

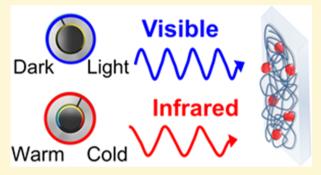
Polymer-Nanoparticle Electrochromic Materials that Selectively Modulate Visible and Near-Infrared Light

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Supporting Information

ABSTRACT: In this manuscript, we describe a class of hybrid electrochromic materials utilizing polythiophenes and tin-doped indium oxide (ITO) nanoparticles that independently modulate visible and near-infrared (NIR) light. By altering the voltage applied across electrodes modified with these composite materials, the electrodes can be repeatedly switched between three distinct modes of operation. These "bright and warm", "bright and cool", and "dark and cool" modes vary in their visible and NIR transmission properties and are targeted toward the development of smart windows that can control both solar lighting and heating fluxes. Electrodes containing the composite films, which are fabricated by electropolymerizing polythiophenes on transparent



electrodes coated with ITO nanoparticles, possess fast switching times (<90 s), moderate durability, and contrast ratios similar to those of the individual composite components. The maximum contrast ratios of the composite systems are 47% at 700 nm and 39% at 1250 nm. After 200 switching cycles, these contrast ratios degrade by 15-20%. The composite materials developed here represent a new direction of research aimed at modulating light and heat flux in smart windows.

■ INTRODUCTION

The implementation of electrochromic materials in the form of smart windows that dynamically modulate solar light and heat flux could significantly decrease the energy consumption of buildings. 1,2 Electrochromic materials, which change their transmission properties upon the application of a voltage, traditionally modulate visible light.³ The two most commonly studied classes of electrochromics are transition metal oxides (TMOs), exemplified by WO₃,^{4,5} and organic polymers, which include polyanilines and polythiophenes. 6-10

Recently, pioneering work by the Milliron group has focused on developing electrochromic materials that modulate nearinfrared (NIR) light. 11-14 The aim is to design these materials so they can be implemented in smart windows that dynamically control solar heat flux into buildings, thereby decreasing heating and cooling costs. ¹⁵ Milliron et al. have explored the use of a wide range of metal oxide nanomaterials, which include tindoped indium oxide (ITO), aluminum-doped zinc oxide, and WO_{3-x} nanoparticles, as materials that are electrochromic toward NIR light. Coupling these materials with traditional TMOs used for visible light modulation has allowed for the construction of dual electrochromic materials that can independently modulate visible and NIR light. 16 Smart windows utilizing these composite materials could then simultaneously control building lighting and heating.

Polymer-based electrochromic materials targeting visible light offer several potential advantages over TMOs.3 instance, comprehensive work by Reynolds et al. and others has resulted in the synthesis of polymer materials with good

absorption properties over a wide range of colors. 18-21 Such color tuneability is typically more difficult to achieve with inorganic materials. In general, polymer electrochromics also possess faster switching speeds and higher coloration efficiencies than TMOs.3

In this work, we construct proof-of-concept electrochromic systems that combine polythiophenes to modulate visible light with ITO nanoparticles that modulate NIR light. These polymer-nanoparticle hybrid materials can be operated in three distinct voltage regimes, each of which uniquely modulates visible and NIR light. We compare the performance of these composite materials utilizing two polythiophene isomers: poly(3-methylthiophene) (PMeT) and poly(3,3'dimethyl-2,2'-bithiophenyl) (PMe₂T₂).

