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Tuning the bandgaps of polyazomethines containing triphenylamine by different linkage sites of dialdhyde monomers

Jiwei Cai^a, Haijun Niu^{a,b,*}, Cheng Wang^a, Lina Ma^a, Xuduo Bai^{a,**}, Wen Wang^c

^a Key Laboratory of Functional Inorganic Material Chemistry (Heilongjiang University), Ministry of Education, Key Laboratory Macromolecular Chemistry, Harbin 150086, PR China ^b Key Laboratory for Advanced Materials and Institute of Fine Chemicals, East China University of Science and Technology, Shanghai 200237, PR China ^c School of Material Science and Engineering, Harbin Institute of Technology, Harbin 150080, PR China

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ABSTRACT

Two series of conjugated aromatic polyazomethines (PAMs) have been designed and obtained by solution polycondensation of N,N'-bis(4-aminophenyl)-N,N'-di-2-naphthalenyl-4-benzene diamine, N,N'-bis(4-aminophenyl)-N,N'-di-1-naphthalenyl-(1,1'-biphenhyl)-4,4'-diamine with different aromatic dialdehydes, namely terephthalaldehyde, 1,3-isophthalaldehyde, phthaldialdehyde, 4,4'diformyltriphenylamine, 2,5-thiophenedialdehyde, respectively. The structures of polymers were characterized by means of FTIR, ¹H NMR spectroscopy, which showed an agreement with the proposed structure. All the polymers were amorphous determined by XRD technique with good solubility in many organic solvents, such as CHCl₃, THF, N-methyl-2-pyrrolidinone (NMP) and N,N'-dimethylacetamide (DMAc), and could be cast into tough and flexible polymer films. The morphologies of PAMs have been detected by atom force microscopy (AFM) which showed more planar surface.

All polymers displayed outstanding thermal stability, i.e. 20 wt% loss in excess of 515 °C under nitrogen atmosphere. Hybrid density functional theory (DFT) method was used to calculate the optimized geometry and electronic structure of PAMs. The calculated HOMO and LUMO energy levels of these polymers by theory method are in the range of -4.879 to -5.494 and -2.344 to -2.927 eV vs. the vacuum level, respectively, which are similar to the experiment results that indicated the PAMs would be used in organic layer electroluminescent diode (OLED) and photovoltagic cell as hole transporting materials or functional dyes. All obtained PAMs revealed excellent stability of electrochromic characteristics, changing color from original yellowish to red or blue. And multiple reversible colors states were observed upon I2, HCl, FeCl3, UV irradiation doping and dedoping. The properties prove that the PAMs are multifunctional materials which will be subject of hole-transporting, electrochromic, chemical sensor application in near future.

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1. Introduction

Conjugated polymers have been widely recognized as a new class of molecular semiconductors for electronic and optoelectronic devices, such as light emitting diodes [1], thin film transistors [2], and photovoltaic cells [3]. We are particularly interested in conjugated PAMs due to their documented excellent thermal, mechanical, electronic, optical, optoelectronic, and fiber forming properties [4-16]. PAM is isoelectronic with poly-phenylvinylene (PPV) which known as star molecular for OLED and photovoltagic cell, but PAM is easier to be prepared by polymerization of various aldehyde and amine monomers under gentle conditions than other conducting polymers. The energy gap of the PAM is liable to be tuned by changing the monomer with different donor or acceptor electronic properties, and protonation, complexation of carbon-nitrogen double bonded units in the main chain of PAM. Although in the most cases, PSB is insoluble in common solvents which hinder the development of research, many methods could be to enhance the processibility such as introducing bulk block in the main chain [17], longer alkyl groups in the ortho position of the aromatic rings [11a], polycondensation in a mixture of solvents or solvent/salt [18], inclusion of flexible spacers between main chain aromatic rings [19], and polymerization in the cyclodextrin cavity [20].

TPA is a unique star molecule possessing useful function such as redox activity, fluorescence and transport of positive charge via the radical cation species. Being efficient hole conductors, TPA is commonly used as photoconductor. Introducing

^{*} Corresponding author at: Key Laboratory of Functional Inorganic Material Chemistry (Heilongjiang University), Ministry of Education, Key Laboratory Macromolecular Chemistry, Harbin 150086, PR China. Tel.: +86 13684501571; fax: +86 0451 86608131.

^{**} Corresponding author. Tel.: +86 13684501571; fax: +86 0451 86608131. E-mail address: haijunniu@hotmail.com (H. Niu).

