

Reduced coefficient of linear thermal expansion of colorless and transparent polyimide by introducing rigid-rod amide unit: synthesis and properties

Hongtao Zuo¹, Guangtao Qian¹, Haibei Li², Feng Gan³, Yuting Fang¹, Xiuting Li¹, Jie Dong¹, Xin Zhao^{1*},
Qinghua Zhang^{1*}

¹ State Key Laboratory for Modification of Chemical Fibers and Polymer Materials, College of Materials

Science and Engineering, Donghua University, Shanghai 201620, P. R. China

² School of Ocean, Shandong University, Weihai 264209, PR China. ³ School of Textile Materials and
Engineering, Wuyi University, Jiangmen, Guangdong 529020, P. R. China

Corresponding author: X. Zhao (xzhao@dhu.edu.cn), Q. Zhang (qhzhang@dhu.edu.cn)

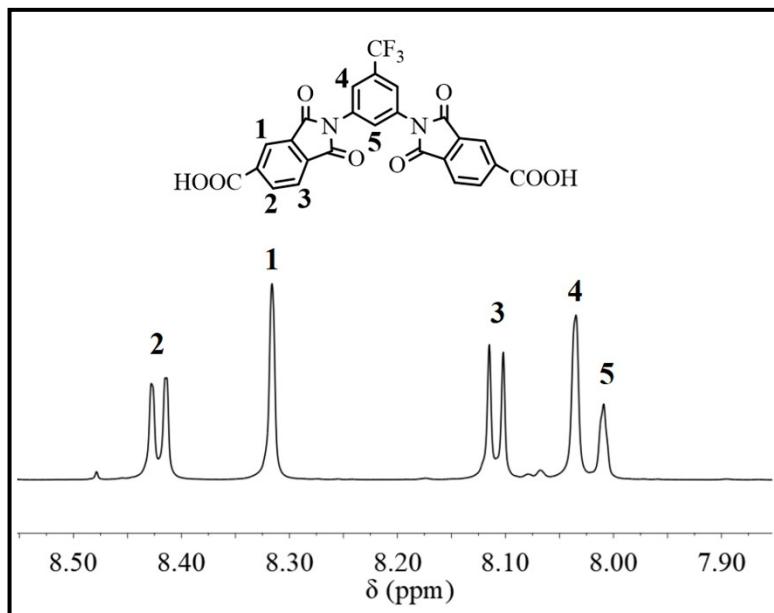


Fig. S1 ¹H-NMR spectra of the 2,2'-(5-(trifluoromethyl)-1,3-phenylene)bis(1,3-dioxoisindoline-5-carboxylic acid) (DAc-1)

