Supporting Information for

Synthesis, crystal structure, and optical properties of fluorinated poly(pyrazole) ligands and in-silico assessment of their affinity for volatile organic compounds

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S.1. Infrared spectroscopy and thermal analysis

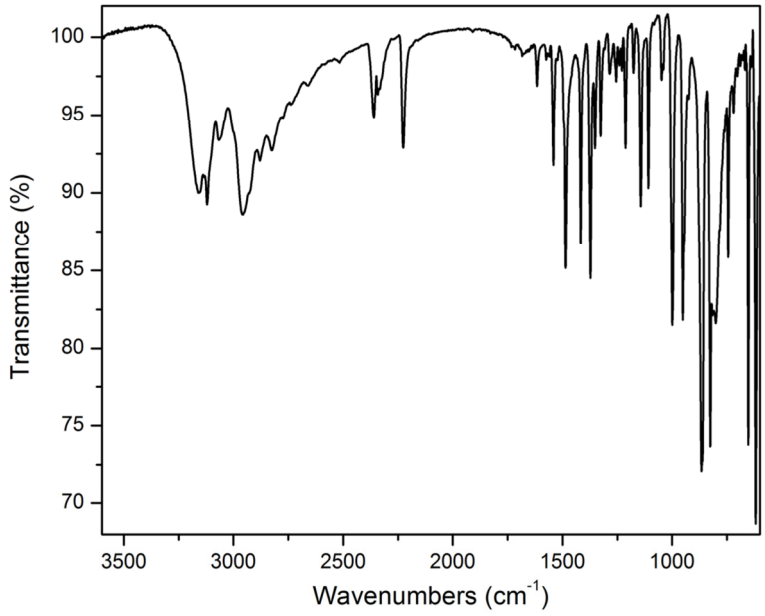

Figure S1. ATR-FTIR spectrum of compound **H_2BPEFB**.

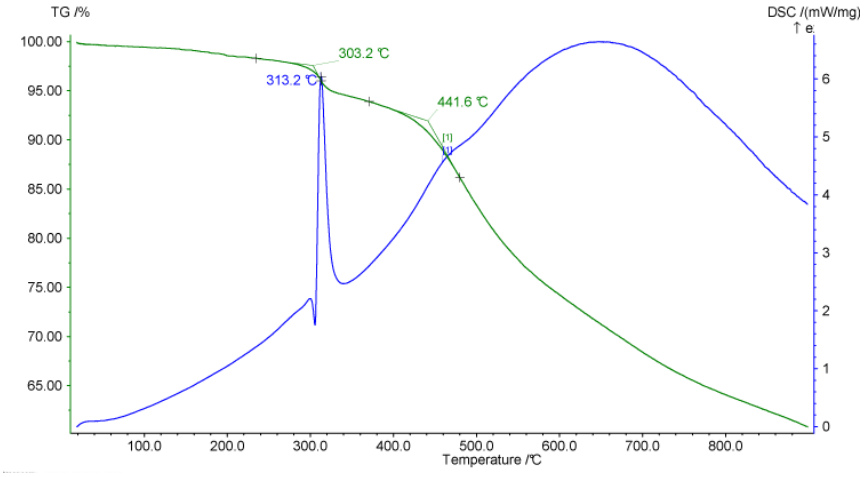

Figure S2. Simultaneous thermal analysis of compound **H_2BPEFB**: thermogravimetric analysis, green trace; Differential scanning calorimetry, blue trace.

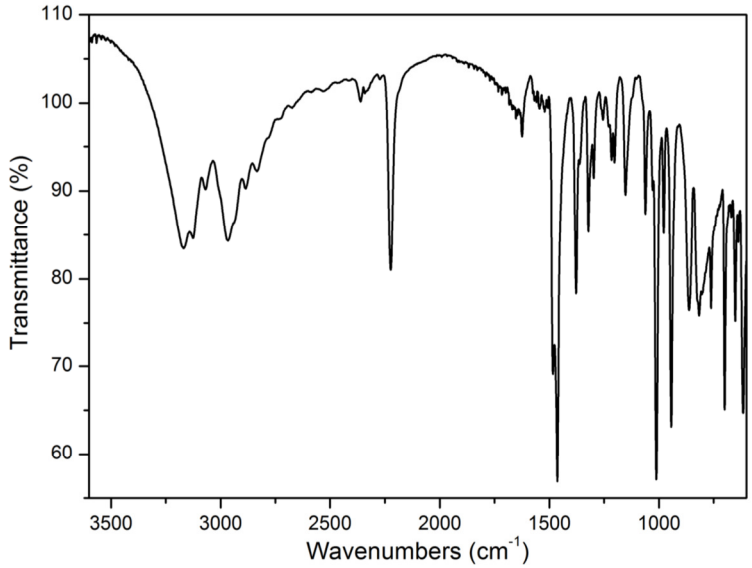

Figure S3. ATR-FTIR spectrum of compound **H_2BPEF_2B**.

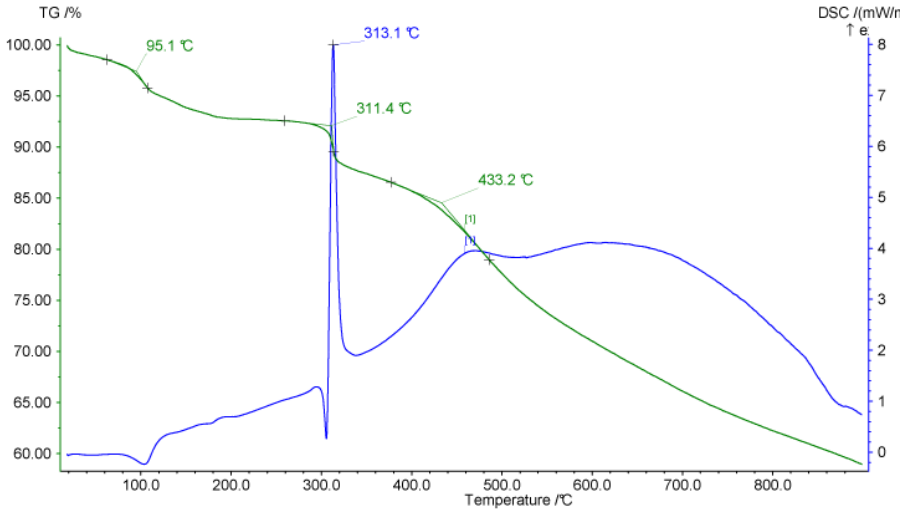

Figure S4. Simultaneous thermal analysis of compound **H_2BPEF_2B**: thermogravimetric analysis, green trace; Differential scanning calorimetry, blue trace.

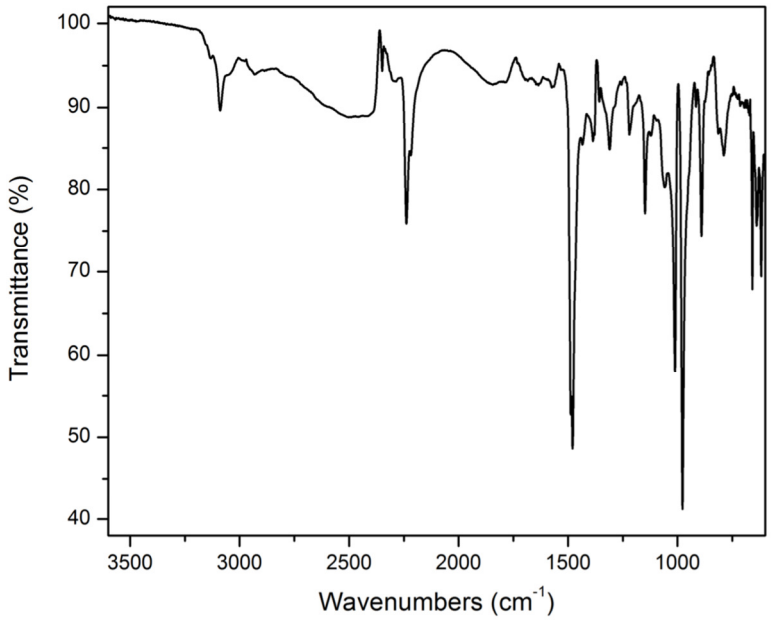

Figure S5. ATR-FTIR spectrum of compound **H_2BPEF$_4$B**.

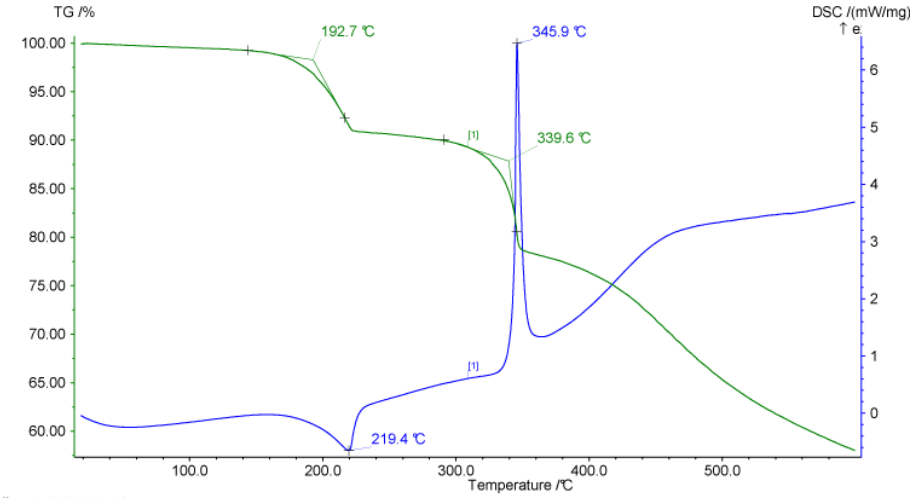

Figure S6. Simultaneous thermal analysis on compound **H_2BPEF$_4$B**: thermogravimetric analysis, green trace; Differential scanning calorimetry, blue trace..