■ EXPERIMENTAL SECTION

Film Preparation. All chemicals were received from commercial sources and used without further purification unless otherwise stated. ITO nanoparticles were synthesized following a procedure based on that by Milliron et al. 11 Electrodes consisting of ITO on glass (10 $\Omega/$ sq, 2 cm \times 2 cm) were cleaned by successively sonicating in deionized H₂O with 5% Extran solution for 15 min, acetone for 15 min, and isopropanol for 15 min. After the electrodes were dried under a stream of N₂, the electrodes were subjected to a UV-ozone treatment for 15 min. For films containing ITO nanoparticles, a dispersion of the assynthesized nanoparticles in 1:1 octane/hexane was deposited via spin-

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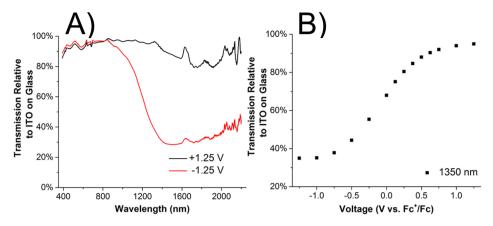


Figure 1. (A) Transmission spectra of an ITO nanoparticle film on an ITO-coated glass electrode polarized at +1.25 V (black) and -1.25 V (red) versus Fc^+/Fc and (B) the percent transmission at 1350 nm as a function of voltage inside a spectroelectrochemical cell containing 1 M LiClO₄ in PC.

casting. After 40 μ L of this dispersion was deposited on the cleaned ITO on glass surfaces, the electrodes were spun at 1000 rpm for 20 s and at 4000 rpm for an additional 20 s. The ligands of the ITO nanoparticles were then exchanged by soaking them in a 1 M solution of formic acid in acetonitrile for 45 min. The electrodes were subsequently rinsed with acetonitrile and dried under a stream of N₂. Finally, the surfaces were annealed at 300 °C in a N₂-filled glovebox (<1 ppm of O₂ and <1 ppm of H₂O) for 30 min. Additional cycles of spin-casting, ligand-exchanging, and annealing were performed to increase the film thickness as necessary.

Electropolymerization Procedures. All electrochemical studies were carried out using a CH Instruments 600 D Electrochemical Workstation (Austin, TX) or a SP-150 Biologic potentiostat. Electropolymerization of polythiophenes was performed using cleaned ITO on glass electrodes or electrodes modified with ITO nanoparticles as the working electrode. Separate Ag wires were used as the counter and reference electrodes. For each experiment, the ferrocenium ion/ ferrocene (Fc+/Fc) redox couple was measured against the Ag quasireference electrode in the same solvent-electrolyte system. All voltage values presented are reported against Fc⁺/Fc. The electropolymerization of PMeT was performed using a solution of 3-methylthiophene (200 mM) and LiClO₄ (100 mM) in propylene carbonate (PC). The working electrode was held at +1.75 V until 20 mC/cm² of charge was passed. The electropolymerization of PMe₂T₂ was performed using a solution of 3,3'-dimethyl-2,2'-bithiophenyl (10 mM) and LiClO₄ (100 mM) in acetonitrile. The working electrode was swept from +0.4 V to +1.6 V and back to +0.4 V three times (unless otherwise specified) at a scan rate of 50 mV/s. After electropolymerization, all electrodes were rinsed with acetonitrile and dried under a stream of N2 before spectroelectrochemical measurements were performed. The thicknesses of films were assessed using a Dektak profilometer and averaged over five positions on each sample (Figure S1). Scanning electron microscopy (SEM) images were obtained using a FEI XL30 Sirion microscope operated at an accelerating voltage of 5 kV.

Spectroelectrochemical Measurements. Spectroelectrochemistry was performed in a glass cuvette with a path length of \sim 2 mm containing a solution of 1 M LiClO $_4$ in PC. Pt and Ag wires were used as the counter and reference electrodes, respectively. Transmission spectra were recorded using a Jasco Model V670 UV–vis-NIR Spectrometer. All transmission spectra are reported after 5 min at the applied potential unless otherwise stated and after background subtracting the transmission spectrum of a bare ITO on glass electrode.

RESULTS AND DISCUSSION

Individual Components of the Hybrid Electrochromic System. To construct a composite electrochromic material that independently modulates visible and NIR light, we first individually optimized the performance of each component of

the polymer—nanoparticle system. To modulate NIR light, we modified ITO-coated glass electrodes with films of ITO nanoparticles following procedures developed by Milliron and co-workers. In brief, ITO nanoparticles ~ 5 nm in diameter doped with $\sim 13\%$ Sn were synthesized with oleylamine capping ligands, spin-casted onto ITO-coated glass electrodes, and treated with formic acid and annealed to remove the ligands. As previously shown by Milliron et al., If films of these ITO nanoparticles effectively modulate light with wavelengths greater than ~ 1300 nm through plasmonic resonance that is sensitive to electrode polarization.

