Synthesis and characterization of fluorinated poly(aryl ether)s with excellent dielectric properties

Hao Zheng,[a,b] Zejun Zheng,[b] Dirong Gong,[a] Chun Tian,*[b] You Wen,*[b] Zhen Wang[b] and Jingling Yan[b]

[a] School of Materials Science & Chemical Engineering, Ningbo University, Ningbo 315211, People's Republic of China

[b] Ningbo Institute of Materials Technology & Engineering, Chinese Academy of Science, Ningbo 315201, People's Republic of China

Corresponding authors: Chun Tian, tianchun@nimte.ac.cn; You Wen, wenyou@nimte.ac.cn

List of Contents for Supplementary Materials:

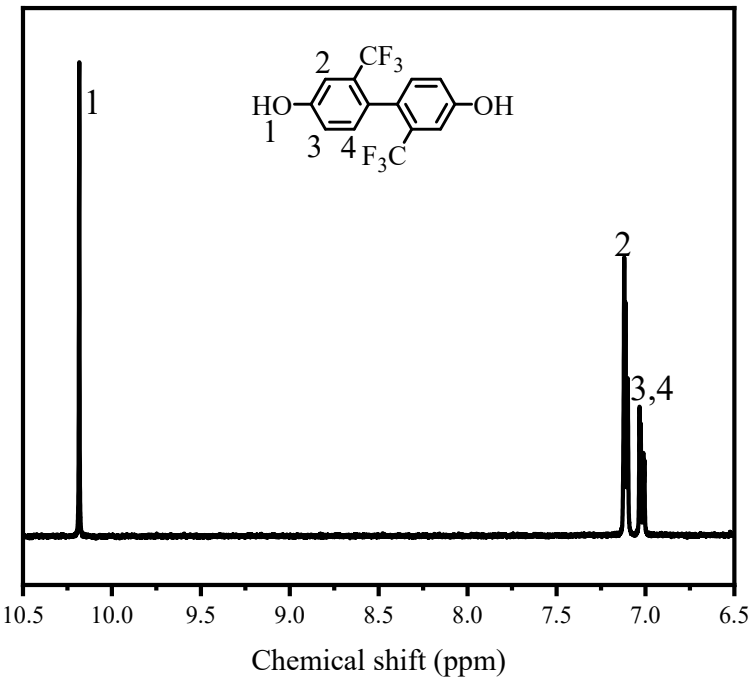


Figure S1. ^{1}H NMR spectrum of TFBP in DMSO-d_6