S.2. NMR Spectroscopy

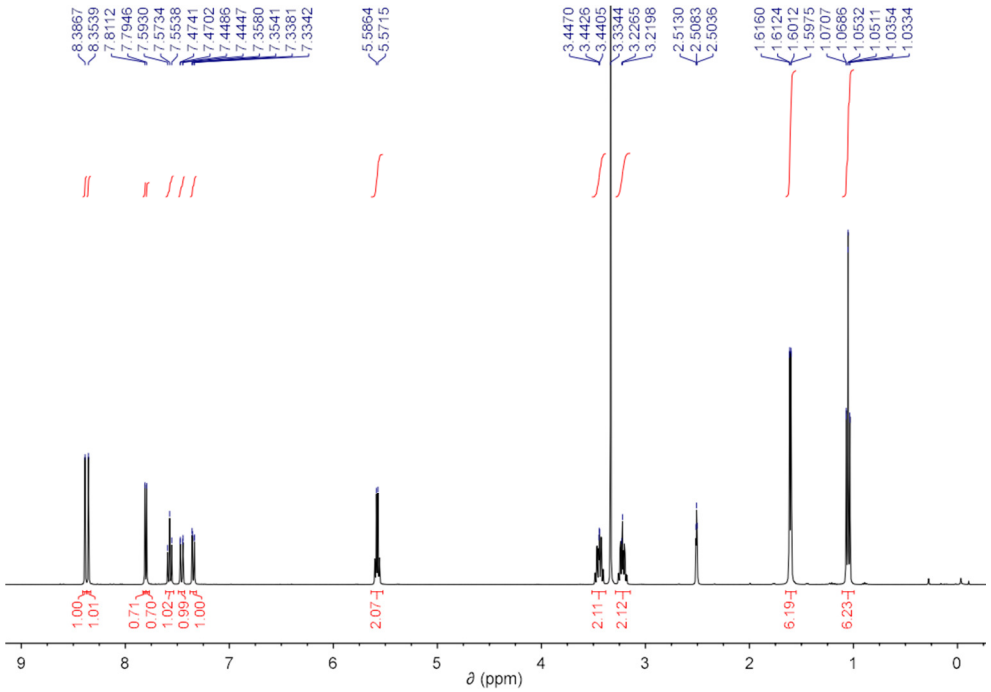

Figure S7. [1]H NMR spectrum (400 MHz, DMSO-*d*6, 298 K) of compound **2a**.

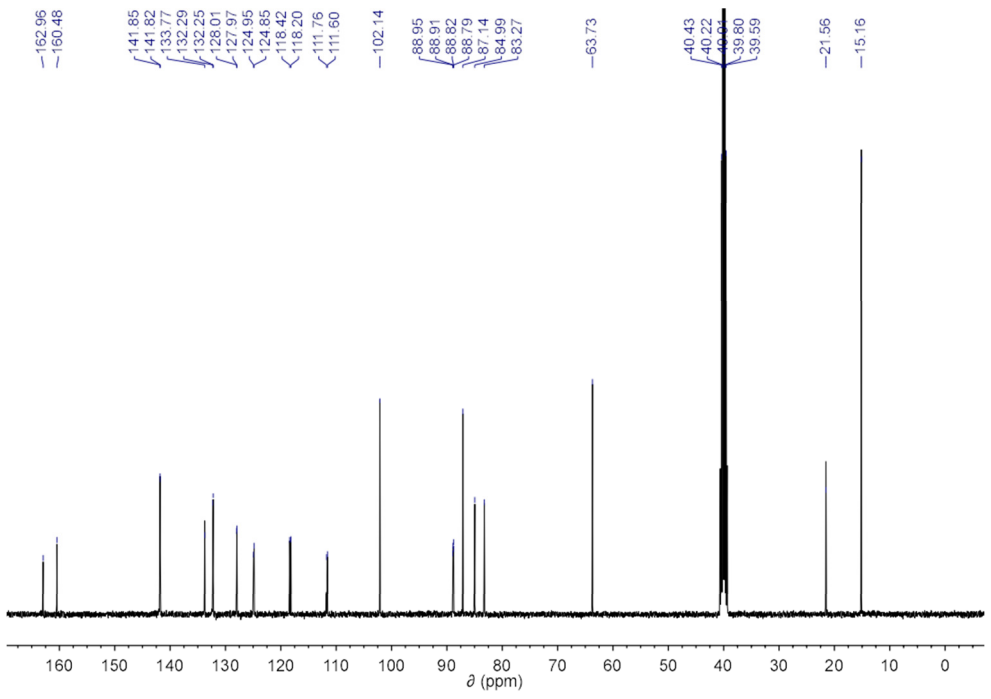

Figure S8. [13]C NMR spectrum (100 MHz, DMSO-*d*6, 298 K) of compound **2a**.

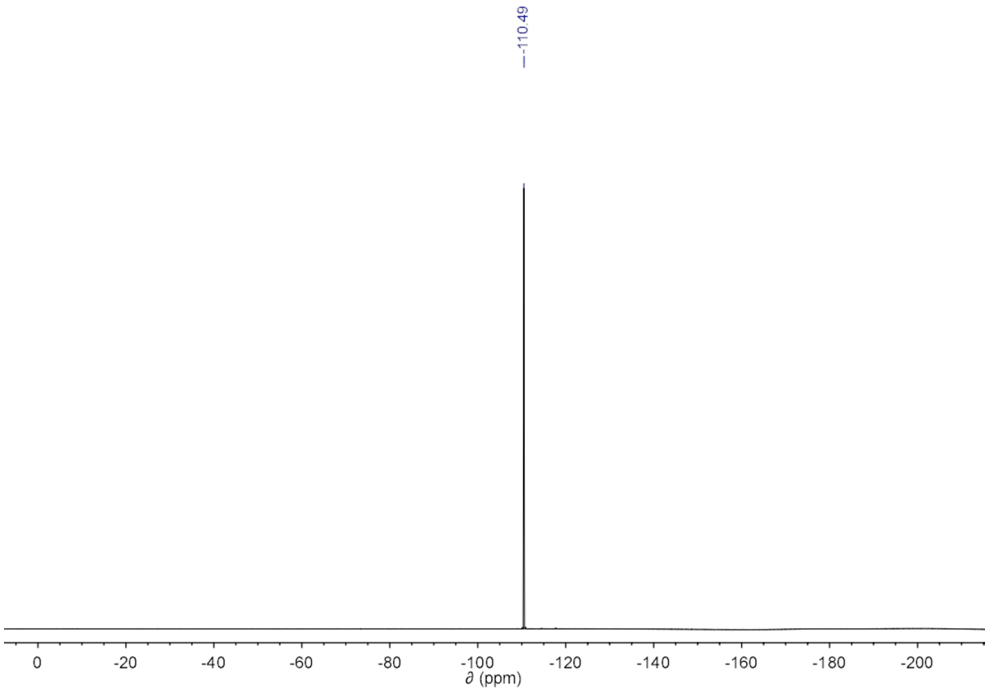

Figure S9. ^{19}F NMR spectrum (376 MHz, DMSO-d_6, 298 K) of compound **2a**.

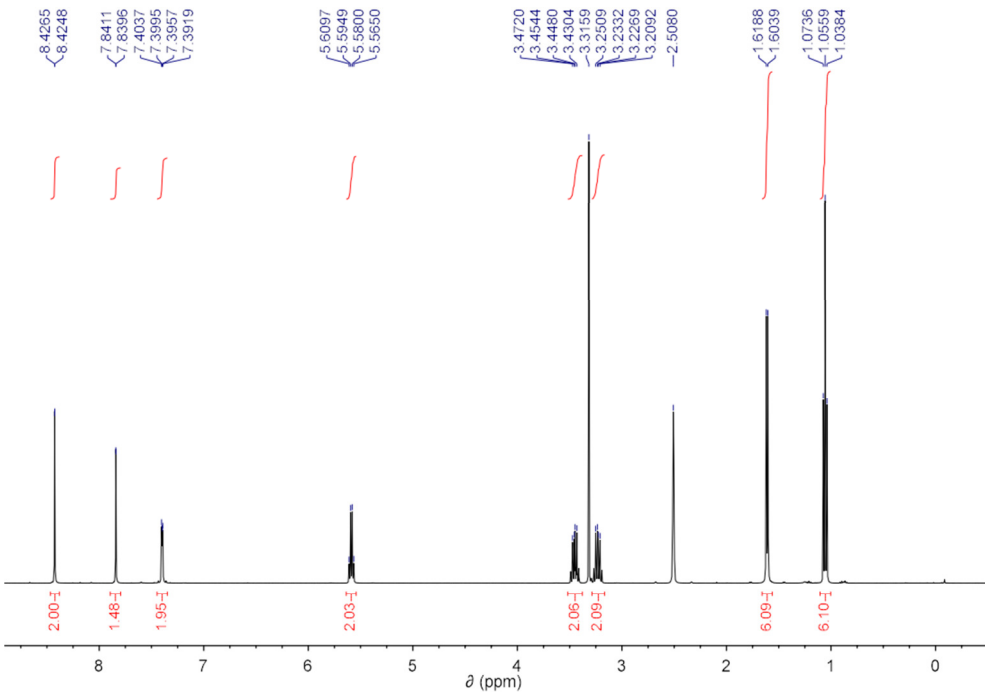

Figure S10. ^{1}H NMR spectrum (400 MHz, DMSO-d_6, 298 K) of compound **2b**.