Under anodic polarization (+1.25 V), the films possess greater than 80% transmission at all wavelengths of light measured (Figure 1A, black line). Upon cathodically polarizing the electrode (-1.25 V), the transmission in the NIR decreases substantially (red line). This decrease in transmission results from plasmonic absorption by the nanoparticles that occur upon the electrochemical injection of charge, which increases the free carrier concentration of the particles. Figure 1, panel B plots the transmission of the films at 1350 nm, the wavelength at which the modulation between the two states is greatest, as a function of applied voltage. As the voltage increases, the transmission at 1350 nm (and all other NIR wavelengths) increases in a sigmoidal fashion. It is crucial to carefully consider the voltage-transmission profile of the ITO nanoparticles when developing a polymer-ITO nanoparticle hybrid electrochromic material. Specifically, to maximize performance of the individual components, the polymer utilized must switch states in a voltage range that is well-separated from the range in which ITO nanoparticle switching occurs.

Poly(3,4-ethylenedioxythiophene) (PEDOT), an electrochromic polymer that is colorless in its oxidized form and deep blue when reduced, is one of the most commonly used polymer-based electrochromic materials. However, since the voltage regime in which PEDOT switches substantially overlaps with that of ITO nanoparticles (Figure S2), we could not construct a hybrid electrochromic material by coupling PEDOT with ITO nanoparticles. Polypyrroles are another class of frequently employed electrochromic polymers. However, we elected not to use these polymers since many polypyrroles including poly(3,4-ethylenedioxypyrrole) (PEDOP) and the parent polymer polypyrrole (PPy) have formal potentials within 300 mV of the redox potential of PEDOT. Therefore, the potentials at which PEDOP and PPy switch states would

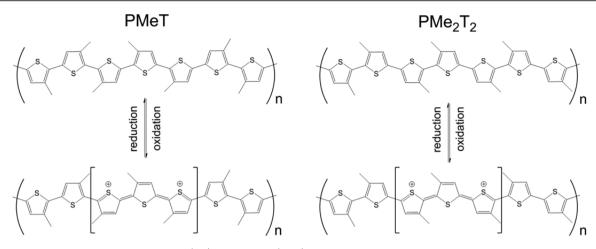


Figure 2. Representative structures of the PMeT (left) and PMe₂T₂ (right) polymers studied in this work and their redox reactions between neutral and bipolaronic states. While the structure of PMeT is regionandom, PMe₂T₂ consists of regionegular dimers.

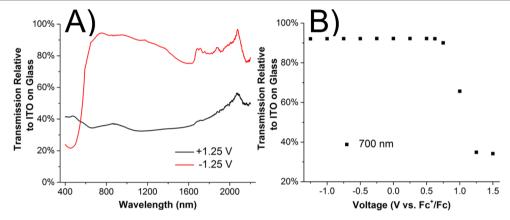


Figure 3. (A) Transmission spectra of a PMe₂T₂ film on an ITO-coated glass electrode polarized at +1.25 V (black) and -1.25 V (red) versus Fc⁺/Fc and (B) the percent transmission at 700 nm as a function of voltage inside a spectroelectrochemical cell containing 1 M LiClO₄ in PC.

