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Supporting Information

Infrared Transmitting Polyimides Based on Chalcogenide Element-Blocks with Tunable High-refractive Indices and Broad Optical Windows

Ki-Ho Nam^a, Aram Lee^b, Seoung-Ki Lee^b, Kahyun Hur^c, Haksoo Han^{a,*}

^a Department of Chemical and Biomolecular Engineering, Yonsei University, 50 Yonsei-ro, Seodaemungu, Seoul 120–749, Republic of Korea

^b Institute of Advanced Composite Materials, Korea Institute of Science and Technology (KIST), 92 Chudong-ro, Bongdong-eup, Wanju-gun, Jeonbuk, 55324, Republic of Korea

^c Center for Computational Science, Korea Institute of Science and Technology, Seoul, 02792, Republic of Korea

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I) Experimental Section

A) Materials and Instrumentation

1,4-Benzenedithiol (>98%), 4,4'-thiobisbenzenethiol (>98%), 4-bromophthalic anhydride (>97%), pyromellitic dianhydride (PMDA, >99%), and bis(4-aminohenyl) sulfide (SDA, >98%) were purchased from Tokyo Chemical Industry Co., Ltd., and used as recieved. 4,4'-[p-phenylenebis(thio)]diphthalic anhydride (2SDEA)^[1] and 4,4'-[p-thiobis(phenylenesulfanyl)]diphthalic anhydride (3SDEA)^[2] were synthesized according to the protocol described in the literature. Potassium carbonate (K₂CO₃), hydrochloric acid (HCl, 35%), *N*,*N*-dimethylformamide (DMF, 99.8%), and toluene (>99%) was purchased from Duksan reagents, and used as recieved. Zirconia nanoparticles (ZrO₂ NPs, 99%) and (3aminopropyl)triethoxysilane (APTES, >98%) was purchased from Sigma-Aldrich, and used as recieved.

Nuclear magnetic resonance (NMR) spectra were obtained with an Agilent 600 MHz Premium COMPACT spectrometer at 600 MHz for ¹H in dimethyl sulfoxide- d_6 (DMSO- d_6) using tetramethylsilane (TMS) as an internal standard. Mass spectroscopy was performed using an Agilent 7890 B. Inherent viscosity measurements were performed using a Malvern Y510 viscometer at 30 °C after dissolving the PAA precursors in NMP (0.5 g/dL). Attenuated total reflection–Fourier transform-infrared (ATR-FT-IR) spectra were obtained with a FTIR-460 Plus (JASCO Co., Japan) with 32 scans per spectrum at 2 cm⁻¹ resolution. Scanning electron microscopy (SEM; JEOL-7800F, JEOL Ltd., Japan) was performed at an acceleration voltage of 10.0 kV. Ultraviolet-visible (UV-vis) spectra were recorded on a JASCO V-670 spectrometer in transmittance mode over wavelength range of 200–3000 nm, resolution of 1 nm, and scanning rate of 400 nm/min. The in-plane (n_{TE}) and out-of-plane (n_{TM}) refractive indices were measured using a prism coupler (Metricon PC-2000); the wavelengths were 404, 532, 632.8, 829, and 1554 nm from a He-Ne laser light source. The birefringence (Δn) between n_{TE} and n_{TM} was calculated and the average refractive index (n_{AV}) was calculated using the following equation.

$n_{\rm AV} = [(2n_{\rm TE}^2 + n_{\rm TM}^2)/3]^{1/2}$

Dynamic mechanical thermal analysis (DMA) was performed using a TA Instruments Q800 at a scanning rate of 3 °C/min with a load frequency of 1 Hz in air. The specimens were prepared in film form (30 mm length, 10 mm wide, and *ca*. 30 μ m thickness). Thermogravimetric analysis (TGA) was performed under a nitrogen gas flow using a TA Instruments Q50 at a heating rate of 20 °C/min. SWIR and MWIR images were taken using a thermos-mini(C-10614-02) thermal emission microscope (Hamamatsu Photonics, Japan) with a 3–5 μ m lens. LWIR images were taken using a Testo, 875-1i camera with a 7–12 μ m lens.