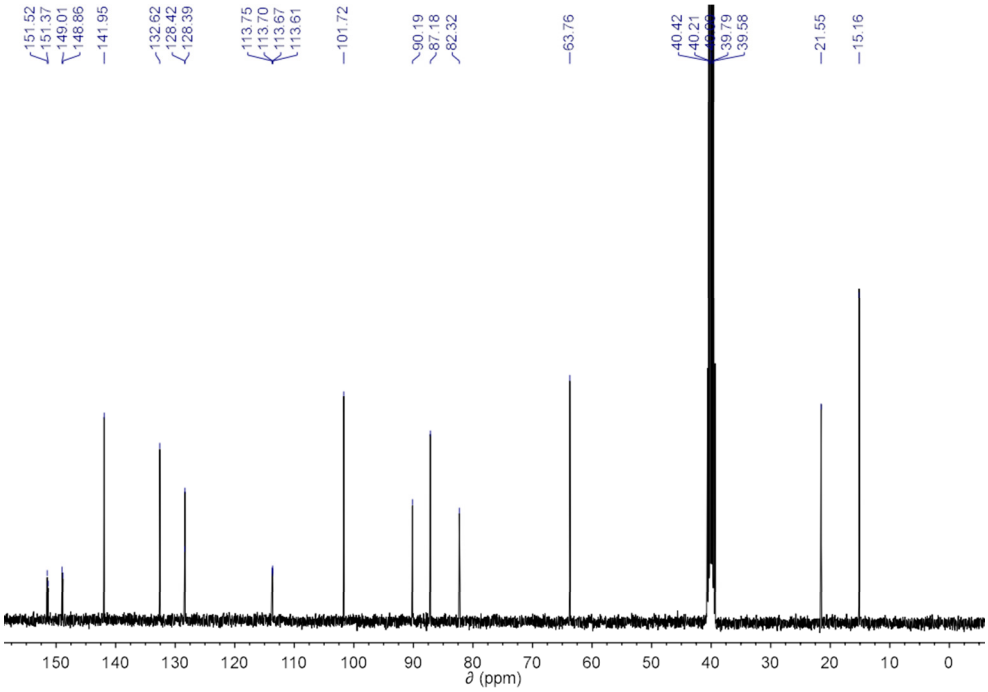

Figure S11. ^{13}C NMR spectrum (100 MHz, DMSO-d_6, 298 K) of compound **2b**.

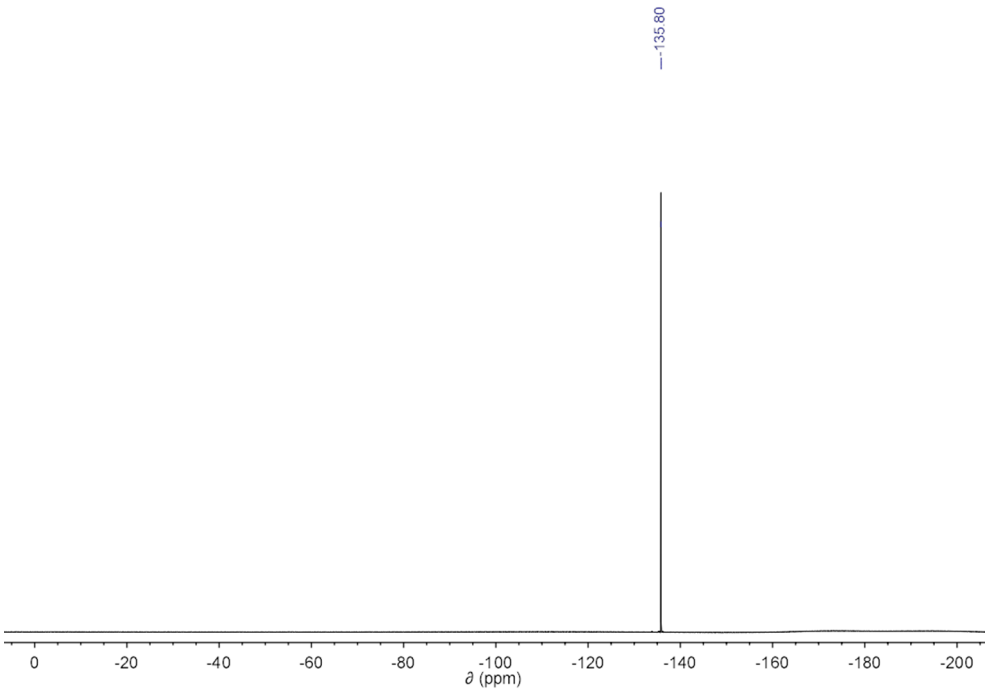

Figure S12. ^{19}F NMR spectrum (376 MHz, DMSO-d_6, 298 K) of compound **2b**.

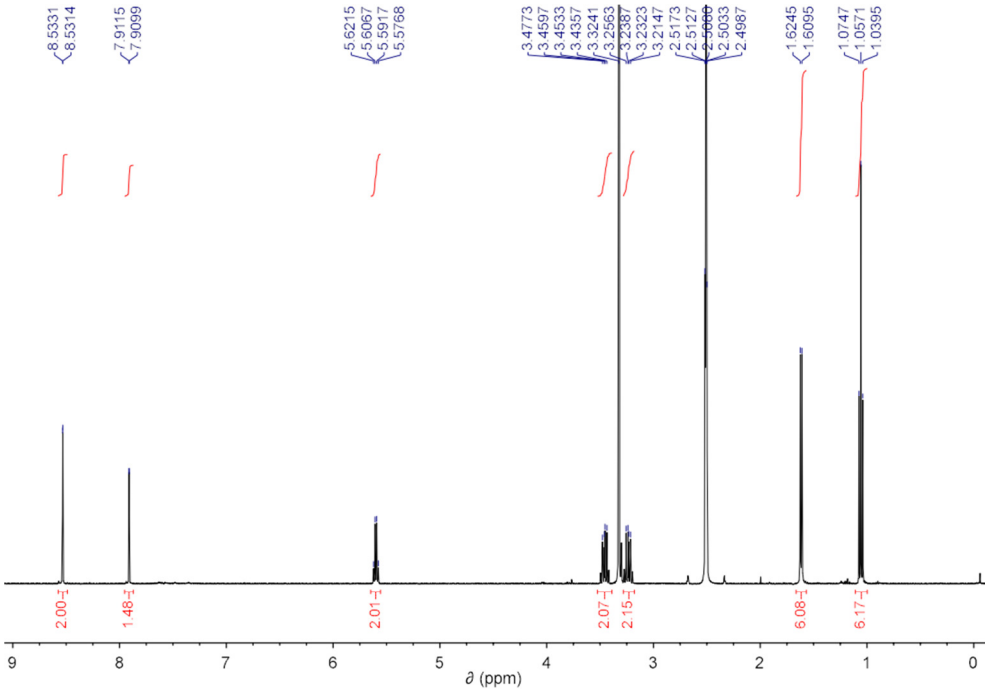

Figure S13. [1]H NMR spectrum (400 MHz, DMSO-*d*6, 298 K) of compound **2c**.

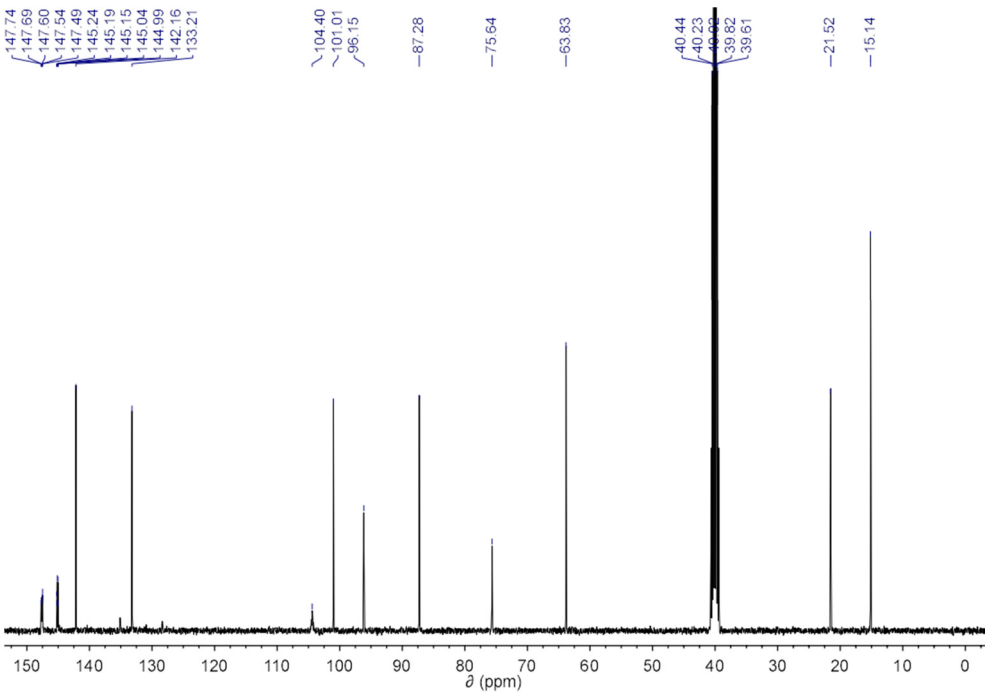

Figure S14. [13]C NMR spectrum (100 MHz, DMSO-*d*6, 298 K) of compound **2c**.

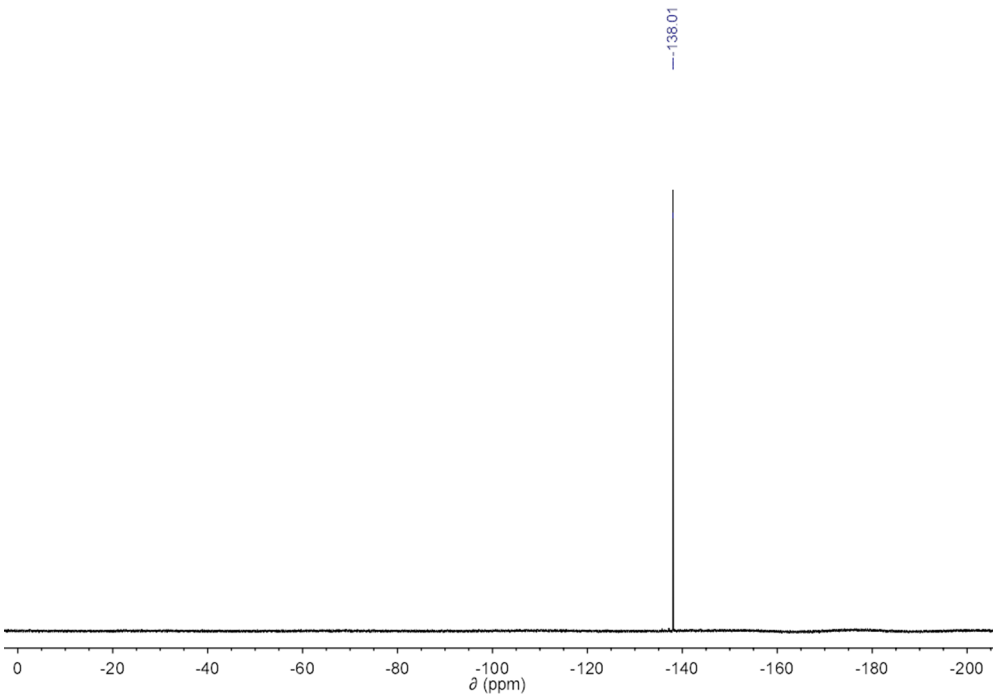

Figure S15. [19]F NMR spectrum (376 MHz, DMSO-d_6, 298 K) of compound **2c**.