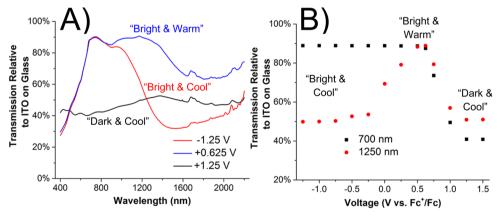


Figure 4. (A) Transmission spectra of a film of the PMe_2T_2 -ITO composite material on an ITO-coated glass electrode polarized at -1.25 V (red), +0.625 V (blue), and +1.25 V (black) versus Fc^+/Fc and (B) the percent transmission at 700 nm (black) and 1250 nm (red) as a function of voltage inside a spectroelectrochemical cell containing 1 M LiClO₄ in PC.

also substantially overlap with those of ITO nanoparticles. For these reasons, we elected to utilize polythiophenes that switch states at much more positive potentials than PEDOT. Representations of the structures and redox reactions of these polythiophenes, PMeT and PMe₂T₂, are shown in Figure 2. Although they possess switching voltages compatible with hybrid electrochromic materials utilizing ITO nanoparticles, polythiophenes with simple alkyl substitutes such as PMeT and

 PMe_2T_2 are less stable with respect to electrochemical switching than those based on dioxythiophenes such as $PEDOT.^6$

Figure 3 displays the transmission spectra of an electrochromic cell containing PMe_2T_2 . When polarized to -1.25 V, PMe_2T_2 exists in its undoped reduced form. In this state, PMe_2T_2 is light yellow and possesses a maximum absorbance at 452 nm (Figure 3A, red line). Upon electrochemical oxidation,

the PMe_2T_2 film turns deep blue as red and NIR light are absorbed by polarons (black line). Figure 3, panel B plots the transmission of the film at 700 nm as a function of applied voltage. At potentials more positive than +0.625 V, the transmission begins to decrease as the film begins to oxidize. At these positive potentials, the ITO nanoparticles have mostly completed their switching, thus rendering PMe_2T_2 a good candidate for the construction of a hybrid polymer—nanoparticle electrochromic cell.

Polymer-ITO Hybrid Electrochromic Systems. We constructed hybrid polymer-ITO nanoparticle systems by electropolymerizing PMeT or PMe2T2 onto films of ITO nanoparticles supported on ITO-coated glass electrodes. The resulting electrodes can be switched between three different states with respect to 700 nm visible light and 1250 nm NIR light. The PMe₂T₂-ITO electrodes outperform the PMeT-ITO system due to the higher band gap and oxidation potential of PMe₂T₂ (Figures S3-S5, Table S1). At -1.25 V, the PMe₂T₂-ITO electrodes are in a "bright and cool" state because the film is relatively transparent to 700 nm light but relatively opaque to 1250 nm light (Figure 4A, red line). In this mode, the PMe₂T₂ is light yellow, and the ITO nanoparticles absorb NIR light. Upon increasing the polarization of the electrode to +0.625 V, the electrode switches to a "bright and warm" state (blue line). At this voltage, the PMe₂T₂ remains light yellow, but the ITO nanoparticles do not absorb NIR light as strongly. Finally, upon further increasing the voltage to +1.25 V, the film enters a "dark and cool" state in which the PMe₂T₂ film becomes deep blue and relatively opaque to 700 nm light (black line). Although at this voltage the ITO nanoparticles do not absorb NIR light to any significant extent, polarons in PMe₂T₂ mediate NIR absorption.

Figure 4, panel B plots the transmission of the PMe_2T_2 –ITO film at 700 and 1250 nm as a function of applied voltage. As the voltage is increased from -1.25 V to +1.5 V, the transmission curve at 700 nm undergoes one transition due to the oxidation of PMe_2T_2 in the composite. In contrast, the transmission curve at 1250 nm undergoes two transitions, the first mediated by a decrease in plasmonic absorption by the ITO nanoparticles, and the second caused by increased polaronic absorption in PMe_2T_2 . These two transmission curves add to give the three unique operating states of the polymer—nanoparticle system.