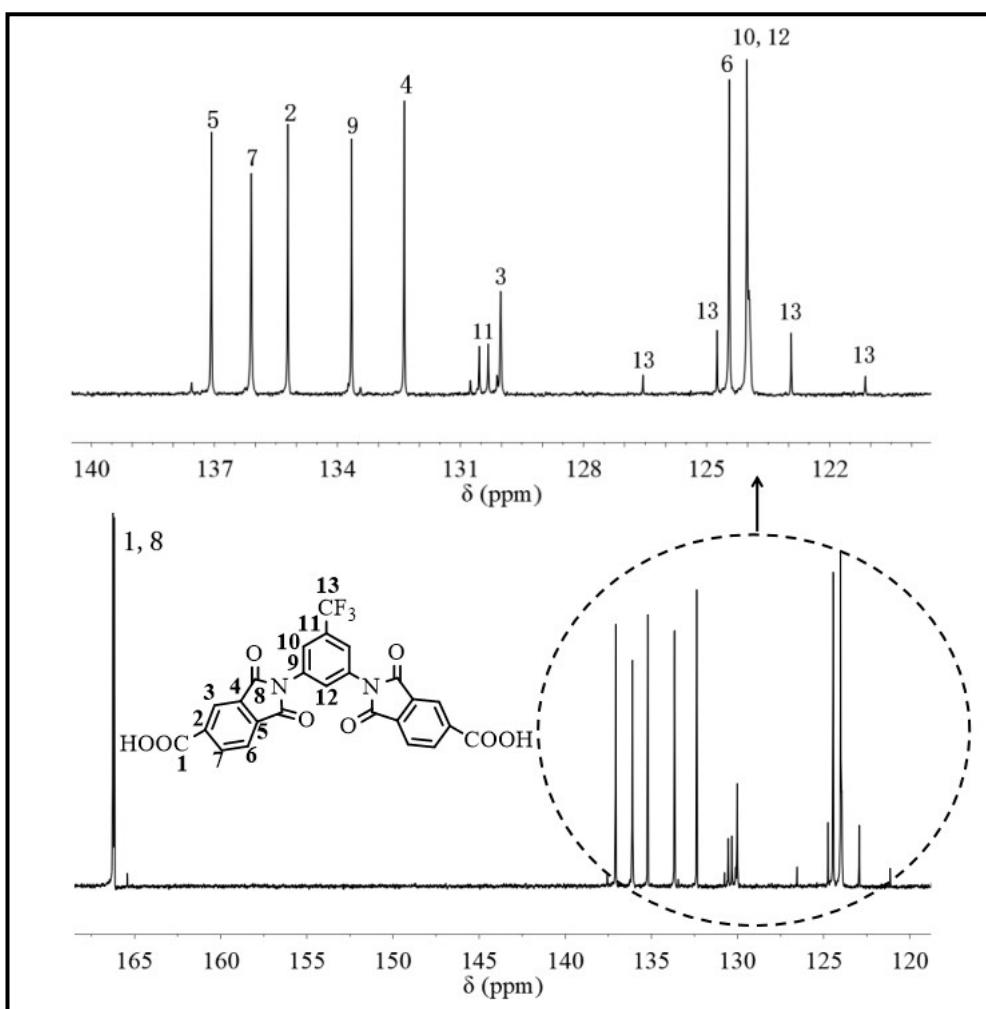


Fig. S2 ¹³C-NMR spectra of the 2,2'-(5-(trifluoromethyl)-1,3-phenylene)bis(1,3-dioxoisindoline-5-carboxylic acid) (DAc-1)

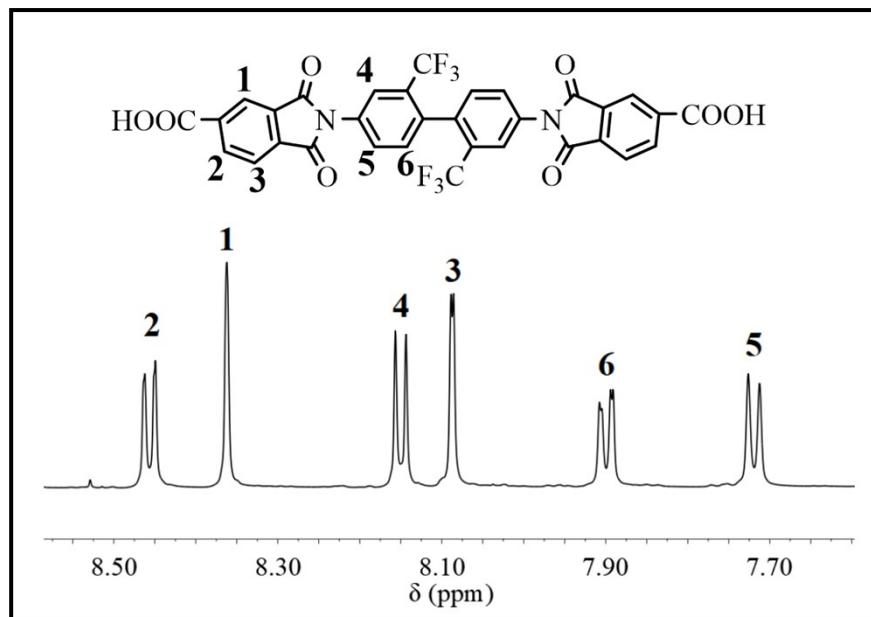


Fig. S3 ¹H-NMR spectra of the 2,2'-(2,2'-bis(trifluoromethyl)-[1,1'-biphenyl]-4,4'-diyl)bis(1,3-dioxoisindoline-5-carboxylic acid) (DAc-2)

