Xm=1/(s+i) | 76.93967565 | 108.895722 | 133.2640836 | 207.9348642 |
| SA (surface area) | 285.2665312 | 403.7488409 | 494.0985588 | 770.9527876 |
| Residual Sum of Squares | 3.61E-05 | 1.99E-05 | 1.12E-05 | 4.99E-06 |
| Pearson's r | 0.994560004 | 0.99375191 | 0.994836658 | 0.994574501 |
| R-Square (COD) | 0.989149602 | 0.987542859 | 0.989699976 | 0.989178439 |
| Adj. R-Square | 0.986437003 | 0.984428574 | 0.98712497 | 0.986473049 |

**[5-7]**

**References**

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