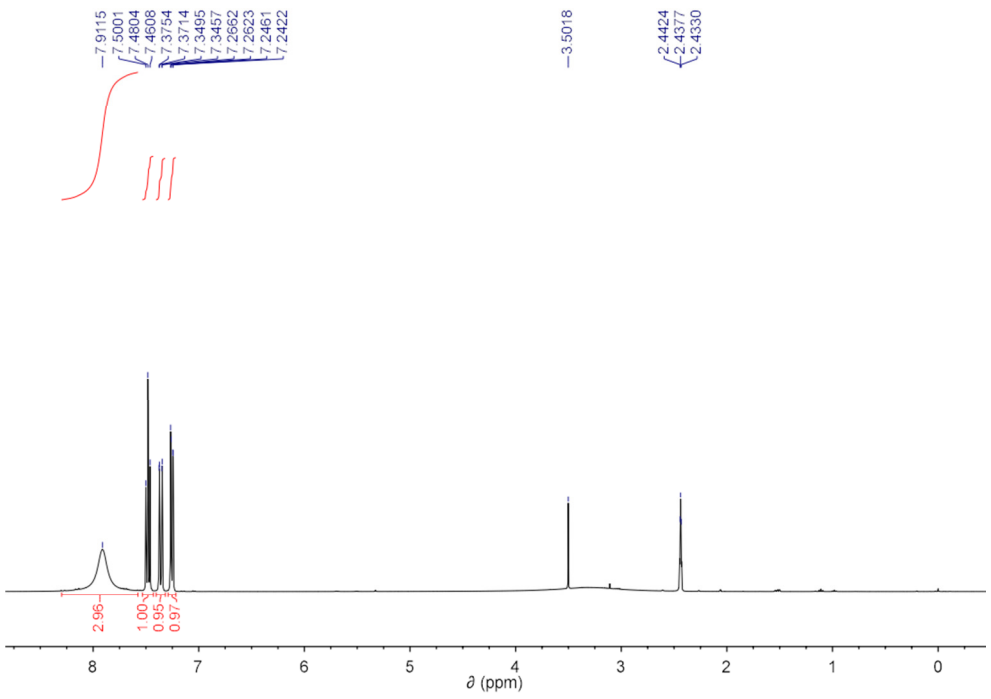

Figure S16. [1]H NMR spectrum (400 MHz, DMSO-d_6, 298 K) of compound **H_2BPEFB**.

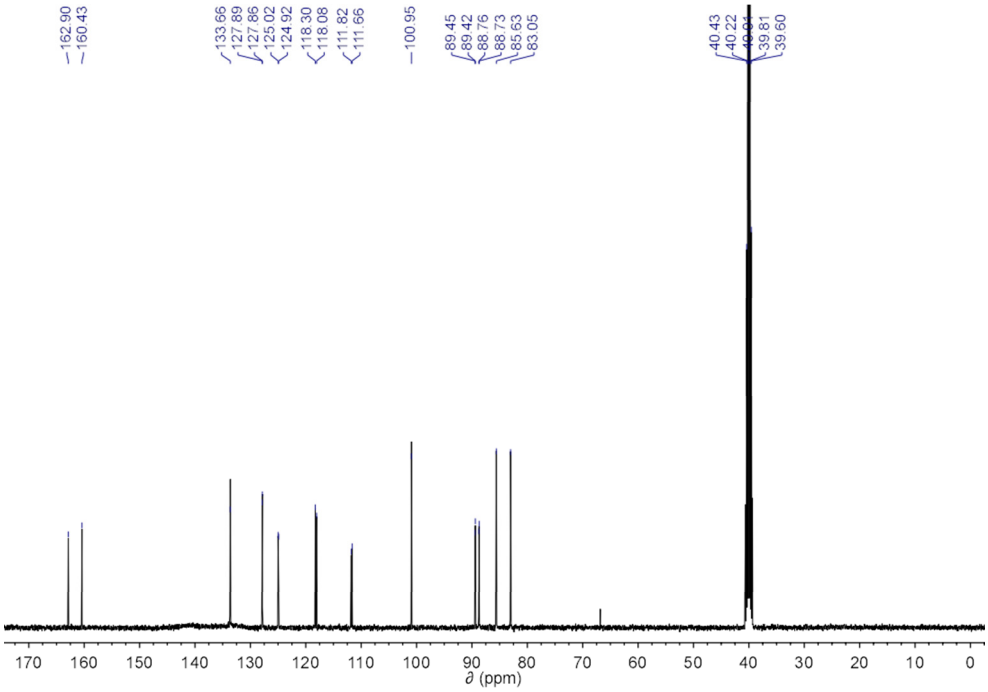

Figure S17. ^{13}C NMR spectrum (100 MHz, DMSO-d_6, 298 K) of compound **H_2BPEFB**.

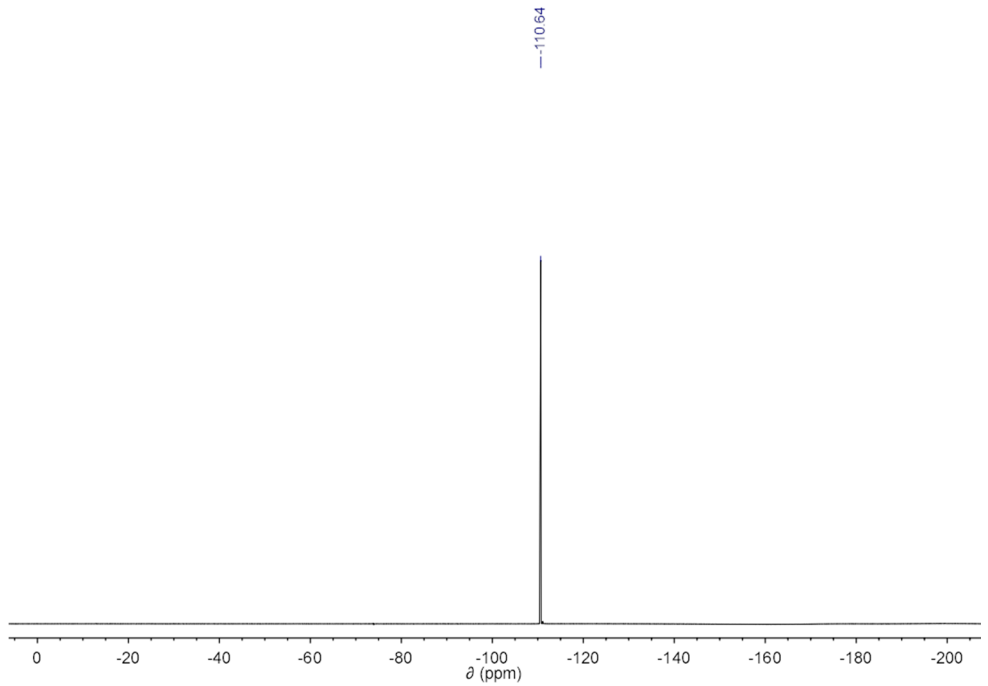

Figure S18. ^{19}F NMR spectrum (376 MHz, DMSO-d_6, 298 K) of compound **H_2BPEFB**.

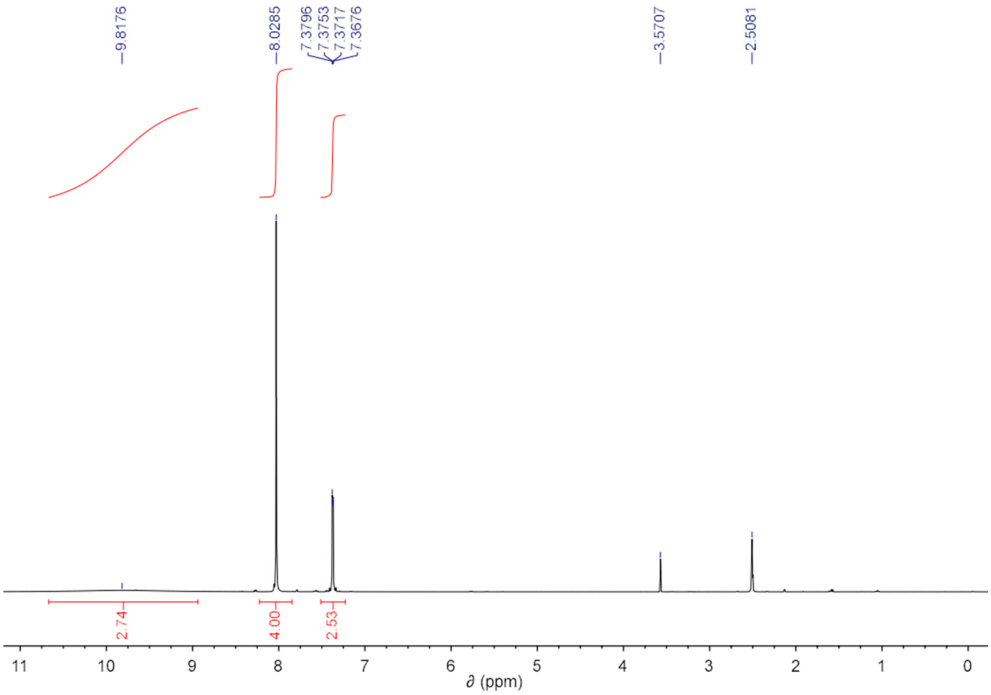

Figure S19. [1]H NMR spectrum (400 MHz, DMSO-*d*6, 298 K) of compound **H2BPEF2B**.