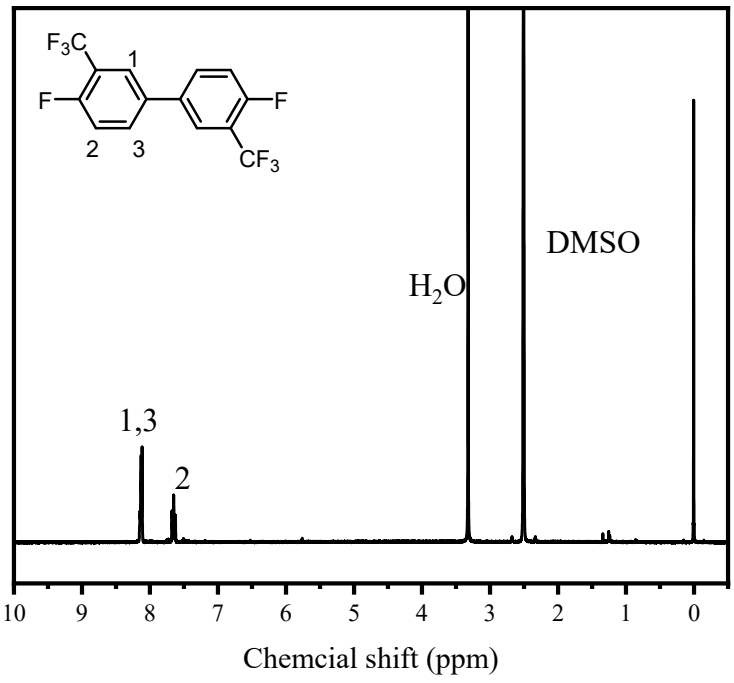


Figure S2. ^{1}H NMR spectrum of BDTF in DMSO-d_6

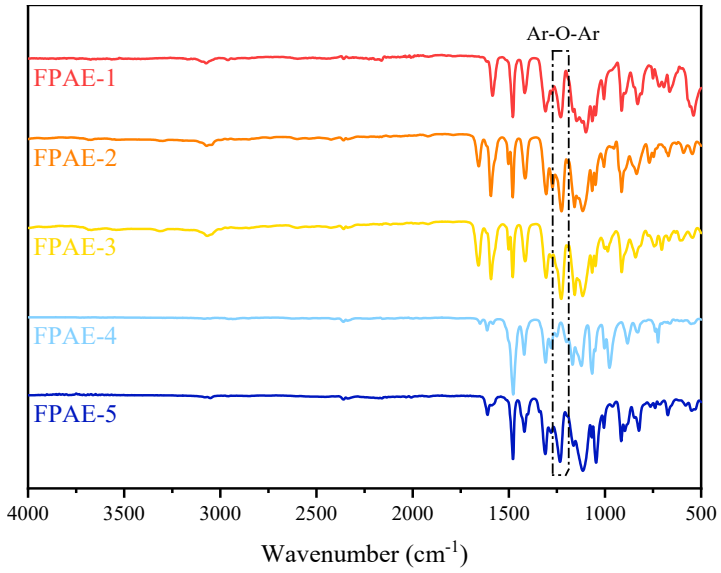


Figure S3. FT-IR spectra of FPAEs

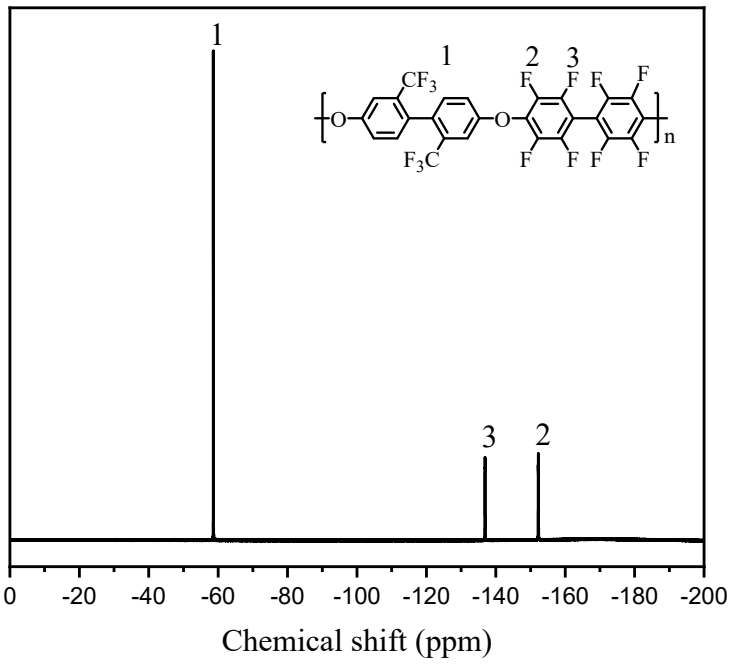


Figure S4. ^{19}F NMR spectrum of FPAE-5 in $CDCl_3$

Figure S5. ^{13}C NMR spectrum of FPAE-4 in $CDCl_3$

Figure S6. HSQC 2D NMR spectrum of FPAE-4 in in $CDCl_3$

Figure S7. HMBC 2D NMR spectrum of FPAE-4 in in $CDCl_3$

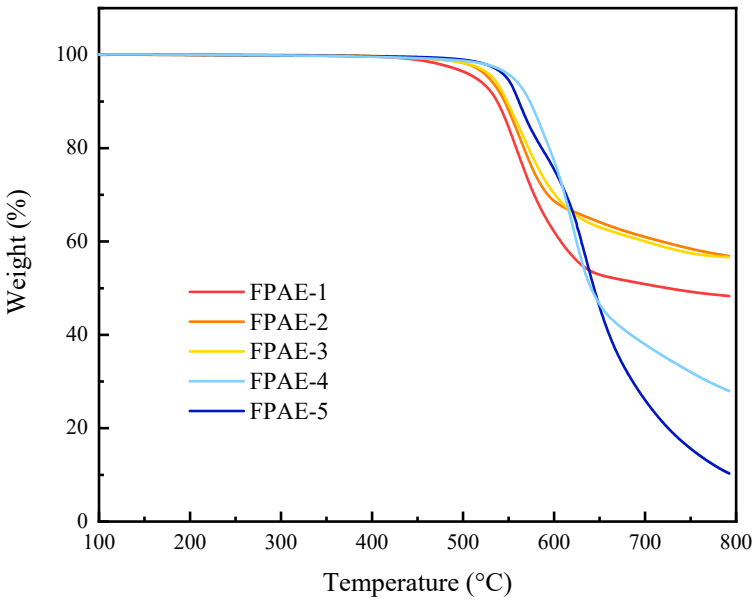


Figure S8. TGA curves of FPAEs in nitrogen

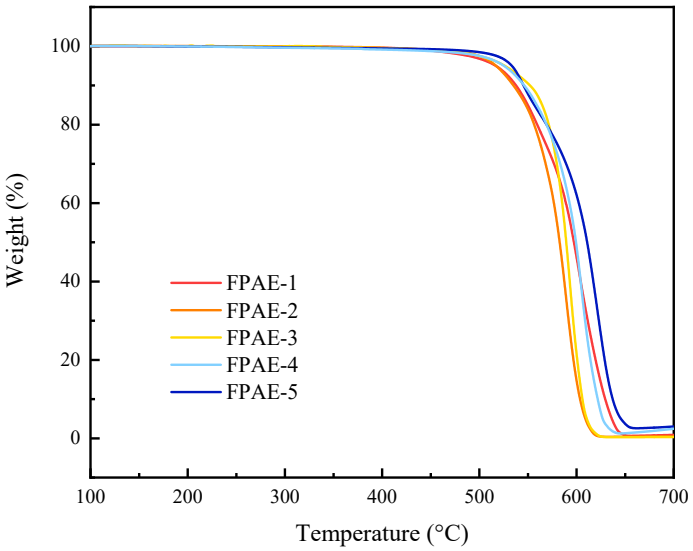


Figure S9. TGA curves of FPAEs in air

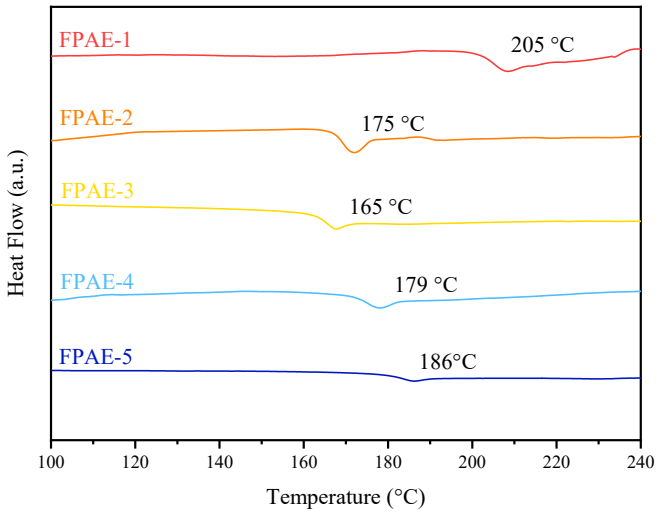


Figure S10. DSC curves of FPAEs

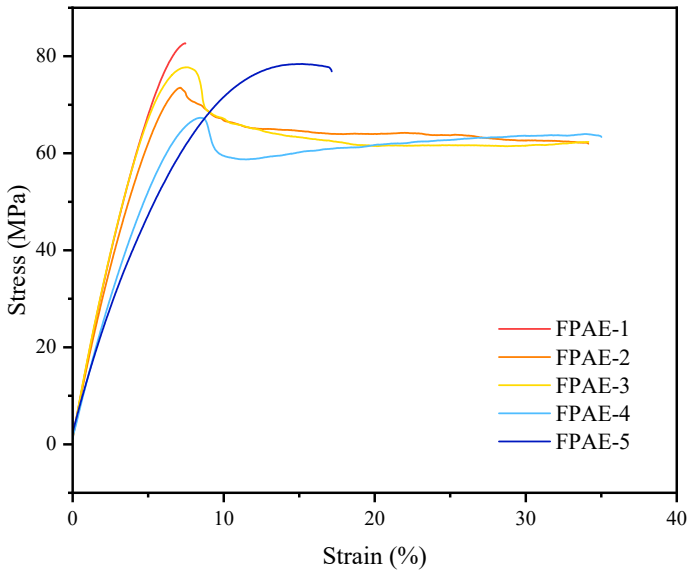