B) Experimental Procedures

1. Synthesis of 4,4'-[p-phenylenebis(thio)]diphthalic anhydride (2SDEA)

In a 250 mL round flask fitted with a magnetic stirrer, condenser, thermometer, and a nitrogen inlet tube, a mixture of 2 g (14.1 mmol) of 1,4-benzenedithiol, 7 g (30.8 mmol) of 4-bromophthalic anhydride, 4.3 g (30.8 mmol) of anhydrous K₂CO₃, and 120 mL of freshly distilled DMF was heated to 130 °C for 12 h. after cooling, the resulting white solid was isolated by filteration and dried in *vacuo* at 130 °C for 12 h. The obtained solid was boiled in a solution (240 mL) of deionized water-HCl conc. (1:1 vol/vol) for 3 h. Then, the mixture was cooled down to room temperature, filtered, and washed with deionized water several times to produce the white solid (the tetra-acid). The solid was first heated in *vacuo* at 120 °C to remove the water. Then, it was heated in *vacuo* at 185 °C for 3 h to dehydrate and afford the 2SDEA tetracarboxylic dianhydride as a yellow crystal (**Figure S1a**). ¹H NMR (600 MHz, DMSO-*d*₆, ppm): δ =7.67–7.69 (d, 2H), δ =7.72–7.76 (m, 4H), δ =7.83–7.88 (d, 2H), δ =7.98–8.02 (d, 2H), and δ =8.04–8.06 (m, 2H). MS (API+): calcd for [C₂₈H₁₄O₈S₃+H]⁺ 434.44; found: 435.04.

2. Synthesis of 4,4'-[p-thiobis(phenylenesulfanyl)]diphthalic anhydride (3SDEA)

4 g (16 mmol) of 4,4'-thiobisbenzenethiol, 8 g (35.2 mmol) of 4-bromophthalic anhydride (35.2 mmol, 8 g), 4.9 g (35.2 mmol) of anhydrous K₂CO₃, and 120 mL of freshly distilled DMF was added to a 250 mL round flask equipped with a magnetic stirrer, condenser, thermometer, and a nitrogen inlet tube and the solution was stirred at 130 °C for 12 h. After cooling, the resulting reaction mixture was filtered and then dried in *vacuo* at 120 °C for 12 h. The crude products were then boiled in a solution (240 mL) of deionized water-HCl conc. (1:1 vol/vol) for 3 h and the solid was collected by filteration and washed with deionized water. The tetra-acid was then dried in *vacuo* at 120 °C for 12 h. Finally yellow crystal was collected after dried in *vacuo* at 185 °C for 3 h (**Figure S1b**). ¹H NMR (600 MHz, DMSO-*d*₆, ppm): δ =7.35–7.51 (d, 4H), δ =7.55–7.61 (d, 4H), δ =7.64 (s, 2H), δ =7.68–7.71 (d, 2H), and δ =7.95–7.98 (d, 2H). MS (API+): calcd for [C₂₈H₁₅O₆S₃+H]⁺ 542.60; found: 543.18.

3. Polyaddition, imidization, and film preparation

The poly(amic acid)s (PAAs) were synthesized by the equimolar polyaddition of tetracarboxylic dianhydride with bis(4-aminohenyl) sulfide (SDA) in anhydrous NMP (30% of the total solid concentration) *via* a two-step method (**Figure S2**). 2 mmol of synthesized SDA and NMP were placed into a 50 mL flask equipped with a magnetic stirrer and nitrogen inlet tube. After the SDA was completely dissolved, 2 mmol of tetracarboxylic dianhydride was slowly added into a flask and the mixture was stirred at room temperature for 24 h to produce a viscous PAA solution. Thereafter, the PAA solution was spin-casted onto a fused silica substrate, followed by a prebaking program (90 °C/2 h) and cyclodehydration curing procedure (110, 130, 160, 190, 220, and 250 °C/30 min) under *vacuo*.