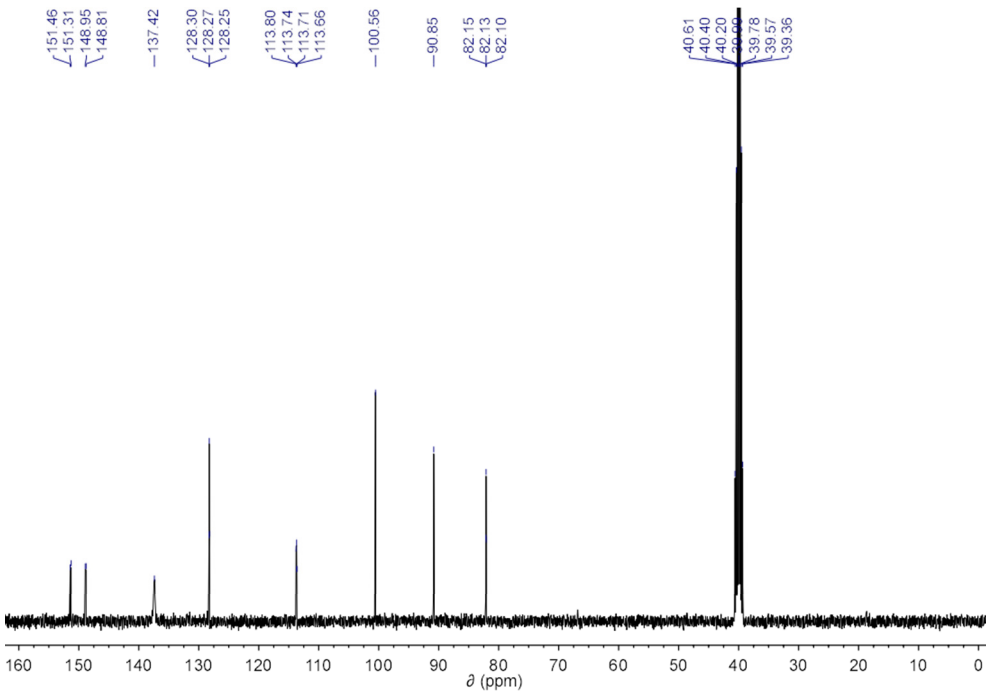

Figure S20. [13]C NMR spectrum (100 MHz, DMSO-*d*6, 298 K) of compound **H2BPEF2B**.

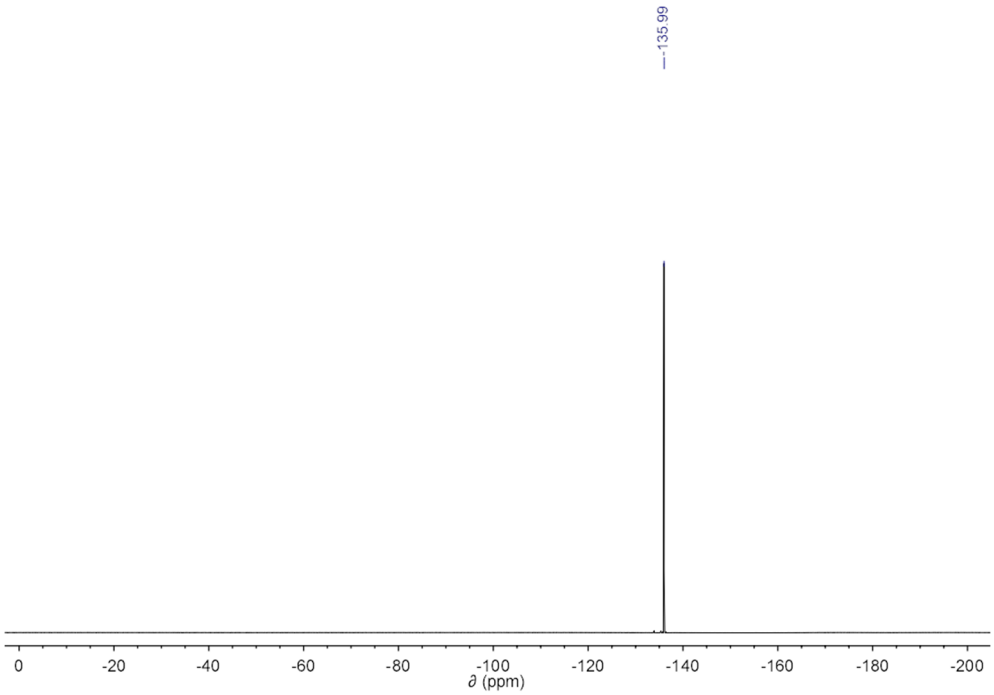

Figure S21. ^{19}F NMR spectrum (376 MHz, DMSO-d_6, 298 K) of compound **H_2BPEF$_2$B**.

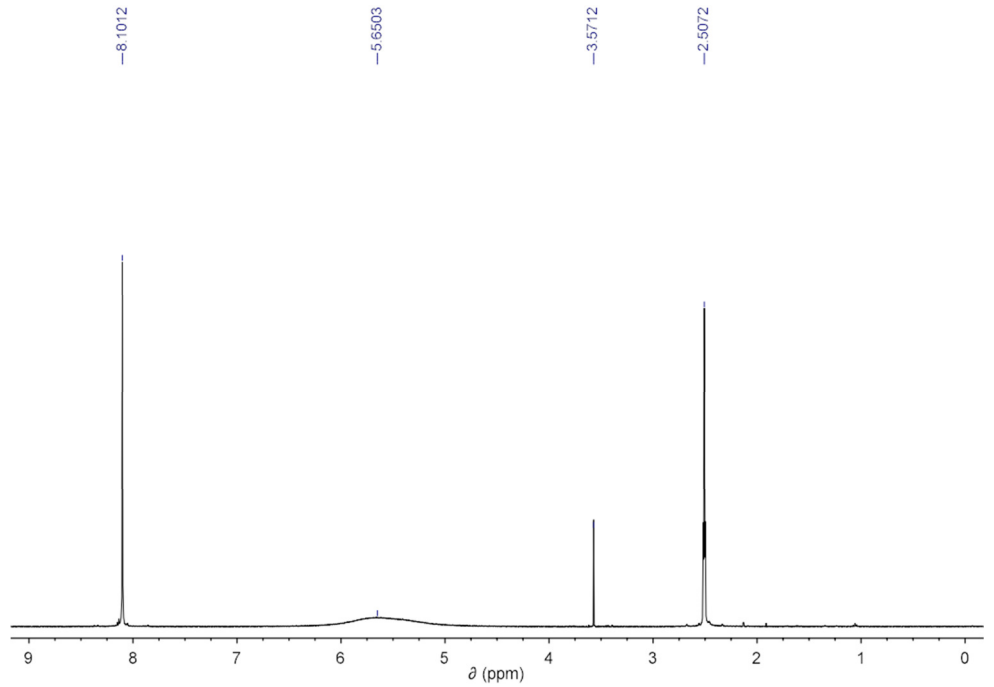

Figure S22. ^{1}H NMR spectrum (400 MHz, DMSO-d_6, 289 K) of compound **H_2BPEF$_4$B**.

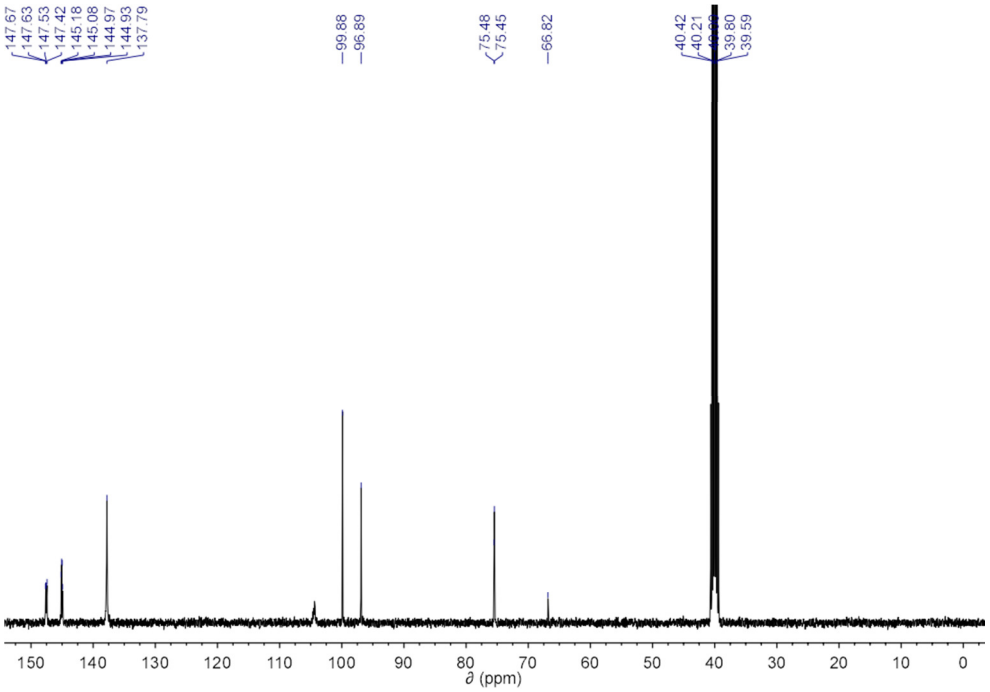

Figure S23. ^{13}C NMR spectrum (100 MHz, DMSO-*d*$_6$, 298 K) of compound **H$_2$BPEF$_4$B**.