To further understand the operation of the PMe₂T₂-ITO hybrid electrochromic system, we performed cyclic voltammetry (CV) of the composite film and its individual components (Figure 5). A film of ITO nanoparticles alone does not produce any significant Faradaic current (black line), indicating that NIR optical modulation of the particles originates from capacitive charging phenomena. This finding is consistent with previous reports indicating that shifts in the plasmonic absorption of these ITO nanoparticles are controlled by changes in the electrochemical double layer and not by redox events. 11 In contrast, the CV of the PMe₂T₂ polymer alone (red line) displays Faradaic peaks corresponding to the formal oxidation and reduction of the polymer. The onset of the oxidative wave begins at potentials greater than +0.625 V, which is the voltage at which the transmission characteristics of the PMe₂T₂ film begin to change (Figure 3B). The CV of the PMe₂T₂-ITO hybrid system possesses not only the main features present in the PMe₂T₂ voltammetry, but also additional features caused by capacitive charging of the ITO nanoparticles (Figure 5, blue line).

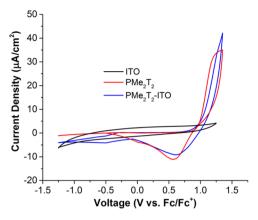


Figure 5. Cyclic voltammograms of films of ITO nanoparticles (black), PMe_2T_2 (red), and the PMe_2T_2 –ITO composite material (blue) in 1 M LiClO₄ in PC starting from -1.25 V at a scan rate of 10 mV/s.

We used SEM to interrogate the morphology of the PMe_2T_2 -ITO composite material and its individual components (Figures 6 and S6). Figure 6, panel A shows a SEM image

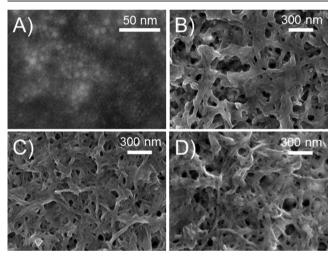


Figure 6. (A) Top-down SEM images of ITO nanoparticles, (B) oxidized PMe_2T_2 , (C) reduced PMe_2T_2 and (D) PMe_2T_2 –ITO with reduced PMe_2T_2 .

of the ITO nanoparticles utilized, which have diameters ranging from about 3–10 nm. The oxidized and reduced forms of PMe_2T_2 exhibit a porous texture that resembles the morphology of PEDOT films electrodeposited under comparable conditions (Figure 6B,C). Top-down microscopy of the PMe_2T_2 –ITO material reveals a porous film that is similar to PMe_2T_2 , indicating that PMe_2T_2 completely covers the bottom layer of ITO nanoparticles (Figure 6D). Interestingly, the ITO nanoparticles are still electrochromic in PMe_2T_2 –ITO even though they are covered by the PMe_2T_2 polymer. This finding indicates that the polymer is porous enough to be permeable toward the ions in the electrolyte, which are needed to facilitate electrochromism in the ITO nanoparticles.

Contrast Ratios of PMe_2T_2 -ITO. Having demonstrated the first proof-of-concept polymer—nanoparticle electrochromic system that switches between three different modes of operation, we now evaluate the contrast ratios of the PMe_2T_2 -ITO material (Table 1). The contrast ratio at 1250 nm is 46% for the ITO nanoparticles alone, and the contrast ratio induced

Table 1. Contrast Ratios for ITO, PMe_2T_2 , and PMe_2T_2 –ITO Electrochromic Systems between Different Electrode Polarizations (vs Fc^+/Fc)

sample	two states	contrast ratio
ITO	"cool" (-1.25 V) and "warm" (+1.25 V)	46% at 1250 nm
PMe_2T_2	"bright" (–1.25 V) and "dark" (+1.25 V)	57% at 700 nm
PMe ₂ T ₂ -ITO	"bright and cool" (-1.25 V) and "bright and warm" $(+0.625 \text{ V})$	1% at 700 nm
		39% at 1250 nm
	"bright and warm" (+0.625 V) and "dark and cool" (+1.25 V)	47% at 700 nm
		38% at 1250 nm

by the nanoparticles (between "bright and cool" and "bright and warm" states) in the hybrid material is 39%. The close correspondence between these two values indicates that the switching voltages of the ITO nanoparticles and PMe_2T_2 polymer are well-separated. In other words, only a small amount of parasitic absorption of NIR light by the ITO nanoparticles occurs at +0.625 V.