The PI film was stripped from the substrate by immersing the PI coated substrate in hot deionized water. The IR spectra of the PI films exhibited characteristic imide absorption peaks at around 1780 cm⁻¹ (asym. C=O str.), 1721 cm⁻¹ (sym. C=O str.), 1490 cm⁻¹ (C=C str.), 1370 cm⁻¹ (C_{arom} -N str.), 1082 cm⁻¹ (Ar–S–Ar), 1083–717 cm⁻¹ (Ar–H str.), and 748 cm⁻¹ (imide ring deformation), respectively **Figure 2b**. The thickness of specimen for yellow index (YI) and UV-vis spectra measurements was adjusted to be 10 µm.

4. Preparation of amine-functionalized ZrO₂ NPs (F@ZrO₂ NPs)

2 g of ZrO_2 NPs were suspended in 20 mL of Toluene by 30 min sonication. Then, 2 g of trimethylamine was added to the mixture under nitrogen atmosphere and stirring, followed by addition of 2 g of APTES. The resulting mixture was stirred at 70 °C for 30 min and then was refluxed at 110 °C for 24 h to accomplish the hydrolysis and condensation of APTES on ZrO_2 surface. F@ZrO₂ NPs were next recovered by centrifugation and latterly washed with ethanol followed by dried in *vacuo* at 50 °C for 12 h.

5. General synthetic procedure for the PI/F@ZrO₂ hybrids

A new class of PI hybrids with chemical bonds between the PI and F@ZrO₂ has been synthesized using an *in situ* polymerization (**Figure S3**). F@ZrO₂ was dissolved in NMP using homogenizer at 800 rpm for 10 min and further ultra-sonicated for 30 min. SDA was added in the suspension, followed by the gradual addition of 3SDEA. The resulting mixture was stirred for a prolonged period of 24 h in nitrogen atmosphere to afford a clear and viscous solution. The PAA/F@ZrO₂ solution was spin-casted onto a fused silica substrate and thermally imidized by sequential temperature programming (110, 130, 160, 190, 220, and 250 °C/30 min) in *vacuo*.



Supplementary Figure S1. Synthesis of tetracarboxylic dianhydrides a) 2SDEA and b) 3SDEA.



Supplementary Figure S2. Synthesis of PIs.



Supplementary Figure S3. Synthesis of PI/F@ZrO₂ hybrids.

II) Results and Discussion Section

¹H nuclear magnetic resonance spectroscopy (NMR) of monomers



Supplementary Figure S4. ¹H NMR spectra of a) 2SDEA and b) 3SEDA.

X-ray photoelectron spectroscopy (XPS) of F@ZrO₂

The intensity loss of transmitted light due to Rayleigh scattering should be avoided to develop transparent high-*n* polymer hybrids.^[3] Thus, the size of the inorganic particles with high-*n* values should be reduced to less than 40 nm (one-tenth of the wavelength of visible light). In addition, the processing in the fabrication of hybrids is important. For example, the direct mixing of inorganic nanoparticles with the polymer matrix induces the agglomeration of nanoparticles. To prevent such agglomeration, the surface of inorganic nanoparticles is generally modified.

Figure S6 shows deconvoluted X-ray photoelectron spectroscopy (XPS) spectra to clarify the surface chemical composition of F@ZrO₂. The observed, well resolved spin-orbit components seen at approximately 181.1 and 183.5 eV respectively correspond to Zr $3d_{5/2}$ and Zr $3d_{3/2}$ electrons, and are owing to the presence of Zr in its oxidation state Zr^{4+} from ZrO_2 .^[4] In O1s XPS curve fitting, the peak at the higher binding energy at 530.4 eV was due to the contributions of the Si–O–Zr bonds, while the other peak at the lower binding energy at 529.1 eV was attributed to the Zr–OH groups.^[5] Furthermore, the peak observed at a higher binding energy position of 531.9 eV is assigned to other chemical states of oxygen (C–O or C=O). In spectrum (c), the typical binding energy peak observed at 398.7 eV is due to the core-level electron of N1s.^[6]



Supplementary Figure S6. XPS depth profile spectra of F@ZrO₂: a) Zr 3d, b) O1s, and c) N1s. The spectra are normalized to aid visualization.

