



Cite this: *Polym. Chem.*, 2018, **9**, 1693

Received 5th November 2017,  
Accepted 21st February 2018

DOI: 10.1039/c7py01858d

rsc.li/polymers

## Cyanotriphenylamine-based polyimidothioethers as multifunctional materials for ambipolar electrochromic and electrofluorochromic devices, and fluorescent electrospun fibers†

Hung-Ju Yen,<sup>a</sup> Cha-Wen Chang,<sup>b</sup> Hui Qi Wong<sup>a</sup> and Guey-Sheng Liou<sup>a,c</sup>

A series of new luminescent and electrochromic polyimidothioethers (PITEs) was prepared from a new triphenylamine-based bismaleimide and commercial dithiols *via* Michael polyaddition. With organo-processability and high thermal stability, the optoelectronic properties of these PITEs were investigated and they demonstrated great potential as multifunctional materials for ambipolar electrochromic and electrofluorochromic devices, and fluorescent electrospun fibers.

### Introduction

Recent studies have already indicated that heteroatom-containing luminogens, such as triphenylamine (TPA) derivatives and cyano (CN) substituents, possess excellent features in light emission.<sup>1</sup> The luminogens are mostly non-fluorescent in solution states but fluorescent in the aggregate/solid states, which are due to the restriction of intramolecular rotation.<sup>2</sup> This phenomenon, namely “aggregation-induced emission (AIE)”, is exactly the opposite of the aggregation-caused quenching<sup>3</sup> observed in most traditional chromophores,<sup>4</sup> and considered as a new approach for designing novel, efficient solid-state emitters.<sup>5</sup> Moreover, the electrospinning (electrospun, ES) technique could further produce an extended chain conformation along the fiber’s orientation, thus enhancing the alignment and is expected to exhibit a

much higher photoluminescence (PL) efficiency than the spin-coated film.<sup>6</sup>

Among the AIE materials, CN-based luminogens have been developed due to its internal steric hindrance, structural simplicity, and high molar polarization.<sup>7</sup> Therefore, we recently incorporated the CN group into TPA-based polymers for developing high-performance electrofluorochromic (EFC) devices with a fast response rate, high fluorescence contrast and long-term stability.<sup>8</sup> EFC deals with the electrically driven reversible optical changes in fluorescence.<sup>9</sup> Reversible switching of the optical status by the electrochemical or photochemical conversion of the UV-vis or PL spectra is a desirable field of investigation in optoelectronics such as displays, sensors, optical memory, and biological analysis.<sup>10</sup> In particular, fluorescent high-performance polymers are promising candidates for application in EFC devices because of their good chemical and radiation resistance, excellent thermal stability, high mechanical strength, low flammability, and good electronic properties.<sup>11</sup>

Under this design concept, we would be able to design new optoelectronic materials by introducing CN-TPA into polyimidothioethers (PITEs). In this contribution, we therefore synthesized a series of PITEs from a new CNTPA-based bismaleimide monomer. The PITEs were chosen because of their facile preparation, which can be readily synthesized from bismaleimides (BMIs) and dithiols *via* Michael polyaddition.<sup>12</sup> Also, the good combination of high thermal stability (from the imido group) and high optical transparency (from the thioether linkage) would make these materials perfect candidates for advanced optical applications. In addition, by combining the carbonyl and TPA groups, the prepared PITEs are expected to reveal great potential for ambipolar electrochromic (EC) and EFC applications.

<sup>a</sup>Institute of Chemistry, Academia Sinica, 128 Academia Road, Section 2, Nankang, Taipei 11529, Taiwan. E-mail: hjyen@gate.sinica.edu.tw

<sup>b</sup>Department of Interface Chemistry, Division of Applied Chemistry, Material and Chemical Research Laboratories, Industrial Technology Research Institute, Hsinchu 30011, Taiwan

<sup>c</sup>Functional Polymeric Materials Laboratory, Institute of Polymer Science and Engineering, National Taiwan University, 1 Roosevelt Road, 4th Sec., Taipei 10617, Taiwan. E-mail: gslou@ntu.edu.tw

† Electronic supplementary information (ESI) available: Experimental section. Figures: IR spectra of compounds and PITE CN-S; NMR spectra of diamide acid compound, CN-BMI, CN-C<sub>2</sub>, CH<sub>2</sub>-C<sub>2</sub>, and CH<sub>2</sub>-S; TGA and DSC curves of PITEs; AEE properties of PITEs; electrochromic behavior of PITE CH<sub>2</sub>-S; electrochromic and electrofluorochromic behaviors of CN-S. Tables: inherent viscosity, molecular weights, solubility behavior, thermal properties, and electrochemical properties of PITEs. See DOI: 10.1039/c7py01858d

## Results and discussion

### Monomer synthesis

The new aromatic BMI **CN-BMI** having the CN-TPA group was successfully synthesized by the cyclodehydration of the bismaleamic acid resulting from the reaction of the diamine compound **1** with maleic anhydride as shown in Scheme 1. Elemental analysis, IR, and NMR spectroscopic techniques were used to identify the structures of the intermediate bismaleamic acid compound and the target monomer **CN-BMI**. The FT-IR spectra of the bismaleamic acid compound and **CN-BMI** are illustrated in Fig. S1b and S1c,<sup>†</sup> respectively, and the IR spectrum of the diamine compound **1** is also shown in Fig. S1a<sup>†</sup> for comparison. The BMI monomer **CN-BMI** exhibited characteristic maleimide absorption bands at around 1714 (C=O stretch), 1595 (C=C stretch), and 1146 cm<sup>-1</sup> (imide ring deformation) with a nitrile characteristic band at around 2220 cm<sup>-1</sup> (C≡N stretching). Fig. S2<sup>†</sup> illustrates the <sup>1</sup>H and <sup>13</sup>C NMR spectra of the bismaleamic acid compound and the BMI monomer **CN-BMI**. The assignments of each carbon and proton are assisted by the two-dimensional NMR spectra as shown in Fig. 1, and these spectra agree well with the proposed molecular structure.