Figure S11. Representative stress-strain curves of FPAEs

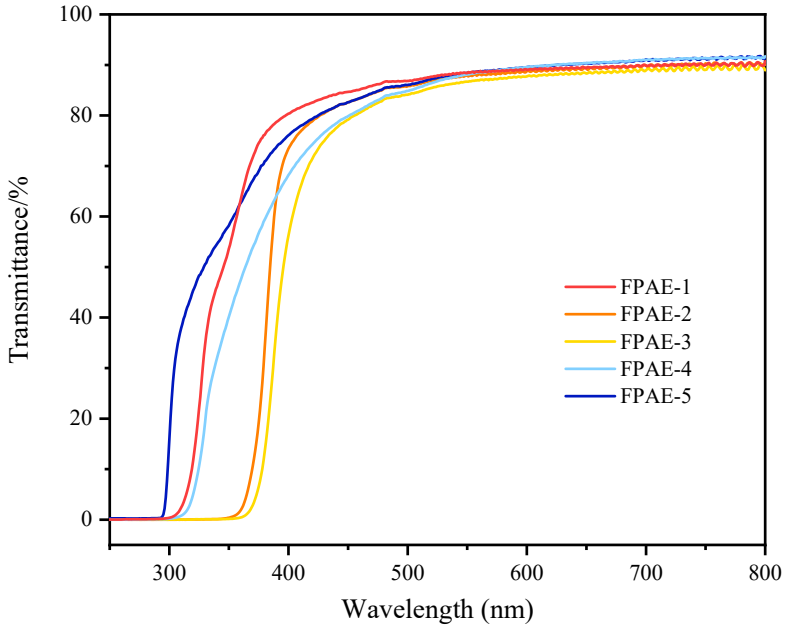


Figure S12. UV-Vis spectra of FPAEs

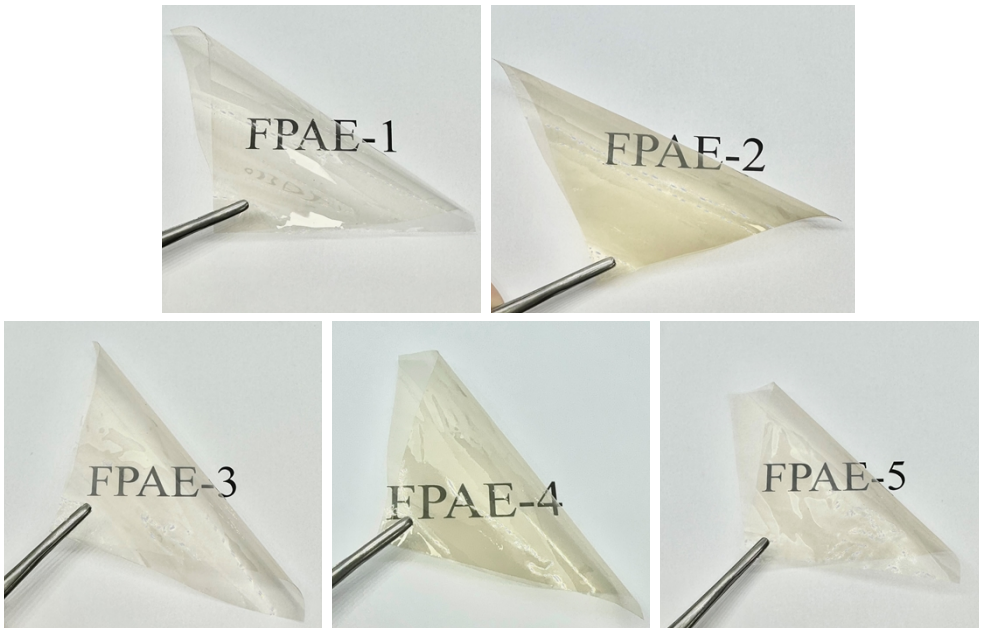


Figure S13. Images of FPAEs films

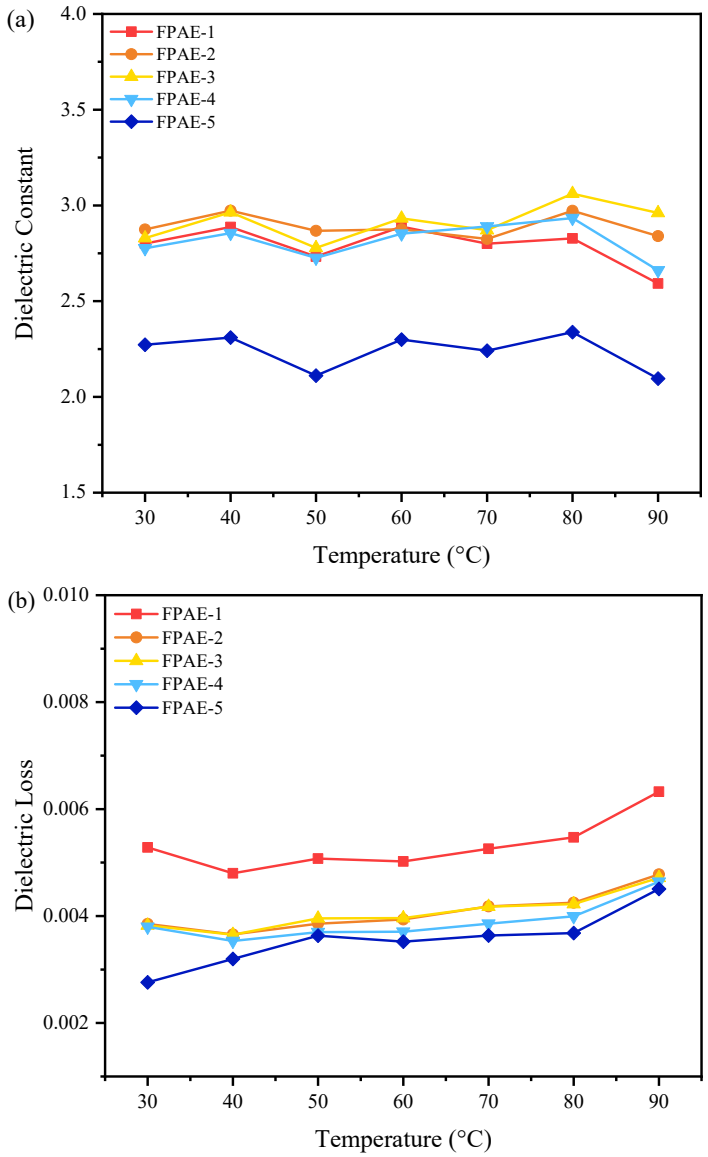


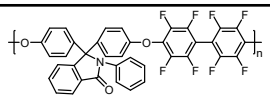
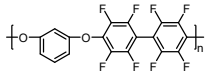
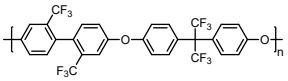
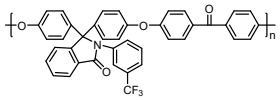
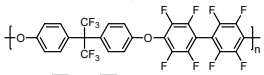
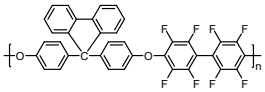
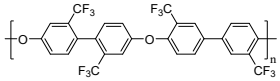
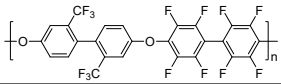
Figure S14. Dielectric properties (a) D_k and (b) D_f of the FPAEs at 11 GHz as a function of temperature