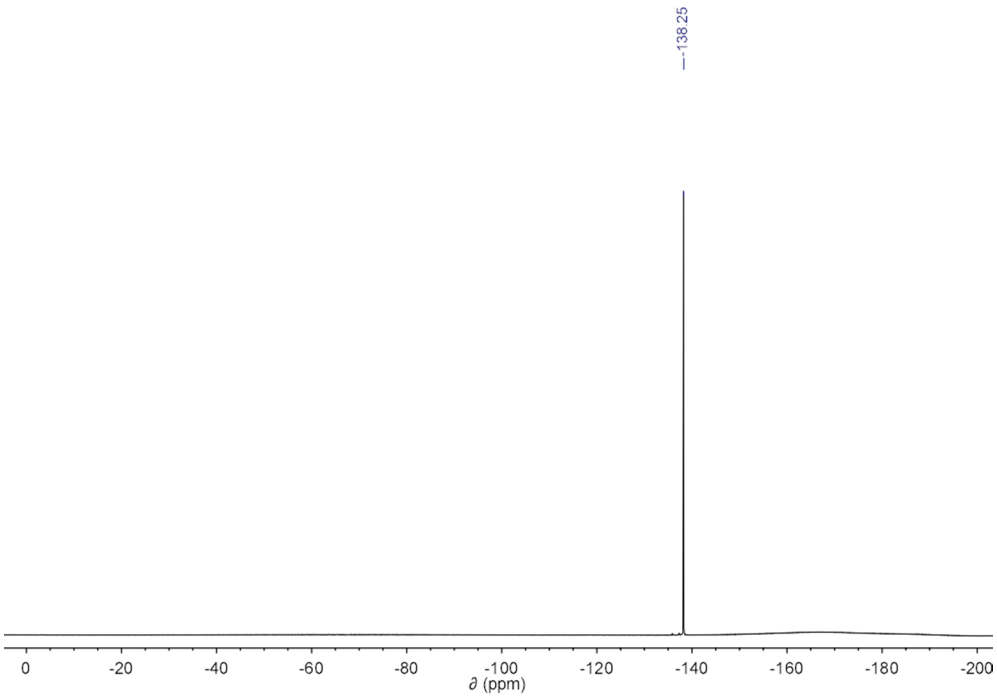

Figure S24. ^{19}F NMR spectrum (376 MHz, DMSO-*d*$_6$, 298 K) of compound **H$_2$BPEF$_4$B**.

S.3. X-ray crystallography

Table S1. Crystal data and structure refinement details for **H_2BPEFB**, **H_2BPEF_2B** and **H_2BPEF_4B**.

	H_2BPEFB	**H_2BPEF_2B**	**H_2BPEF_4B**
Empirical formula	$C_{16}H_9FN_4$	$C_{16}H_8F_2N_4$	$C_{16}H_6F_4N_4$
Formula weight	276.27	294.26	330.25
Temperature/K	190	190.0	190
Crystal system	monoclinic	monoclinic	monoclinic
Space group	$P2_1/c$	$P2_1/c$	$P2_1/c$
a/Å	15.902(2)	7.913(6)	13.3901(6)
b/Å	5.4778(6)	5.411(3)	6.3395(3)
c/Å	7.315(1)	15.519(11)	7.8929(3)
α/°	90	90	90
β/°	90.515(4)	102.200(13)	93.316(2)
γ/°	90	90	90
Volume/Å^3	637.1(1)	649.5(7)	668.88(5)
Z, Z'	4, 2	2	4, 2
ρ_{calc} g/cm^3	1.440	1.505	1.640
μ/mm^{-1}	0.100	0.114	0.141
F(000)	284.0	300.0	332.0
Crystal size/mm^3	0.05 × 0.04 × 0.03	0.1 × 0.05 × 0.02	0.05 × 0.03 × 0.03
Radiation	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)
2Θ data collection/°	7.868 to 51.464	5.372 to 51.64	7.114 to 51.478
Refl. Collec./Indep.	14592/ 1213 [R_{int} = 0.0841]	13572/1247 [R_{int} = 0.0596]	15225/1269 [R_{int} = 0.0412]
Data/restraints/param.	1213/0/100	1247/10/136	1269/0/113
Goodness-of-fit on F^2	1.072	1.072	1.069
R_1 [I>=2σ (I)]	0.0845	0.0447	0.0508
wR_2 [I>=2σ (I)]	0.1646	0.1018	0.1386
Peak/hole / e Å^{-3}	0.33/-0.33	0.18/-0.18	0.46/-0.25

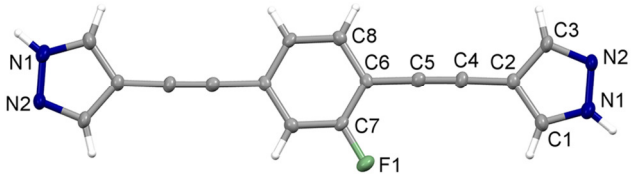

Figure S25. Molecular structure of **H_2BPEFB** with thermal ellipsoids drawn at the 30% probability level. Only one component of the disordered aromatic ring is reported for clarity. Colour code: carbon, grey; hydrogen, white; fluorine, light green; nitrogen, blue.

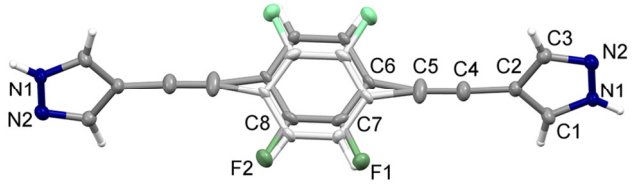

Figure S26. Molecular structure of **H_2BPEF$_2$B**, highlighting the disordered aromatic ring. Thermal ellipsoids drawn at the 30% probability level. Colour code: carbon, grey; hydrogen, white; fluorine, light green; nitrogen, blue.

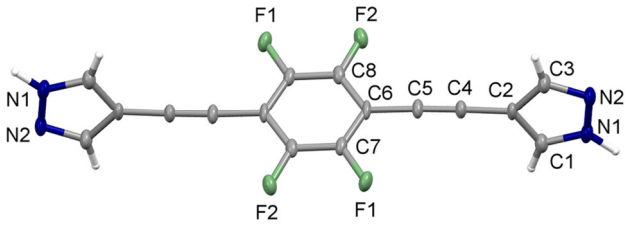

Figure S27. Molecular structure of **H_2BPEF$_4$B**, with thermal ellipsoids drawn at the 30% probability level. Colour code: carbon, grey; hydrogen, white; fluorine, light green; nitrogen, blue.

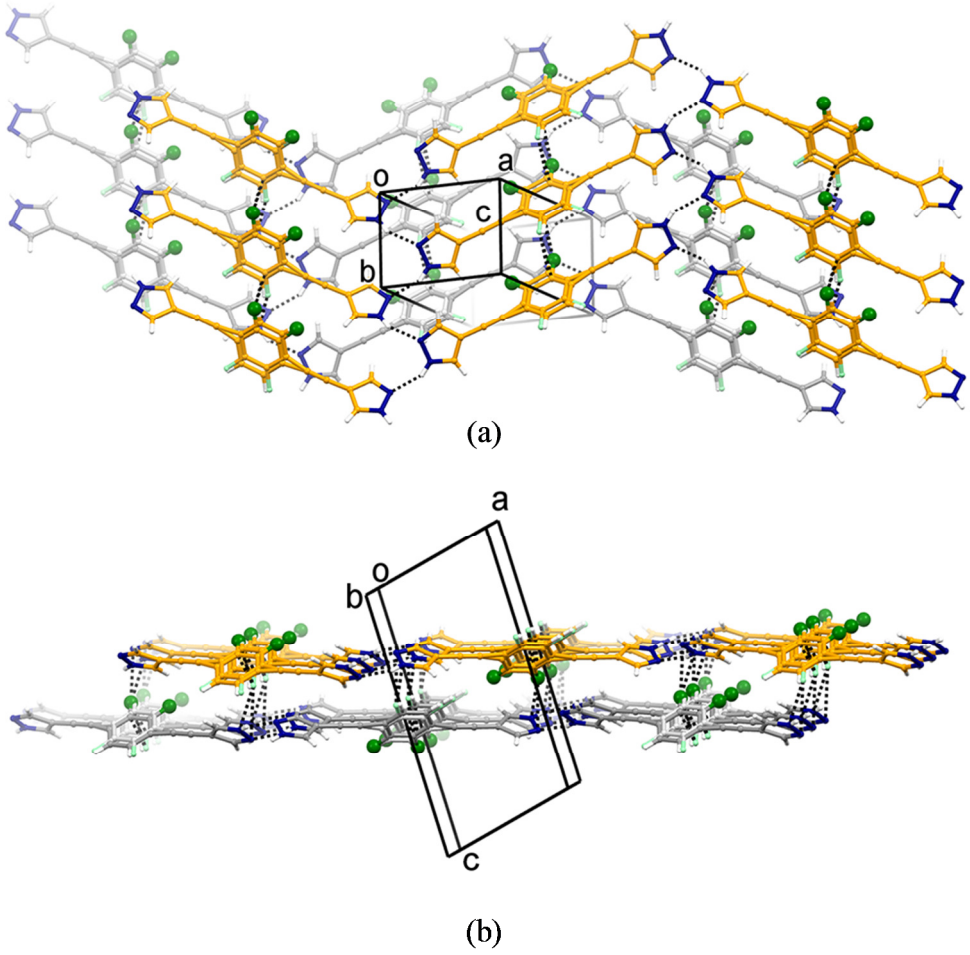

Figure S28. Portion of the crystal structure of **H_2BPEF_2B** viewed, in perspective, along the crystallographic directions (a) [001] and (b) [010]. The carbon atoms of two consecutive 2-D layers are highlighted in yellow and gray, respectively. Non-bonding interactions are represented with dashed lines. Colour code: hydrogen, white; fluorine, green; nitrogen, blue.