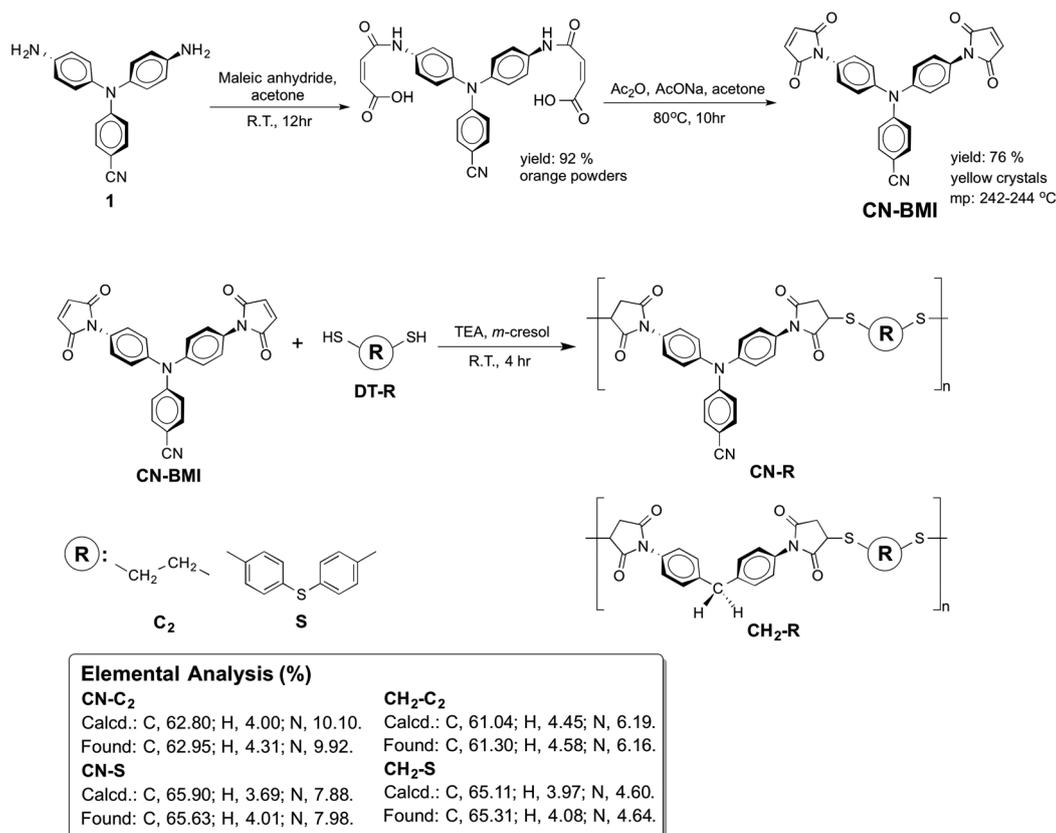
### Polymer synthesis

According to the Michael polyaddition technique described by Crivello,<sup>13</sup> a series of new PITEs was synthesized from **CN-BMI**

and commercial dithiols (Scheme 1). Michael polyaddition was chosen due to its attraction for the synthesis of step-growth polymers with high molecular weights from BMIs and dithiols, and the reaction was carried out at room temperature for 4 h in the presence of a catalytic amount of triethylamine as a basic catalyst in *m*-cresol. The polymerization proceeded homogeneously throughout the procedure and afforded clear, viscous polymer solutions in high yield with no evolution of volatile molecules. All the PITEs precipitated in white fiber-like forms when the resulting polymer solutions are slowly poured into acidified methanol and their resultant inherent viscosities and molecular weights are summarized in Table S1.<sup>†</sup> Elemental analysis, IR, and NMR spectroscopic techniques were used to identify the structure of PITEs. As shown in Fig. S1d,<sup>†</sup> a typical IR spectrum for PITE **CN-S** exhibited characteristic absorption bands of the imide at around 1714 (C=O stretch) and 1180 cm<sup>-1</sup> (thioether C–S–C stretch) with a nitrile characteristic band at around 2221 cm<sup>-1</sup> (C≡N stretching). The NMR spectra shown in Fig. 2 and Fig. S3<sup>†</sup> were in perfect agreement with the proposed molecular structures. Furthermore, the elemental composition of the polymers was confirmed by elemental analysis and is summarized in Scheme 1.

### Polymer properties

**Basic characterization.** The PITEs were readily soluble in polar aprotic organic solvents such as *N*-methyl-2-pyrrolidinone



Scheme 1 Synthetic route to the CNTPA-based **CN-BMI** and PITEs with the elemental analysis results.