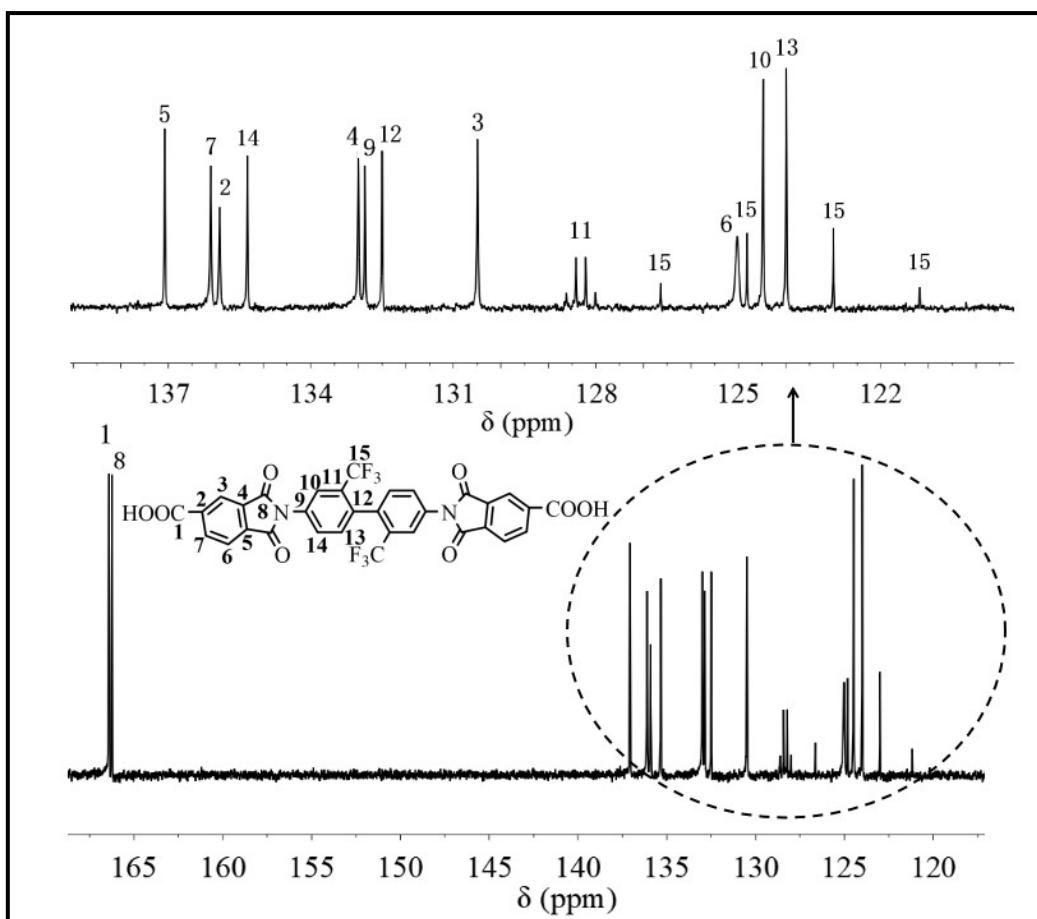


Fig. S4 ¹³C-NMR spectra of the 2,2'-(2,2'-bis(trifluoromethyl)-[1,1'-biphenyl]-4,4'-diyl)bis(1,3-dioxoisoindoline-5-carboxylic acid) (DAc-2)