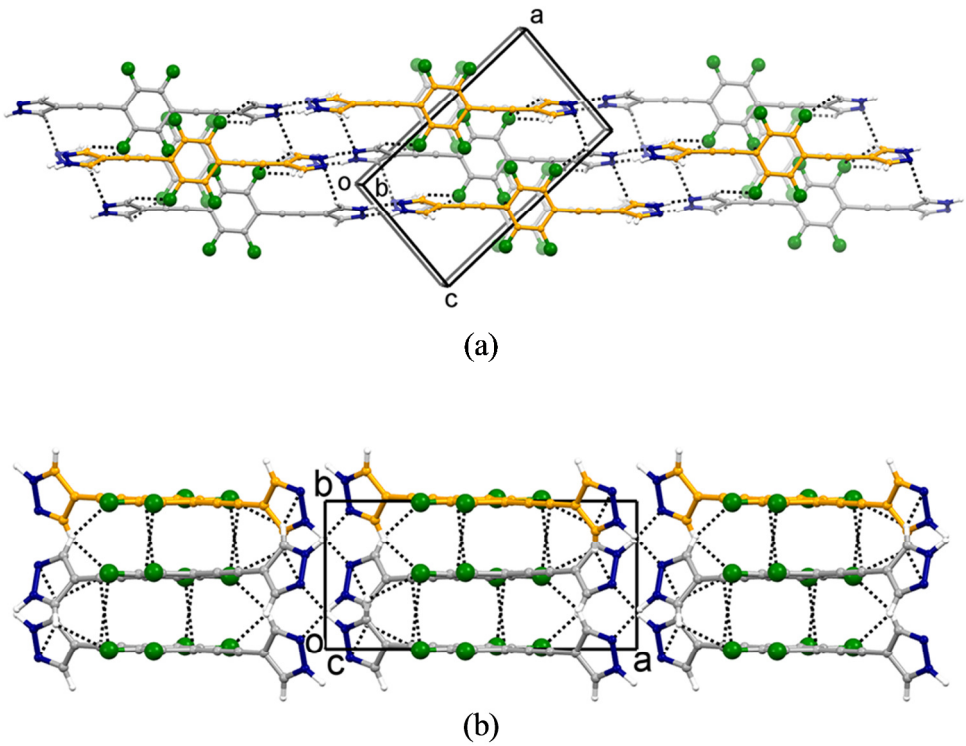

Figure S29. Portion of the crystal structure of **H_2BPEF$_4$B** viewed, in perspective, along the crystallographic directions (a) [011] and (b) [001]. The carbon atoms of two consecutive 2-D layers are highlighted in yellow and gray, respectively. Non-bonding interactions are represented with dashed lines. Colour code: hydrogen, white; fluorine, green; nitrogen, blue.

S.4. Electronic state transition spectroscopy

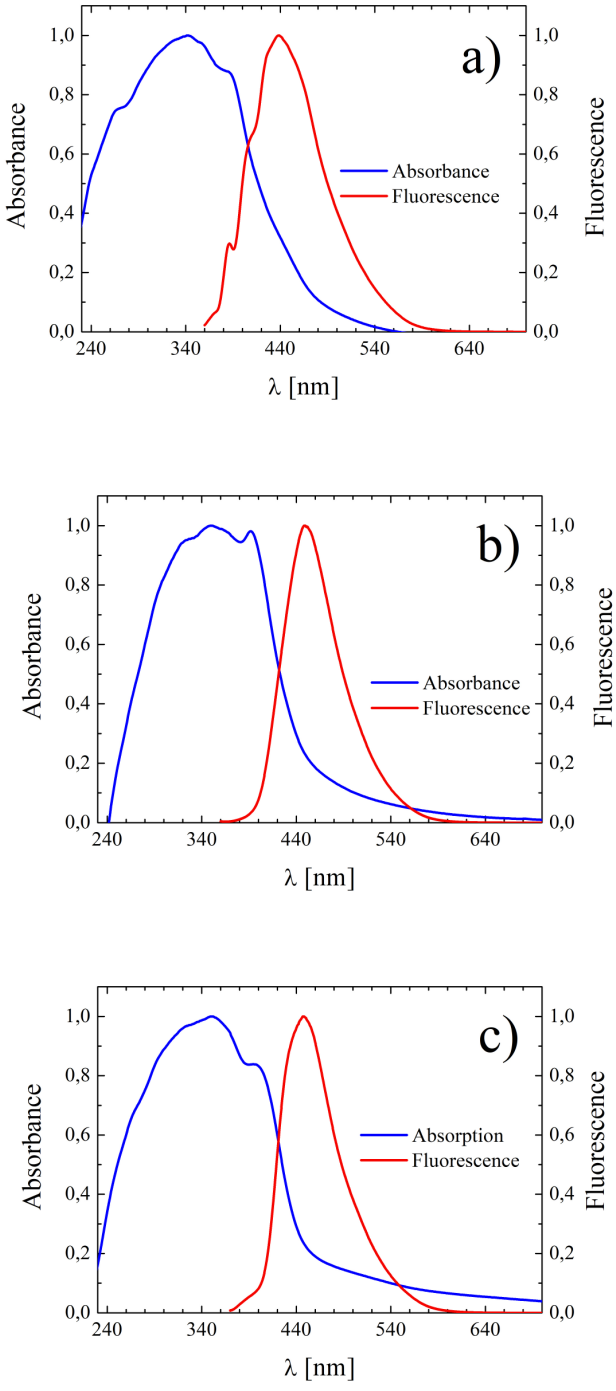

Figure S30. Solid-state absorption (blue) and fluorescence (red) spectral line-shapes of a) **H₂BPEFB**, b) **H₂BPEF₂B**, and c) **H₂BPEF₄B**.

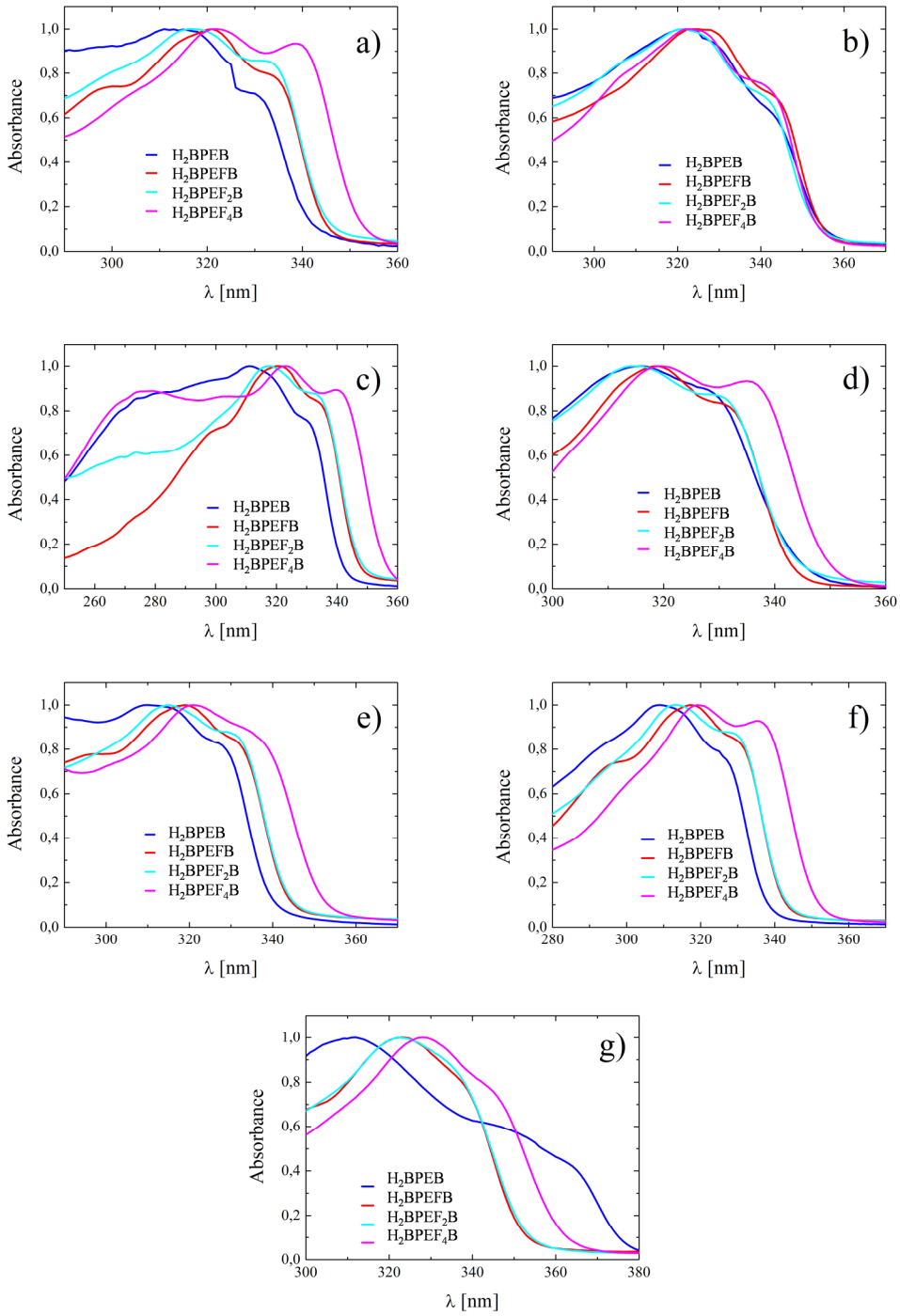

Figure S31. Absorption spectra of compounds **H2BPEB** (blue), **H2BPEFB** (red), **H2BPEF2B** (cyan), and **H2BPEF4B** (magenta) in: a) toluene, b) chloroform, c) tetrahydrofuran, d) dichloromethane, e) ethyl acetate, f) ethanol, and g) dimethylsulfoxyde.