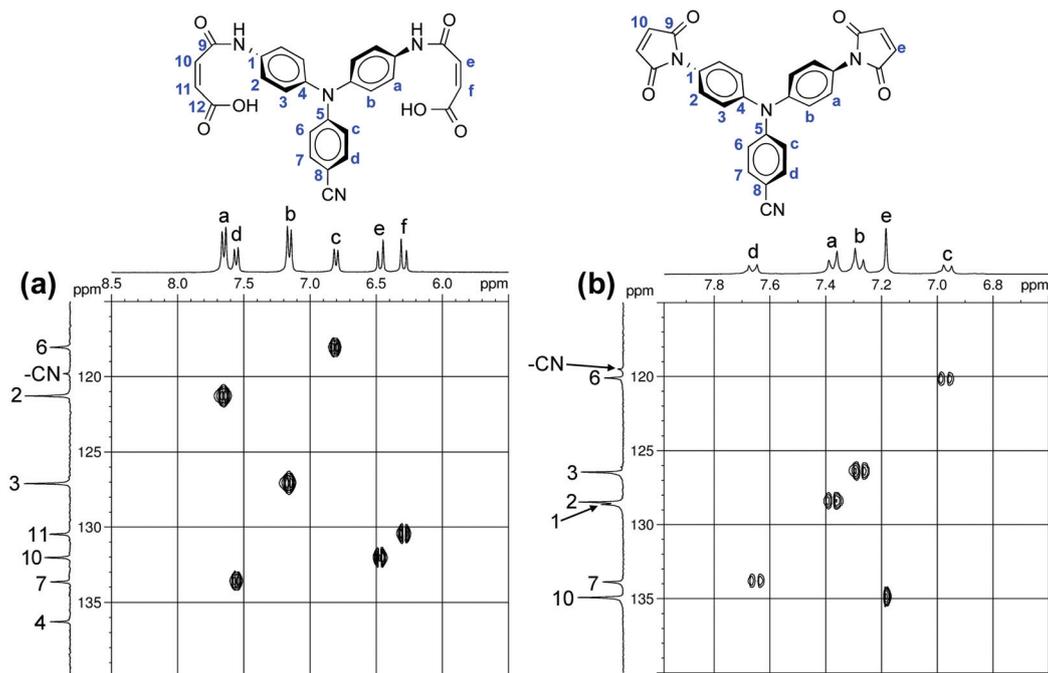


Fig. 1 C–H HMQC spectra of (a) diamic acid compound and (b) monomer CN-BMI in DMSO- $d_6$ .

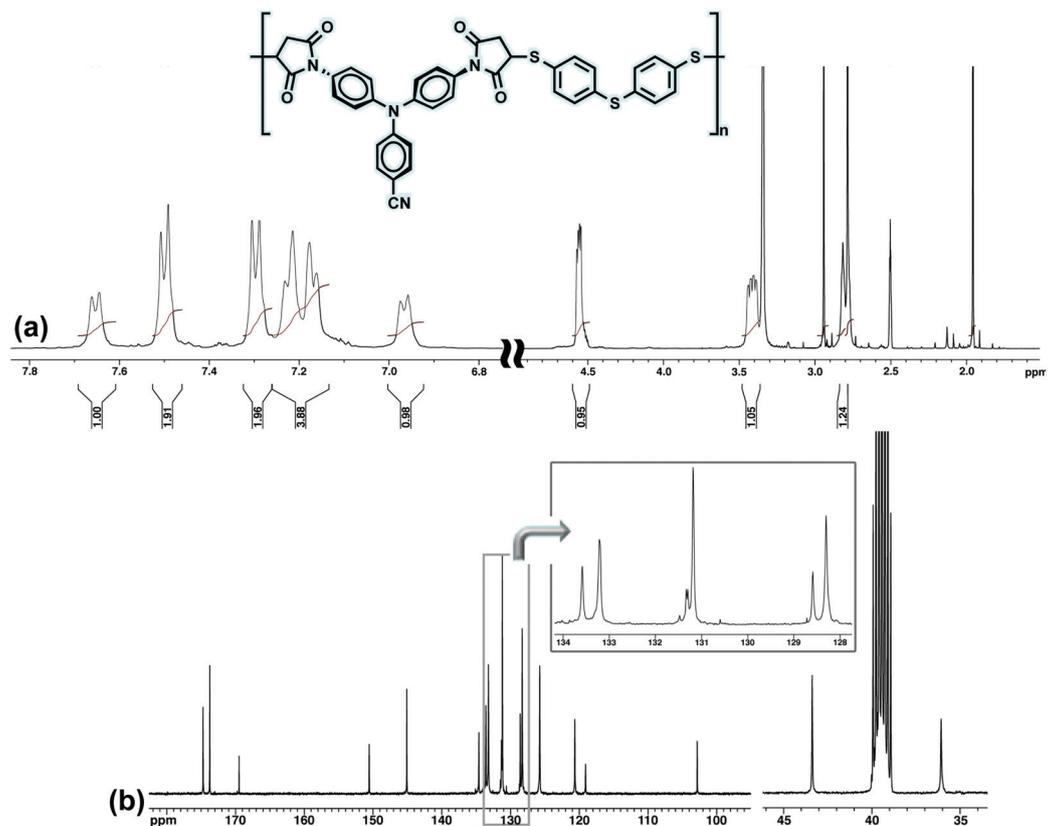


Fig. 2 (a)  $^1\text{H}$  and (b)  $^{13}\text{C}$  NMR spectra of PITE CN-S in DMSO- $d_6$ .

(NMP), *N,N*-dimethylacetamide (DMAc), *N,N*-dimethylformamide (DMF), and *m*-cresol, and partially soluble in tetrahydrofuran (THF) and chloroform (Table S2†). Their high solubilities could be attributed to the incorporation of the bulky and noncoplanar CN-TPA moiety along the polymer backbone, which results in high steric hindrance to close packing, and thus reduces their crystallization tendency. Besides, stereoisomerism also plays an important role in that the preference of the stereoisomer from the bis-attack on the opposite sides of this plane could result in the formation of a polymer with a less ordered structure that can be reflected in the enhancement of solubility. Thus, excellent solubility makes these polymers potential candidates for practical applications by spin-coating or inkjet-printing processes to afford high performance thin films for optoelectronic devices.