Morphological structure of PI hybrid films

To investigate the comprehensive dispersion state of $F@ZrO_2$ in the PI matrix, scanning electron microscopy (SEM) and 3D X-ray computer tomographic (CT) analyses were conducted. The fracture morphologies of various PI hybrids are shown in **Figure S7**. Additionally, the elemental mapping data supported the composition of the PI hybrids. Compared with the continuous phase of pristine PI, the cross-sectional morphology of PI/F@ZrO₂ hybrid films showed uniformity and good compatibility between the PI matrix and F@ZrO₂ owing to favorable interfacial interactions and covalent bonding. Furthermore, the 3D X-ray CT tomography image of the PI hybrids shown in **Figure 2** illustrates that the F@ZrO₂ (green spots) were homogeneously dispersed within the PI matrix. Because the detection resolution of the sample scan was 150 nm, sizes smaller than the resolution limit may not appear in the 3D X-ray CT image.



Supplementary Figure S7. SEM fracture surface images and EDX spectrum of PI hybrids possessing a) 0 wt%, b) 0.5 wt%, c) 1 wt%, and d) 3 wt% of F@ZrO₂.

Analysis of refractive indices of PI hybrid films as a function of F@ZrO₂ loading

Supplementary Table S1. Prism coupling measured refractive indices for parallel (TE), perpendicular (TM) polarizations, and calculated average refractive indices and Abbe's numbers at varying wavelengths of the PI films

Commission de		Wavelength (nm)							
Sample code	Mode	404	532	632.8	829	1554			
	TE	1.9551	1.7393	1.6866	1.6435	1.6259			
PMDA-SDA	TM	1.9276	1.7126	1.6729	1.6264	1.6098			
	$n_{\rm AV}$ ^a	1.9459 1.7304 1.682 1.6		1.6378	1.6205				
	V _D ^b			6.43					
	TE	1.9715	1.7577	1.7072	1.6657	1.6473			
2SDE 4-SD 4	ТМ	1.9677	1.7400	1.6754	1.6598	1.6414			
25DEA-5DA	$n_{\rm AV}$ ^a	1.9702	1.7518	1.6966	1.6637	1.6453			
	V_{D} b	7.96							
	TE	1.9880	1.7840	1.7305	1.6917	1.6716			
	ТМ	1.9772	1.7703	1.7146	1.6903	1.6703			
35DEA-5DA	n _{AV} ^a	1.9844	1.7794	1.7252	1.6912	1.6711			
	$V_{\mathrm{D}}^{\mathrm{b}}$	6.28							
	TE	2.0318	1.7861	1.7315	1.7036	1.6849			
F@ 7r O-0 5%	ТМ	1.9852	1.7791	1.7279	1.6938	1.6755			
$F(\underline{W}\Sigma IO_2 0.3 76$	$n_{ m AV}$ ^a	2.0163	1.7837	1.7303	1.7003	1.6817			
	V_{D} b	TE 1.9880 TM 1.9772 n_{AV}^{a} 1.9844 V_{D}^{b} V_{D}^{b} TE 2.0318 TM 1.9852 n_{AV}^{a} 2.0163 V_{D}^{b} V_{D}^{b} TE 2.0342 TM 2.0030		6.49					
F@ZrO ₂ 1%	TE	2.0342	1.7941	1.7320	1.7063	1.6887			
	ТМ	2.0030	1.7816	1.7301	1.6969	1.6778			
	$n_{\rm AV}$ ^a	2.0238	1.7899	1.7313	1.7031	1.685			
	V _D ^b	7.39							
F@7r0 20/	TE	2.1213	1.7957	1.7396	1.7120	1.6926			
1 (102 570	ТМ	2.0231	1.7873	1.7349	1.7080	1.6877			

n _{AV} ^a	2.0891	1.7929	1.738	1.7106	1.6909
V _D b			7.71		

^aAverage refractive index measured at each wavelength. ^bAbbe's number is given by $V_{\rm D} = n_{589.3} - 1/n_{486.1} - n_{656.3}$.