Figure S7 plots the total visible and NIR solar transmittances of the PMe₂T₂-ITO system when integrated over the intensities at each wavelength of the solar spectrum (air mass 1.5 G). These values are important when considering light and heat flux through electrochromic materials used in smart windows. When incorporating all wavelengths of the visible or NIR spectrum, the contrast ratios in the material decrease as compared to when they are calculated solely at 700 or 1250 nm since the material does not modulate all wavelengths equally effectively. For example, the PMe₂T₂-ITO system possesses a lower contrast ratio between 1600 nm (35%) and 2200 nm (19%) as compared to 1400 nm (47%) between the "bright and cool" and "bright and warm" states. Increasing the total solar integrated contrast ratio for visible light could be improved through the use of, for example, complementary cathodically coloring polymers at the counter electrode. Improvement of the total solar integrated NIR contrast ratio could be achieved by incorporating recently developed WO3-x nanocrystals or other nanomaterials, which are electrochromic across a broader range of the NIR than ITO nanoparticles, into this architecture.

Effect of Polymer Thickness on PMe_2T_2 –ITO. In this section, we evaluate the effect of the thickness of PMe_2T_2 on the performance of the PMe_2T_2 –ITO composite. The electrode containing PMe_2T_2 –ITO described in the preceding section was fabricated by electropolymerizing PMe_2T_2 on an electrode modified with ITO nanoparticles by performing three CV cycles from +0.4 V to +1.6 V at a scan rate of 50 mV/s in a solution containing the monomer of PMe_2T_2 .

By varying the number of CV cycles from one to five, the thickness of electropolymerized PMe_2T_2 films can be modulated (Figure S8). As expected, longer electropolymerization times lead to thicker films, which in turn decrease the transmission of the films (Figure S9). Electropolymerization using three CV cycles yields PMe_2T_2 films with thicknesses of \sim 400 nm that possess greater contrast ratios at 700 nm than the thicker or thinner films tested.

For the PMe₂T₂–ITO system, when only two CV cycles are performed to electropolymerize the polymer, the PMe₂T₂–ITO electrode can still be switched between three different states with respect to 700 nm visible light and 1250 nm NIR light (Figure 7A). However, the contrast ratio at 700 nm between the "bright and warm" and "dark and cool" states is only 22% as compared to 47% for the PMe₂T₂–ITO material fabricated using three CV cycles. This result follows from the fact that the polymer incorporated in the material synthesized via two electropolymerization cycles is thinner. Moreover, the contrast ratios at 1250 nm between the "bright and cool" and "bright and warm" states are similar (37% vs 39%) for these two cases since this contrast ratio is determined by the ITO nanoparticles, not the polymer layer.

When PMe_2T_2 is electropolymerized using five CV cycles to construct PMe_2T_2 —ITO, the electrode can also still be switched between three different states with respect to 700 and 1250 nm light (Figure 7B). In this case, however, the polymer layer is too thick for optimal material performance, and the transmission characteristics of the electrode are dominated by the absorption of the polymer. Taken together, these studies varying the thickness of PMe_2T_2 in PMe_2T_2 —ITO indicate that optimizing the thickness of the polymer layer in dual polymer—nanoparticle electrochromic materials is necessary to maximize the contrast ratios of these materials.

Switching Speeds and Durability of PMe_2T_2 -ITO. In addition to the transmission characteristics of the PMe_2T_2 -ITO electrode, we also evaluated the speeds with which the

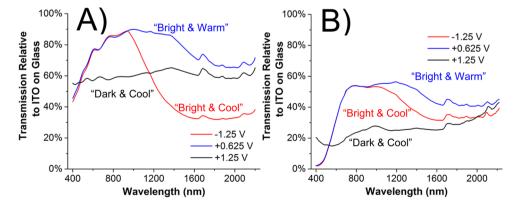


Figure 7. Transmission spectra of films of the PMe_2T_2 -ITO composite material fabricated using (A) two and (B) five CV cycles of electropolymerization on electrodes modified with ITO nanoparticles polarized at -1.25 V (red), +0.625 V (blue), and +1.25 V (black) versus Fc^+/Fc .