The thermal properties of PITEs were examined by DSC and TGA, and the results are summarized in Table S3.† As shown in Fig. S4a,† the glass-transition temperatures ( $T_g$ ) of PITEs could be easily measured in the DSC thermograms as 202 and 205 °C for CN-C<sub>2</sub> and CN-S, respectively, depending upon the stiffness of the polymer chain. In addition, the typical TGA curves of PITEs are shown in Fig. S4b.† All the prepared PITEs exhibited good thermal stability with insignificant weight loss up to 450 °C under a nitrogen atmosphere. The melting-process window ( $\Delta T$ ) termed the region between  $T_g$  and  $T_d$ <sup>5</sup> for these materials was around 270 °C, revealing their great potential for the injection molding process.

### Optical properties of PITEs and their electrospun fibers

The UV-Vis absorption and PL spectra of PITEs as solution (conc.:  $10^{-5}$  mol L<sup>-1</sup>), solid film, and ES fiber states are shown in Fig. 3. These soluble polymers exhibited maximum UV-Vis

absorption bands at 307 and 316 nm in NMP solutions, due to the  $\pi$ - $\pi^*$  transitions of the aromatic chromophores, *e.g.*, TPA units and phenyl rings. The UV-Vis absorptions of CN-TPA-based PITEs in film states showed single absorbance at around 315 nm. These CN-TPA-based PITEs exhibited a blue PL emission maximum in the NMP solutions with quantum yields of 4.3% and 2.6%. In the film state, the PL quantum yields of PITEs were 10.4 and 6.1% for CN-C<sub>2</sub> and CN-S, respectively. These polymers revealed a blue shift of the maximum PL peak from the NMP solution to the film state, which is attributed to the solvent effect<sup>14</sup> and could be explained by using THF as a solvent (as shown in Table 1). In addition, the enhanced  $\Phi_{PL}$  of the solid films implies that the triarylamine derivatives have inherited the aggregation-enhanced emission (AEE) features. To further confirm the AEE attribution, the PL spectra of the PITEs in NMP-methanol diluted solutions were studied with different THF fractions, and the results with images are summarized in Fig. S5.† Since the PITEs were not soluble in methanol but soluble in NMP, therefore by increasing the methanol fraction in the mixed solvent their existing forms could be changed from a solution in pure NMP to the aggregated luminogen particles in the mixtures, which will cause obvious changes in their PL behavior. The enhancement in PL intensity can be attributed to an AEE effect caused by the formation of molecular aggregates, in which the restriction of intramolecular rotations leads to an increase in fluorescence emission.<sup>6d,14b</sup> Moreover, the polymeric ES fibers of PITEs were further fabricated to investigate and confirm the AEE phenomenon of the high quantum yield in solid film states. The field-emission scanning electron microscopy (FE-SEM) images of these two ES fibers shown in Fig. 3a exhibited

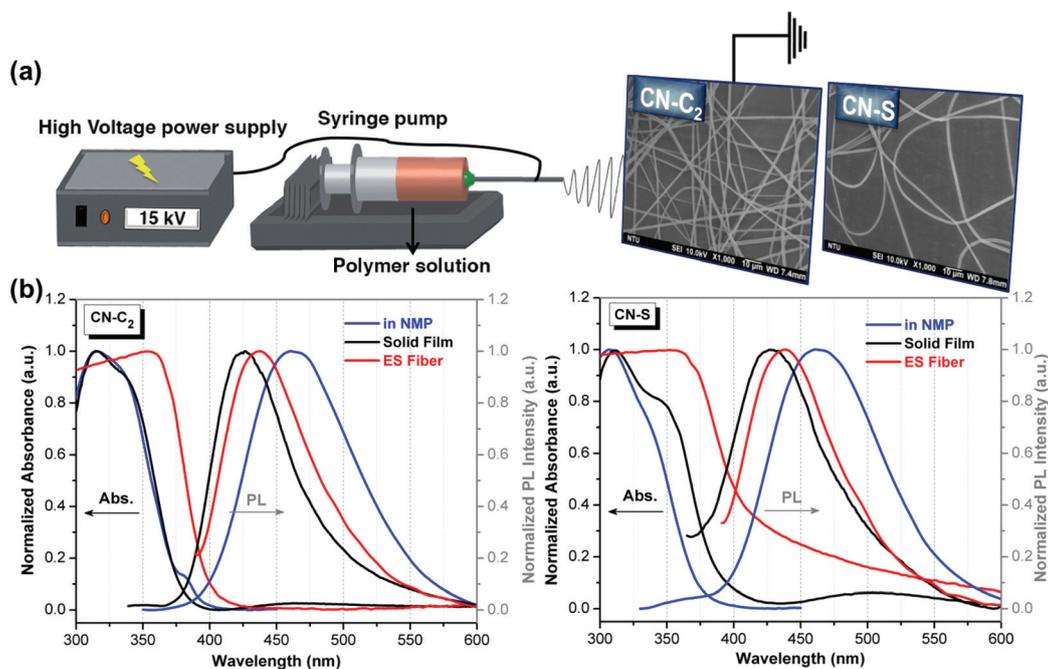


Fig. 3 (a) Scheme of a typical ES setup and the ES fibers of CN-C<sub>2</sub> and CN-S. (b) Normalized absorbance and photoluminescence (PL) spectra of PITEs in solution, solid film, and ES fiber states.