Analysis of color and optical transparency of PI hybrid films as a function of F@ZrO₂ loading

Supplementary Table S2. Coordinates of color and transmittance of the PI films

Samula aada	Color coordinate ^a			Luminance	Yellow	Whiteness	$\lambda_0^{ m f}$	T ₅₀₀ g	T ₂₇₅₀ g
Sample code	$L^{*b} = a^{*c} = b^{*d} (cd/m^2) = index^{e}$	index ^e	index	(nm)	(%)	(%)			
PMDA-SDA	80.65	6.70	54.90	65.05	128	-187.96	478	10.7	41.9
2SDEA-SDA	94.68	-14.85	28.50	89.64	42.91	-64.53	425	90.2	81.9
3SDEA-SDA	96.29	-9.15	18.93	92.71	28.67	-11.43	403.5	90.2	91.7
F@ZrO ₂ 0.5%	91.31	-15.85	33.09	83.38	52.68	-89.26	429.5	80.9	83.9
F@ZrO ₂ 1%	85.30	-12.65	30.83	72.77	54.33	-77.53	397.5	71.5	82.6
F@ZrO ₂ 3%	78.68	-9.67	26.96	61.90	52.79	-59.32	418.5	56.8	85.2

^aThe color parameters were calculated according to a CIE LAB equation, using papers as a standard. ^b*L** is lightness; 100 means white, while 0 implies black. ^cA positive *a** means red color, while a negative *a** indicated green color. ^dA positive *b** means yellow color, while a negative *b** implies blue color. ^eYI values were calculated in conformity with yellowness index of samples and computing the colors of objects by using the CIE system which were imputed to the computer program into the colorimeter. ^f λ_0 defined as the point at which the transmittance becomes less than 1%. ^gOptical transmittance at 500 and 2750 nm, respectively.



Supplementary Figure S8. UV-Visible-NIR transmission spectra for PI hybrids and commerical polymer films.



Supplementary Figure S9. Digital image of USAF glass slide resolution target (chrome pattern on clear background) utilized in the MWIR imaging experiments.



Supplementary Figure S10. a) Thermogram of USAF glass slide resolution target acquired with a IR camera through b) 3SDEA–SDA hybrid film (0.5 wt% F@ZrO₂), c) PMMA film, and d) Kapton[®] film. The sample was placed diagonal orientation.



Supplementary Figure S11. a) Digital image of chrominum photomask utilized in the MWIR imaging experiments. Thermogram of photomask acquired with a IR camera through b) 3SDEA–SDA hybrid film (0.5 wt% F@ZrO₂) and c) glass slide. The sample was placed on the right.

Analysis of thermal properties of PI hybrid films as a function of F@ZrO₂ loading

Sample code	T _g (°C)	T _{5%} (°C) ^a	Char yield (%) ^b
CPMDA-SDA	370.5	549.3	63.7
2SDEA-SDA	227.6	516.9	62.9
3SDEA-SDA	200.2	508.4	56.8
F@ZrO ₂ 0.5%	210.6	502.7	58.9
F@ZrO ₂ 1%	212.3	496.1	60.2
F@ZrO ₂ 3%	211.6	480.2	64.3

Supplementary Table S3. Thermal and thermooxidative behaviors of the PI films

^aDecomposition temperature at 5% weight loss. ^bWeight percentage of char residues at 800 °C.

References

[1] X. Huang, W. Huang, L. Fu, and D. Yan, J. Polym. Res., 2012, 19, 9790.

[2] J.-G. Liu, Y. Nakamura, Y. Shibasaki, S. Ando, and M. Ueda, J. Polym. Sci. Polym. Chem., 2007, 45, 5606–5617.

[3] H. I. Elim, B. Cai, Y. Kurata, O. Sugihara, T. Kaino, T. Adschiri, A.-L. Chu, and N. Kambe, *J. Phys. Chem. B*, 2009, **113**, 10143–10148.

[4] C. Morant, J. M. Sanz, L. Galan, L. Soriano, and F. Rueda, Surface Sci., 1989, 218, 331-345.

[5] A. P. Dementiev, O. P. Ivanova, L. A. Vasilyev, A. V. Naumkin, D. M. Nemirovsky, and D. Y. Shalaev, *J. Vac. Sci. Technol. A*, 1994, **12**, 423–427.

[6] M. A. Ali, S. Srivastava, P. R. Solanki, V. Reddy, V. V. Agrawal, C. Kim, R. John, and B. D. Malhotra, *Sci. Rep.*, 2013, **3**, 1.