Table 2. Half Switching Times for Three Different Electrochromic Systems between Different Electrode Polarizations (vs Fc⁺/Fc)

sample	initial state	final state	wavelength	half switching time
ITO	"cool" (-1.25 V)	"warm" (+1.25 V)	1350 nm	1.1 s
	"warm" (+1.25 V)	"cool" (-1.25 V)	1350 nm	1.2 s
PMe_2T_2	"bright" (-1.25 V)	"dark" (+1.25 V)	700 nm	78 s
			1350 nm	92 s
	"dark" (+1.25 V)	"bright" (-1.25 V)	700 nm	22 s
			1350 nm	29 s
PMe ₂ T ₂ -ITO hybrid	"bright and cool" (-1.25 V)	"dark and cool" (+1.25 V)	700 nm	68 s
	"dark and cool" (+1.25 V)	"bright and cool" (-1.25 V)	700 nm	19 s
	"bright and warm" (+0.625 V)	"dark and cool" (+1.25 V)	700 nm	75 s
			1350 nm	65 s
	"bright and warm" (+0.625 V)	"bright and cool" (-1.25 V)	1350 nm	33 s
	"bright and cool" (-1.25 V)	"bright and warm" (+0.625 V)	1350 nm	71 s

electrode switches between its three modes of operation (Figure S10). Table 2 lists the times it takes the composite material and its individual components to reach halfway through the transition for various initial and final states. Although the half switching times for the ITO nanoparticles are $\sim\!1$ s, which are similar to previous reports, 11 the PMe₂T₂ half switching times are on the order of 20–100 s. Interestingly, the switching times of the composite system are similar to the polymer alone. These values compare favorably with inorganic-based dual electrochromic materials, which, in some cases, possess switching times over several minutes. 13,16

Lastly, we evaluated the durability of the PMe₂T₂-ITO hybrid system. After 200 cycles of switching, the PMe₂T₂-ITO electrode still can be operated in three different states (Figure S11A). However, the contrast ratios at 1350 nm mediated by the ITO nanoparticles and at 700 nm mediated by PMe₂T₂ degraded by 15% and 18%, respectively, after 200 switching cycles. The degradation in the NIR contrast ratio results from a redshift in the plasmonic absorption previously ascribed to leaching of Sn from the ITO nanoparticles that occurs after extensive cycling. 11 The rate of PMe₂T₂ degradation witnessed in the PMe₂T₂-ITO electrode is similar to that of the PMe₂T₂ polymer alone (20% at 700 nm after 200 cycles, Figure S11B). The capacitances of electrodes modified with PMe₂T₂ and PMe₂T₂-ITO also degrade over the course of 200 switching cycles (Figure S12). It is likely that the composite materials developed here undergo further degradation when operated in sunlight due to the presence of UV light, a process analogous to the UV-mediated degradation observed in organic photovoltaics.²⁵ In both cases, the effects of UV degradation can be mitigated through the use of a UV filter. Nonetheless, it is certain that the durability of the materials presented in this manuscript must substantially improve if these electrochromic materials are to be used for smart window applications.

CONCLUSIONS

We have constructed the first class of electrochromic materials that utilizes a composite of polymers and nanoparticles to independently tune the transmission of visible and NIR light across three distinct modes of operation. The materials are easily fabricated through the electropolymerization of a polythiophene on transparent electrodes modified with ITO nanoparticles. We assess the performance of films containing polythiophene structural isomers, PMeT or PMe₂T₂. Electrodes containing PMe₂T₂ exhibit superior performance due to the higher band gap and oxidation potential of this polymer. These

hybrid materials exhibit contrast ratios on par with the polymer and nanoparticle individual components, good switching times, but only modest durability. Taken together, these results represent a new avenue of research in composite electrochromic materials aimed at managing light and heat flux for smart window applications.

ASSOCIATED CONTENT

S Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.chemmater.5b04811.

Further characterization of the PMe_2T_2 -ITO and PMeT-ITO systems (PDF)

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Notes

The authors declare no competing financial interest.

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