Table 1 Optical properties of polyimidothioethers

Index	NMP (10 $\mu$ M) solution			Solid film			ES fiber		
	$\lambda_{\text{abs}}$ (nm)	$\lambda_{\text{em}}^a$ (nm)	$\Phi_{\text{PL}}^b$ (%)	$\lambda_{\text{abs}}$ (nm)	$\lambda_{\text{em}}^a$ (nm)	$\Phi_{\text{PL}}^c$ (%)	$\lambda_{\text{abs}}$ (nm)	$\lambda_{\text{em}}^a$ (nm)	$\Phi_{\text{PL}}^c$ (%)
CN-C <sub>2</sub>	314 (319) <sup>d</sup>	454 (427)	4.3 (17.2)	316	427	10.4	354	436	19.6
CN-S	307 (311)	456 (425)	2.6 (3.8)	312	429	6.1	357	440	21.5

<sup>a</sup> They were excited at  $\lambda_{\text{abs}}$  for both solid and solution states. <sup>b</sup> The quantum yield was measured by using quinine sulfate (dissolved in 1 N H<sub>2</sub>SO<sub>4</sub> at a concentration of 10  $\mu$ M, assuming a photoluminescence quantum efficiency of 0.546) as a standard at 24–25 °C. <sup>c</sup> PL quantum yields of polymer thin films determined using a calibrated integrating sphere. <sup>d</sup> Data in the parentheses are measured in THF (10  $\mu$ M) solution.

smooth fiber-like structures without bead formation. The absorption spectra of the ES fibers showed a bathochromic shift to their solution and film states, suggesting light scattering caused by the ES fibers and could be observed by the trailing end of the spectrum in the visible range (400–600 nm). As per the summarized optical properties in Table 1, the ES fibers of CN-C<sub>2</sub> and CN-S exhibited obviously higher PL emissions with enhanced quantum yields up to 21.5% compared to their corresponding solid films. The molecular weight of polymer chains affects remarkably the formation of the appropriate conformations of the chromophores and hence their emissions. With good consistency with the reported reference,<sup>2d,g</sup> the polymer CN-S with a lower degree of polymerization would gain more emission intensity with increasing aggregation under nonsolvent conditions compared to CN-C<sub>2</sub>. The molecular weight difference varied AEE emission behaviors, which were explained in terms of the conformational difference between the low and high molecular weight analogues. Also, the AIE phenomenon has been attributed to the suppression of nonradiative decay pathways. Confinement in the rigid environment of CN-S attenuates vibrations, which leads to higher levels of photoluminescence from the conformationally restricted excited states when compared to CN-C<sub>2</sub>.<sup>2j</sup> Further enhancement of the PL quantum yield of the AIE luminogen in the fiber state implying the judicious combination of the AIE feature and ES nanofiber fabrication is an essential approach and could be potentially used for the application of optoelectronic materials.

### Electrochemical and electrochromic properties

Typical CV curves of PITEs are shown in Fig. 4a and the electrochemical properties are summarized in Table S4.† All the PITEs exhibited reversible oxidation and reduction processes implying their high electrochemical stability for both p- and n-doping (ambipolar) processes. The reversible oxidation redox wave represents the formation of a stable radical cation originating from the electrochemical redox reactions of the TPA. To understand the reduction behavior of PITEs, we chose and synthesized the simplest structures of PITEs, CH<sub>2</sub>-C<sub>2</sub> and CH<sub>2</sub>-S,<sup>12</sup> to conduct electrochemical reduction. The cyclic voltammograms for CH<sub>2</sub>-C<sub>2</sub> and CH<sub>2</sub>-S are also shown in Fig. 4a. The succinimide segment undergoes one electron transfers with the onset potential ( $E_{\text{onset}}$ ) around –0.80 V corresponding to the reduction of the neutral form to the anion state, con-

firmed the imide's carbonyl group as the electroactive site (Fig. S6†). During the electrochemical oxidation of the PITE thin films, the color of the film changed from colorless to blue. On the other hand, the film changed the color to red when electrochemically reduced.

Therefore, spectroelectrochemical experiments were used to evaluate the optical properties of the EC films. The UV-Vis absorbance curves correlated to the applied potentials of CN-C<sub>2</sub> and CN-S films are depicted in Fig. 4 and Fig. S7,† respectively. The strong absorption of CN-C<sub>2</sub> at around 316 nm, characteristic of the triarylamine unit in the neutral form (0 V), decreased and new peaks at 367 nm and 736 nm grew up steadily upon electrochemical oxidation (increasing the applied voltage from 0 to 1.70 V), corresponding to the one-electron oxidation product, a stable monocation radical TPA of CN-C<sub>2</sub>. The PITE CN-C<sub>2</sub> film switched from a transmissive neutral state ( $L^*$ , 99;  $a^*$ , 0;  $b^*$ , 0) to a highly absorbing blue ( $L^*$ , 42;  $a^*$ , 12;  $b^*$ , –48) at the oxidized state with a high optical transmittance change ( $\Delta\%T$ ) of 71% at 736 nm. Moreover, coloration changes upon reduction were also observed and monitored. As shown in Fig. 4c, the PITE film changed from colorless at neutral form to red at the reduced state ( $L^*$ , 61;  $a^*$ , 20;  $b^*$ , 14) with a good contrast in the visible region at around 500 nm. Another PITE CN-S showing similar ambipolar EC behavior is also summarized in Fig. S7a and S7b.†