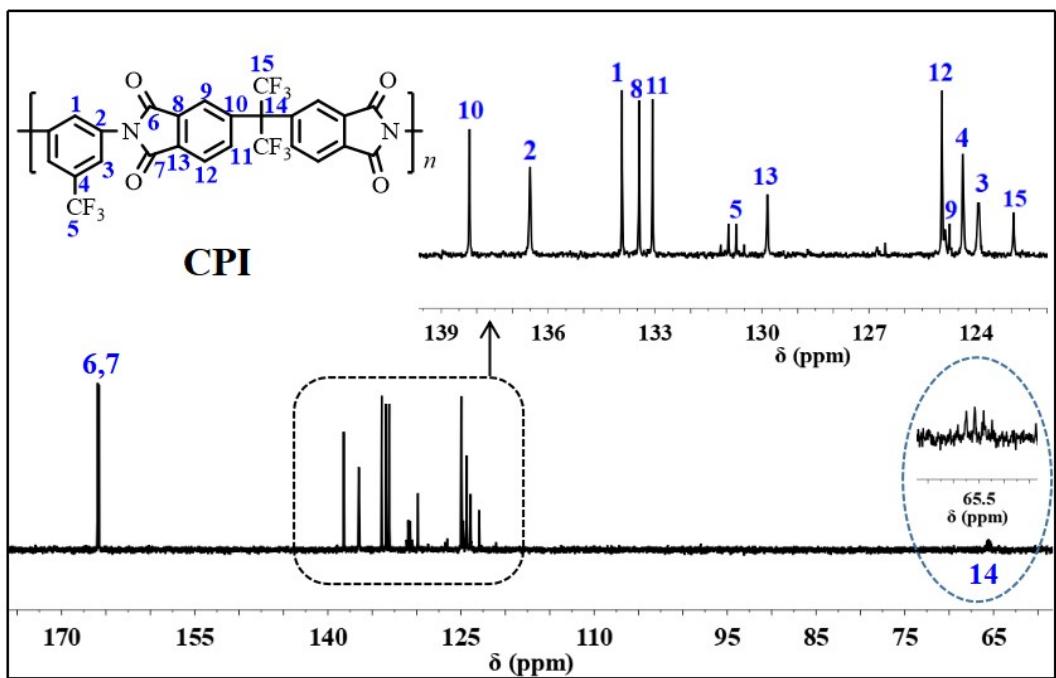


Fig. S5 ^{13}C -NMR spectra of CPI

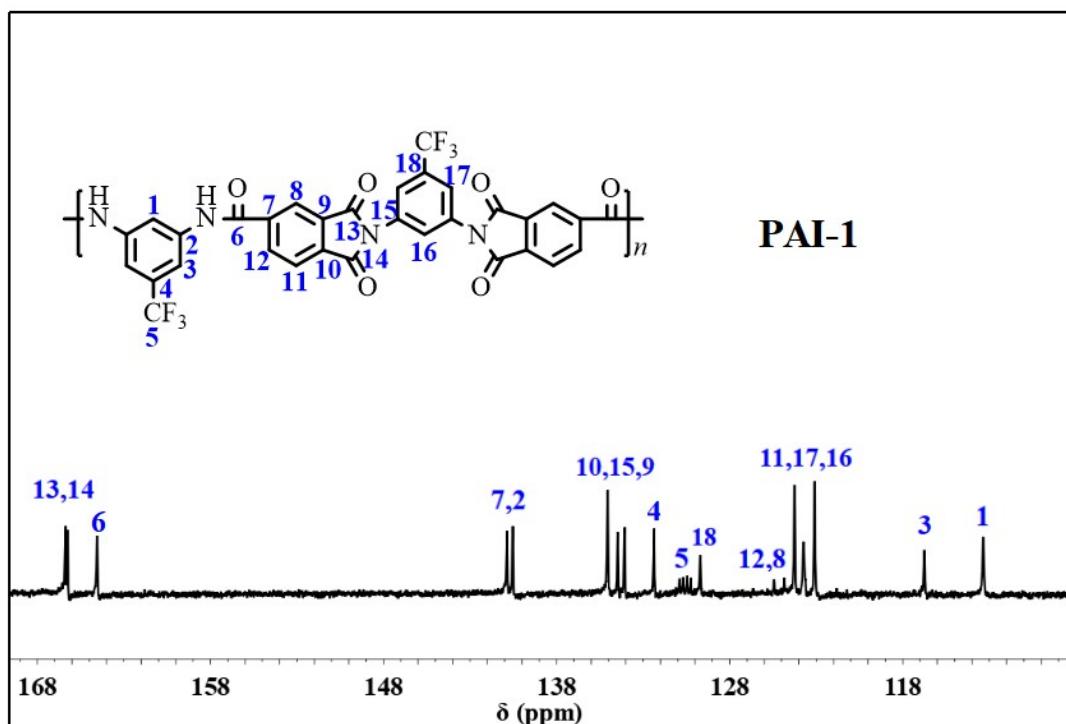


Fig. S6 ^{13}C -NMR spectra of PAI-1

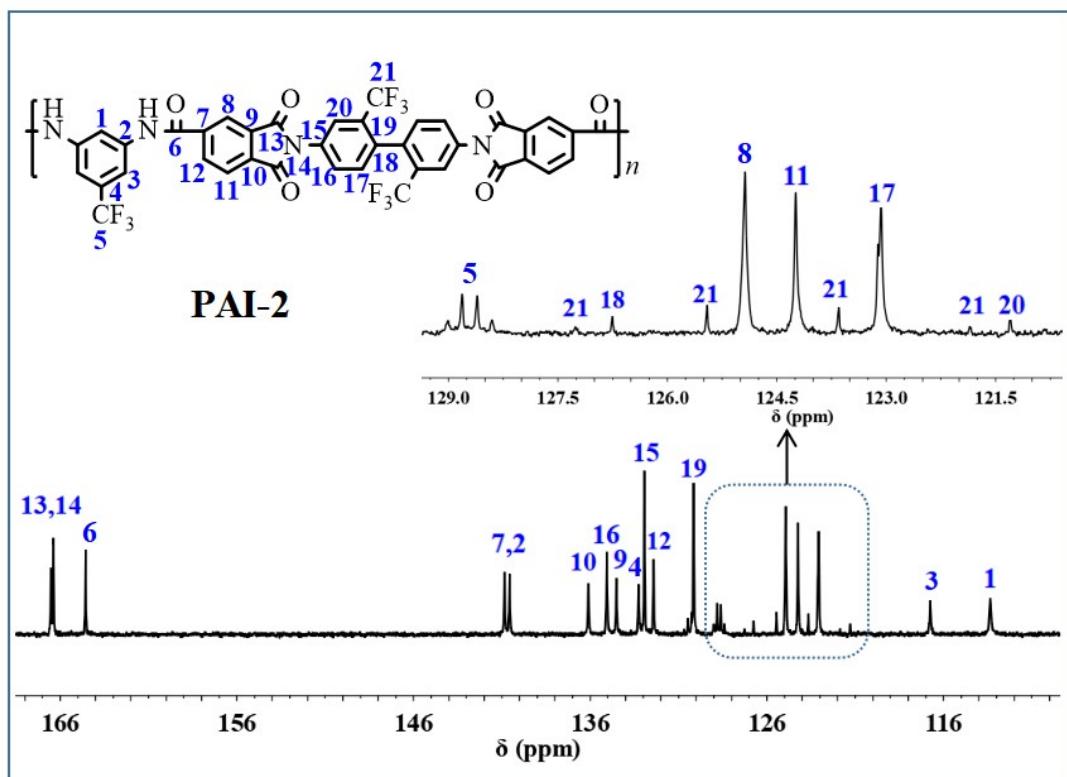


Fig. S7 ^{13}C -NMR spectra of PAI-2

Table S1 Summary of the GIWAXS peak positions

In-plane	Peak position (nm ⁻¹)	Characteristic distance (Å)	Assignment	Out-of-plane	Peak position (nm ⁻¹)	Characteristic distance (Å)	Assignment
CPI	6.61	9.50		CPI	6.66	9.43	
	9.00	6.98	ch-pack		9.00	6.98	ch-pack
	12.8	4.93			11.6	5.50	π -π stack
					12.8	4.91	
PAI-1	8.47	7.41	ch-pack	PAI-1	8.49	7.40	ch-pack
	11.1	5.64			11.5	5.48	
	13.9	4.51			12.1	5.19	π -π stack
					14.3	4.38	
PAI-2	8.58	7.32	ch-pack	PAI-2	8.35	7.52	ch-pack
	11.4	5.50			11.5	5.45	
	14.4	4.36			11.8	5.30	π -π stack
					14.3	4.40	

Table S2 Birefringence of CPI and PAIs films

Code	n_{TE}^a	n_{TM}^b	n_{AV}^c	Δn^d
CPI	1.561	1.555	1.559	0.0060
PAI-1	1.654	1.598	1.635	0.056
PAI-2	1.663	1.564	1.630	0.098

^a n_{TE} : the in-plane refractive index. ^b n_{TM} : the out-of-plane refractive index. ^c n_{av} : the average refractive index ($n_{av} = (2n_{TE} + n_{TM})/3$). ^d Δn : birefringence ($n_{TE} - n_{TM}$).

Table S3 The solubility of CPI and PAIs films

Code	Solvent ^a					
	DMAc	DMF	NMP	DMSO	m-Cresol	THF
CPI	++	++	++	+	+	+
PAI-1	++	+	++	+	+	++
PAI-2	++	++	++	++	+	++

^a Legend: (++) soluble at room temperture, (+) partially soluble at room temperture, soluble on heating 80 °C. The solubility was determined using 10 mg film in 1 ml of solvent.