Table S1. Solubility properties of FPAEs [a]

Entry	NMP	*m*-cresol	DMAc	DMF	THF	1,4-Dioxane	DMSO	$CHCl_3$
FPAE-1	++	++	++	++	++	++	++	++
FPAE-2	++	++	++	++	++	++	-	++
FPAE-3	++	++	++	++	++	++	+-	++
FPAE-4	++	-	++	++	++	++	-	++
FPAE-5	++	-	++	++	++	++	-	++

[a] Determined at a concentration of 0.1g·dL^{-1}, ++: soluble at room temperature; +-: soluble on heating; -: insoluble on heating.

Table S2. Comparison of FPAEs in this work and other reported FPAEs

Ref.	FPAEs	%F [a]	D_k	D_f	T_g [b] (°C)	σ_t [c] (MPa)	E [d] (%)
[1]		22.1	2.66 (1 MHz)	0.0063 (1 MHz)	260		
[2]		37.6	2.31 (10 KHz)	0.0046 (10 KHz)	127		
[3]		36.7	2.81 (1 MHz)	-	181		
[4]		8.9	3.04 (10 GHz)	0.0048 (10 GHz)	213		
[5]		42.2	2.61 (100 KHz)	-	182	36.5	12
[5]		23.6	2.30 (100 KHz)	-	262		
This work		37.5	2.26 (10 GHz)	0.004 (10 GHz)	195	72.7	33.0
This work		43.2	2.07 (10 GHz)	0.002 (10 GHz)	200	73.2	35.0

[a] Fluorine content; [b] Measured by DMA; [c] Tensile strength; [d] Elongation-at-break.

Reference

(1) Wang, L.; Wang, Z.; Qu, M.; Zhou, G. Characterization of fluorinated poly(aryl ether) with low dielectric constant synthesized by nucleophilic polycondensation. *J. Polym. Res.*, 2023, **30**, 348.

(2) Tkachenko, I. M.; Belov, N. A.; Yakovlev, Y. V.; Vakuliuk, P. V.; Shekera, O. V.; Yampolskii, Y. P.; Shevchenko, V. V. Synthesis, gas transport and dielectric properties of fluorinated poly(arylene ether)s based on decafluorobiphenyl. *Mate. Chem. Phys.*, 2016, **183**, 279-287.

(3) Chung, I. S.; Kim, K. H.; Lee, Y. S.; Kim, S. Y. Poly(arylene ether)s with trifluoromethyl groups via meta-activated nitro displacement reaction. *Polymer*, 2010, **51**, 4477-4483.

(4) Liu, X.; Sun, Y.; Chen, Y.; Zhao, Z.; Wang, Z.; Zhou, G. Design and synthesis of novel poly (aryl ether ketones) containing trifluoromethyl and trifluoromethoxy groups. *Des. Monomers Polym.*, 2023, **26**, 140-149.

(5) Goodwin, A. A.; Atkinson, J. R.; Hay, J. N.; Mercer, F. W. Dielectric relaxation behaviour of fluorinated aromatic poly(ether)s and poly(ether ketone)s. *Polymer*, 1999, **40**, 1515-1524.