### Electrofluorochromism

The fluorescence switching of PITEs was monitored by applying electrical positive and negative potentials, and the results are summarized in Fig. 5 and Fig. S7.† The setup of the EFC cell was similar to that of the spectroelectrochemical cell, which was placed in the optical path of the sample light beam in a fluorometer (Fig. 5b). Upon increasing the applied voltage from 0 to 1.70 V, the emissions of PITE thin films were significantly extinguished to dark (Fig. 5c and Fig. S7c†), which is due to the formation of the monocation radical of TPA as an effective fluorescence quencher. While bringing the potential down to –2.0 V, the obviously decreased emission is attributed to the reduction of imide's carbonyl group (Fig. 5a and Fig. S7d†). The decrease of fluorescence intensity occurred without a shift in the emission band upon the potential changes, indicating that the fluorescence quenching originated from the electrochemical oxidation of the CN-TPA unit

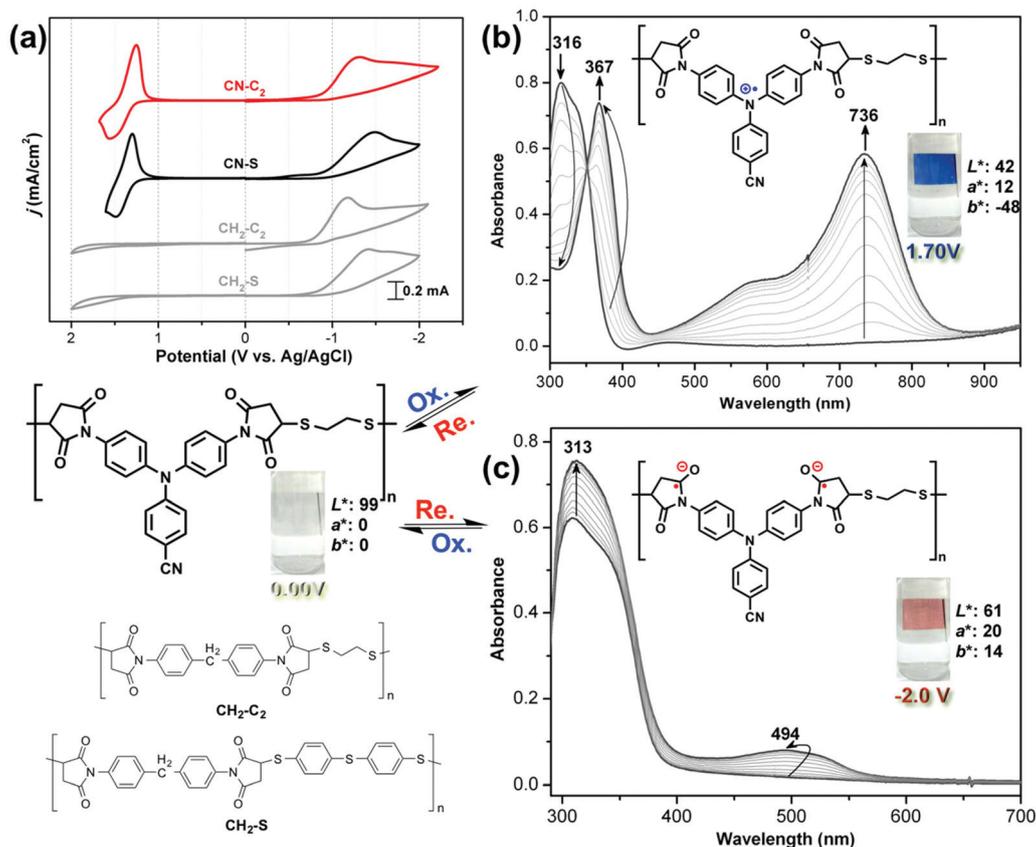


Fig. 4 (a) Cyclic voltammograms of the PITE films on an indium tin oxide (ITO)-coated glass substrate in 0.1 M TBAP/CH<sub>3</sub>CN at a scan rate of 50 mV s<sup>-1</sup>. Spectroelectrochemistry of a PITE CN-C<sub>2</sub> thin film (~100 nm in thickness) by increasing and decreasing the applied voltage to (b) 1.70 and (c) -2.0 (V vs. Ag/AgCl), respectively. The inset shows the color change of the polymer film at indicated potentials.

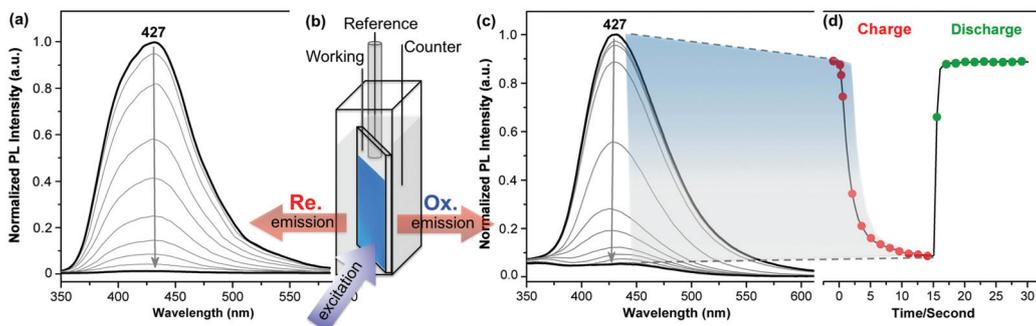


Fig. 5 (a) Fluorescence intensity changes of CN-C<sub>2</sub> (~100 nm in thickness) by applying the electric voltage to -2.0 (V vs. Ag/AgCl). (b) Scheme of a typical electrofluorochromic cell, (c) fluorescence intensity changes, and (d) monitored switching behavior of CN-C<sub>2</sub> (~100 nm in thickness) by increasing the applied voltage to 1.70 (V vs. Ag/AgCl).

or reduction of the succinimide group without the production of any side products. The polymer film turned back to original fluorescence when the potential was subsequently set back at 0 V (Fig. 5c). The other PITE CN-S shows an ambipolar EFC similar to that of CN-C<sub>2</sub>. Notably, the CNTPA-based CN-C<sub>2</sub> having an AEE feature is highly emissive in the solid state, which could be quenched upon the application of step potentials with a relatively high contrast ratio ( $I_f/I_{f0}$ ) of 92, implying

that the judicious combination of the AEE and EC features is a promising approach for EFC materials.