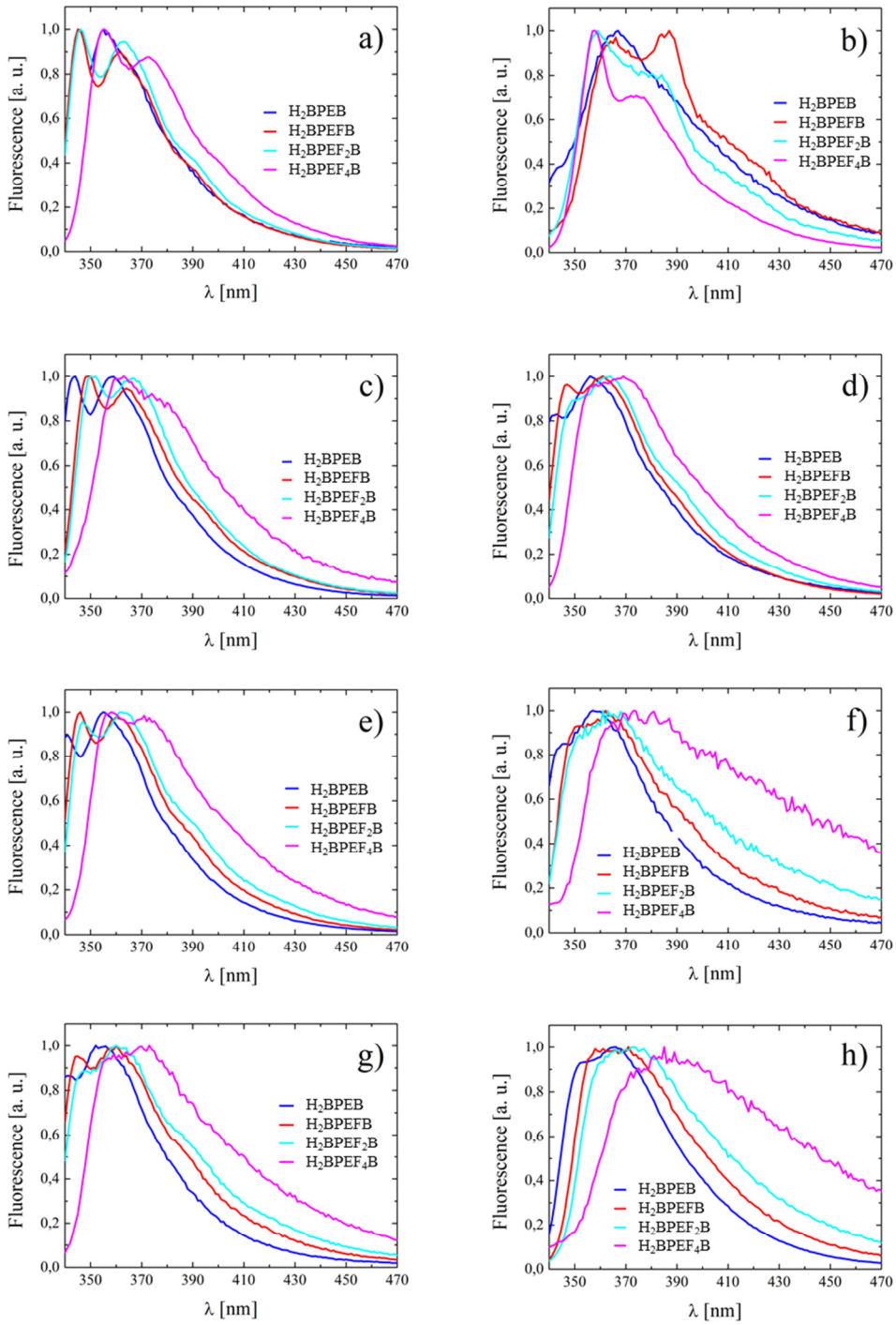

Figure S32. Fluorescence emission spectra of compounds **H2BPEB** (blue), **H2BPEFB** (red), **H2BPEF2B** (cyan), and **H2BPEF4B** (magenta) in: a) toluene, b) chloroform, c) tetrahydrofuran, d) dichloromethane, e) ethyl acetate, f) acetone, g) ethanol, and h) dimethylsulfoxyde.

S.5. Dielectric properties and hydrophobicity

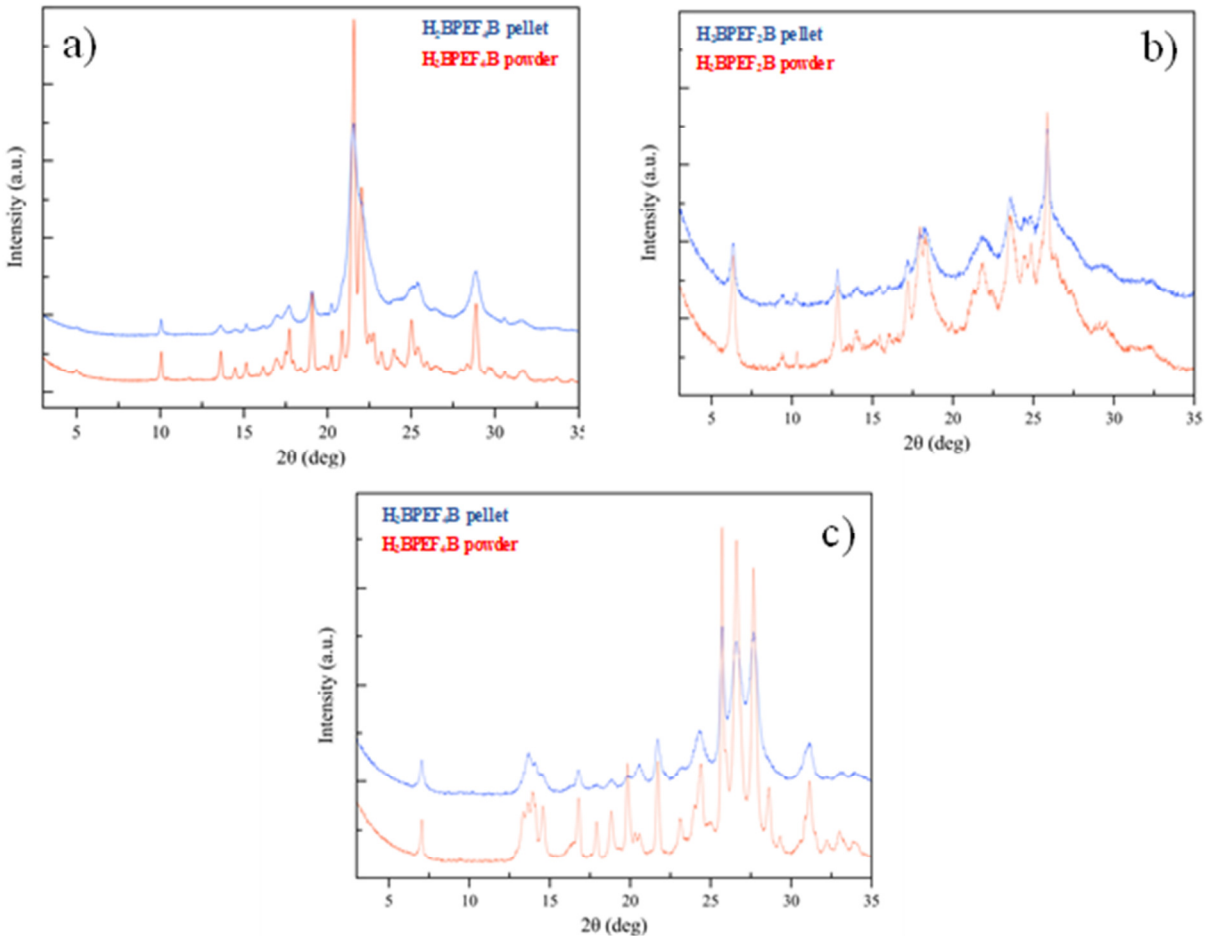

Figure S33. Powder X-ray diffraction patterns of a) **H2BPEFB**, b) **H2BPEF2B** and c) **H2BPEF4B** as synthesized (red trace) and after pellettization (blue trace).

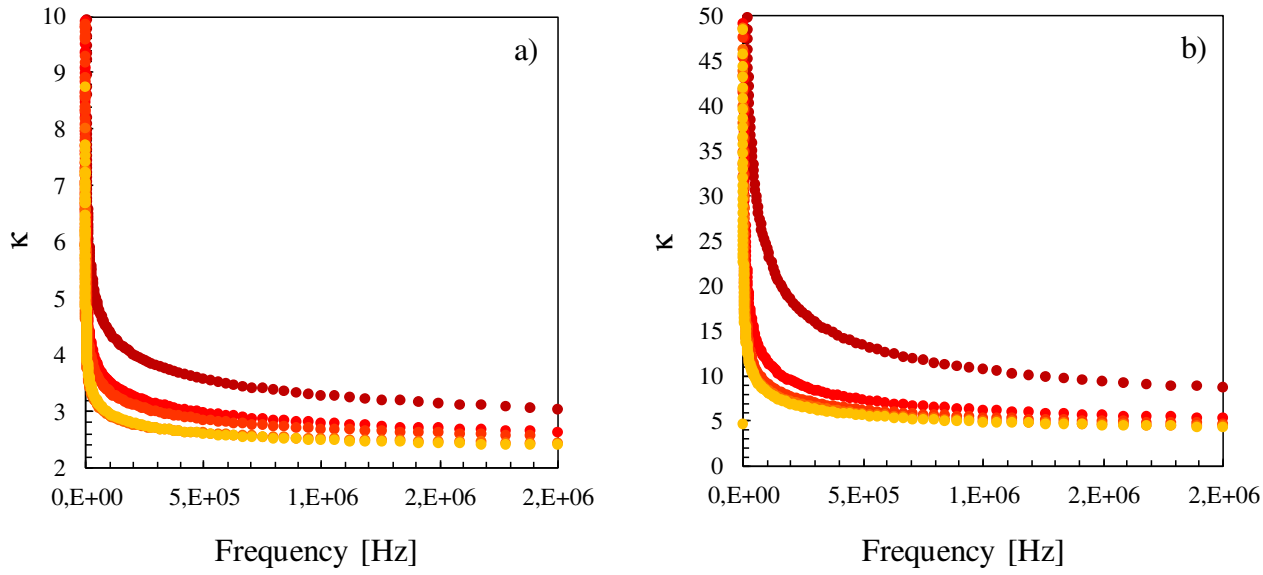

Figure S34. From dark red to light orange: first-to-fifth measurement of the dielectric constant as a function of the AC frequency for a) **H_2BPEFB** and b) **H_2BPEF_2B**, after pellet exposure to a water vapour saturated environment.