## Conclusions

A series of electroactive TPA-based PITEs was readily prepared from the new TPA-based BMI and dithiols *via* Michael polyad-

dition. The PITEs with good processability and thermal stability were utilized to prepare nanofibers by the ES method. Notably, the CN-TPA-based polymers having AEE features are highly emissive in the solid state and could be further enhanced in the form of ES nanofibers (up to 21% of PL quantum yield). The PITEs also revealed interesting ambipolar EC characteristics with color changes from colorless to blue in the oxidized state and to red in the reduced state. Furthermore, electrochemical fluorescence switching was measured and it demonstrated that a fluorescent neutral state changes to non-fluorescent oxidized and reduced states under a low working potential, giving rise to a high contrast ratio ( $I_f/I_{f0}$ ) of 92. These results demonstrate that the incorporation of EC and AEE-active CN-TPA chromophores into high-performance polymers is a feasible approach to prepare multifunctional materials for efficiently emitting, ambipolar electrochromic and electrofluorochromic devices by both solution casting and injection molding techniques.

## Conflicts of interest

There are no conflicts to declare.

## Acknowledgements

The authors thank the Ministry of Science and Technology of Taiwan for financial support. H.-J. Yen also acknowledges the start-up fund from the Academia Sinica.

## References

- (a) B. K. An, S. K. Kwon, S. D. Jung and S. Y. Park, *J. Am. Chem. Soc.*, 2002, **124**, 14410; (b) S. Jayanty and T. P. Radhakrishnan, *Chem. – Eur. J.*, 2004, **10**, 791; (c) J. Xu, L. Wen, W. Zhou, J. Lv, Y. Guo, M. Zhu, H. Liu, Y. Li and L. Jiang, *J. Phys. Chem. C*, 2009, **113**, 5924.
- (a) J. D. Luo, Z. L. Xie, J. W. Y. Lam, L. Cheng, H. Y. Chen, C. F. Qiu, H. S. Kwok, X. W. Zhan, Y. Q. Liu, D. B. Zhu and B. Z. Tang, *Chem. Commun.*, 2001, 1740; (b) W. Z. Yuan, P. Lu, S. Chen, J. W. Y. Lam, Z. Wang, Y. Liu, H. S. Kwok, Y. Ma and B. Z. Tang, *Adv. Mater.*, 2010, **22**, 2159; (c) Y. Liu, S. Chen, J. W. Y. Lam, P. Lu, R. T. K. Kwok, F. Mahtab, H. S. Kwok and B. Z. Tang, *Chem. Mater.*, 2011, **23**, 2536; (d) L. Wang, G. Fang and D. Cao, *J. Macromol. Sci., Part A: Pure Appl. Chem.*, 2014, **51**, 668; (e) X. Wang, W. Wang, Y. Wang, J. Z. Sun and B. Z. Tang, *Polym. Chem.*, 2017, **8**, 2353; (f) J.-B. Xiong, Y.-X. Yuan, L. Wang, J.-P. Sun, W.-G. Qiao, H.-C. Zhang, M. Duan, H. Han, S. Zhang and Y.-S. Zheng, *Org. Lett.*, 2018, **20**, 373; (g) C. Shang, N. Wei, H. Zhuo, Y. Shao, Q. Zhang, Z. Zhang and H. Wang, *J. Mater. Chem. C*, 2017, **5**, 8082; (h) J. Wang, X. Gu, P. Zhang, X. Huang, X. Zheng, M. Chen, H. Feng, R. T. K. Kwok, J. W. Y. Lam and B. Z. Tang, *J. Am. Chem. Soc.*, 2017, **139**, 16974; (i) X. Li, M. Jiang, J. W. Y. Lam, B. Z. Tang and J. Y. Qu, *J. Am. Chem. Soc.*, 2017, **139**, 17022; (j) J. Sturala, M. K. Etherington, A. N. Bismillah, H. F. Higginbotham, W. Trewby, J. A. Aguilar, E. H. C. Bromley, A.-J. Avestro, A. P. Monkman and P. R. McGonigal, *J. Am. Chem. Soc.*, 2017, **139**, 17882; (k) K. Matsuoka, K. Albrecht, K. Yamamoto and K. Fujita, *Sci. Rep.*, 2017, **7**, 41780; (l) Z. Zhao, S. Gao, X. Zheng, P. Zhang, W. Wu, R. T. K. Kwok, Y. Xiong, N. L. C. Leung, Y. Chen, X. Gao, J. W. Y. Lam and B. Z. Tang, *Adv. Funct. Mater.*, DOI: 10.1002/adfm.201705609.
- (a) T. P. I. Saragi, T. Spehr, A. Siebert, T. Fuhrmann-Lieker and J. Salbeck, *Chem. Rev.*, 2007, **107**, 1011; (b) J. Liu, J. W. Y. Lam and B. Z. Tang, *Chem. Rev.*, 2009, **109**, 5799.
- (a) S. Hecht and J. M. J. Fréchet, *Angew. Chem., Int. Ed.*, 2001, **40**, 74; (b) L. Chen, S. Xu, D. McBranch and D. Whitten, *J. Am. Chem. Soc.*, 2000, **122**, 9302.
- (a) Y. Hong, J. W. Y. Lam and B. Z. Tang, *Chem. Commun.*, 2009, 4332; (b) M. Wang, X. Pan, X. Q. Fang, L. Guo, W. Q. Liu, C. N. Zhang, Y. Huang, L. H. Hu and S. Y. Dai, *Adv. Mater.*, 2010, **22**, 5526; (c) H. Wang, F. Li, I. Ravia, B. R. Gao, Y. P. Li, V. Medvedev, H. B. Sun, N. Tessler and Y. G. Ma, *Adv. Funct. Mater.*, 2011, **21**, 3770.
- (a) C. C. Kuo, C. H. Lin and W. C. Chen, *Macromolecules*, 2007, **40**, 6959; (b) S. Chuangchote, T. Sagawa and S. Yoshikawa, *J. Appl. Phys.*, 2008, **47**, 787; (c) L. Xu, H. W. Song, B. A. Dong, Y. Wang, X. Bai, G. L. Wang and Q. Liu, *J. Phys. Chem. C*, 2009, **113**, 9609; (d) H. J. Yen, C. J. Chen and G. S. Liou, *Chem. Commun.*, 2013, **49**, 630.
- (a) A. Qin, J. W. Y. Lam and B. Z. Tang, *Prog. Polym. Sci.*, 2012, **37**, 182; (b) Y. N. Hong, J. W. Y. Lam and B. Z. Tang, *Chem. Soc. Rev.*, 2011, **40**, 5361.
- (a) H. J. Yen and G. S. Liou, *Chem. Commun.*, 2013, **49**, 9797; (b) J. H. Wu and G. S. Liou, *Adv. Funct. Mater.*, 2014, **24**, 6422.
- (a) G. Hennrich, H. Sonnenschein and U. Resch-Genger, *J. Am. Chem. Soc.*, 1999, **121**, 5073; (b) R. Martínez, I. Ratera, A. Tàrraga, P. Molina and J. Veciana, *Chem. Commun.*, 2006, 3809; (c) J. Yoo, T. Kwon, B. D. Sarwade, Y. Kim and E. Kim, *Appl. Phys. Lett.*, 2007, **91**, 241107; (d) S. Seo, Y. Kim, Q. Zhou, G. Clavier, P. Audebert and E. Kim, *Adv. Funct. Mater.*, 2012, **22**, 3556; (e) J. Zhang, Z. Chen, X.-Y. Wang, S.-Z. Guo, Y.-B. Dong, G.-A. Yu, J. Yin and S.-H. Liu, *Sens. Actuators, B*, 2017, **246**, 570; (f) P. Audebert, G. Clavier and C. Allain, in *Progress in Heterocyclic Chemistry*, ed. G. W. Gribble and J. A. Joule, Elsevier, 2017, vol. 29, p. 483; (g) X. Wang, W. Li, W. Li, C. Gu, H. Zheng, Y. Wang, Y.-M. Zhang, M. Li and S. Xiao-An Zhang, *Chem. Commun.*, 2017, **53**, 11209; (h) S. Abraham, S. Mangalath, D. Sasikumar and J. Joseph, *Chem. Mater.*, 2017, **29**, 9877.
- (a) R. A. Bissell, A. P. de Silva, H. Q. N. Gunaratne, P. L. M. Lynch, G. E. M. Maguire and K. R. A. S. Sandanayake, *Chem. Soc. Rev.*, 1992, **21**, 187; (b) J. Kim, J. You and E. Kim, *Macromolecules*, 2010, **43**, 2322; (c) Y. Kim, Y. Kim, S. Kim and E. Kim, *ACS Nano*, 2010, **4**, 5277; (d) J. Sun, Y. Chen and Z. Liang, *Adv. Funct. Mater.*,

- 2016, **26**, 2783; (e) R. Chen, X. Gao, X. Cheng, A. Qin, J. Z. Sun and B. Z. Tang, *Polym. Chem.*, 2017, **8**, 6277.
- 11 (a) G. S. Liou and H. J. Yen, in *Polyimides, in Polymer Science: A Comprehensive Reference*, ed. K. Matyjaszewski and M. Möller, Elsevier BV, Amsterdam, 2012, vol. 5, pp. 497–535; (b) J. Sun, X. Lv, P. Wang, Y. Zhang, Y. Dai, Q. Wu, M. Ouyang and C. Zhang, *J. Mater. Chem. C*, 2014, **2**, 5365; (c) J. Sun, Y. Dai, M. Ouyang, Y. Zhang, L. Zhan and C. Zhang, *J. Mater. Chem. C*, 2015, **3**, 3356; (d) J. Sun and Z. Liang, *ACS Appl. Mater. Interfaces*, 2016, **8**, 18301.
- 12 H. J. Yen and G. S. Liou, *J. Mater. Chem.*, 2010, **20**, 4080.
- 13 J. Crivello, *J. Polym. Sci., Polym. Chem. Ed.*, 1976, **14**, 159.
- 14 (a) H. J. Yen and G. S. Liou, *J. Polym. Sci., Part A: Polym. Chem.*, 2008, **46**, 7354; (b) H. J. Yen, J. H. Wu, W. C. Wang and G. S. Liou, *Adv. Opt. Mater.*, 2013, **1**, 668.