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tional materials such as promising candidates for photo-and electro-luminescence materials based on the synergistic effect of both of them, which arose much attention. Because of bulky, less trend of aggregation, three-dimensional TPA units along the polymer backbone, most of PAMs containing triphenylamine are amorphous and soluble in many organic solvents. Recently, the group of Sek has synthesized many PAMs containing 4,4'diformyltriphenylamine with various diamines and undertaken a detailed study of the structure spectroscopic properties [21]. From about the year of 2005, Liou have investigated deeply on a series of TPA-based high-performance polyimides, polyamides, polyazomethines with attractive electrochromic properties bearing triphenylamine deritives such as N,N'-bis(4-aminophenyl)-N,N'diphenyl -4,4'-biphenyldiamine, and N,N'-bis(4-aminophenyl)-N,N'-diphenyl-1,4-phenylenediamine [22]. They found that the polymer based on TPA as core exhibited stable, excellent, multicolor, electrochromic characteristic, furthermore the corporation of electron-donating substituents at the para positions of triarylamines afforded stable radical cations. The series of PAMs also have donor-acceptor architecture (-TPA-N=CH-Ar-CH=N-) and two kinds of basic nitrogen atoms, which can largely account for the diverse chromogenic phenomena observed. We also prepared PAMs synthesized by two kinds of diamines owned different conjugated length, conformation with five kinds of different substituted dialdehydes which owned various conjugated degrees [23], and observed unique and interesting optical functions similar to work of Sek [24] and contrary to the results of Jenekhe [25]. At the same time, we also investigated the influence of different diamines on the optical properties of PAMs.

In this paper, we demonstrate photochromism, acidichromism, electrochromism of ten kinds of novel PAMs with color and photoluminescence shift stimulated by irradiation, acid and electrooxidation. To the best of our knowledge, this is the first report on the design and discussion of the multifunctional PAMs based on N,N'-bis(4-aminophenyl)-N,N'-di-2-naphthalenyl-1,4- benzenediamine and N,N'-bis(4-aminophenyl)-N,N'-di-1naphthalenyl-[1,1'-biphenhyl]-4,4'-diam-inetriphenylamine containing naphthalene groups.

2. Experimental

2.1. Materials

N,N'-di(1-naphthyl)-4,4'-benzidine, was bought from Qinhuandao Bright Chemical Co. LTD., N,N'-di(2-naphthyl)-1,4-benzenediamine,1,3-isophthalaldehyde were purchased from TCI Co.; 2,5-thiophenedialdehyde was bought from Aldrich–Sigma Co.; Pd/C (10%) was purchased from Acros: 4-fluoronitrobenzene, triphenylamine, terephthalaldehyde, phthaldialdehyde, DMSO(dimethyl sulfoxide), DMF(N,Ndimethylformamide), NMP(N-methyl-2-pyrrolidinone), THF (tetrahydrofuran), N,N-dimethylacetamide (DMAc) were supplied from Sinopharm Chemical Reagent Co., Ltd., China and used as received. 4,4'-Diformyltriphenylamine was prepared by the Vilsmeier reaction according to the method described in the literature we had reported [26].

2.2. Synthesis of monomers

N,N'-bis(4-aminophenyl)-N,N'-di-2-naphthalenyl-1,4-benzenediamine (3), N,N'-bis(4-aminophen yl)-N,N'-di-1-naphthalenyl-[1,1'-biphenhyl]-4,4'-diamine (3') were synthesized with modified method in according to the literature [27,28] in Supporting information (shown in Scheme 1).

2.3. Synthesis of polymers

The synthesis of PId was used as an example to illustrate the general synthetic procedure. To a three necked 50 ml glass reactor fitted with a magnetic stirrer, Dean-stark trap and reflux condenser was charged with 0.542 g (1×10^{-3} mol) N,N'-bis(4-aminophenyl)-N,N'-di-2-naphthalenyl-1,4-benzene diamine (compound 3), and 10 ml DMAc, 3 ml of toluene. To the stirred solution was added 0.3013 g $(1 \times 10^{-3} \text{ mol})$ 4,4'-diformyltriphenylamine three times every 20 min, and the solution was heated at 160°C for 12 h to remove water under nitrogen reflux. After the reaction, the obtained polymer solution was poured slowly into 50 ml of ice frozen methanol. The precipitate was collected by filtration, washed thoroughly with hot methanol in a Soxhlet apparatus for 48 h, then was dried under vacuum at 70 °C overnight. Reprecipitations of the polymer by NMP/methanol were carried out twice for further purification. Yield: 0.4961 g, 64.34%, yellow.

FTIR spectrum (KBr pellet): 3434 (N-H stretching), 1694 (H-C=O stretching), 1625 (CH=N stretching), 1594, 1501, (aromatic ring of benzene), 1313, 1281(C-N stretching), 1167 (C-C stretching), 833 (p-substituted benzene), 696 (single substituted benzene).

¹H NMR (400 MHz, CDCl₃, ppm): 8.46 (d, –CH=N–): 7.75–7.72 (m, aromatic ring of benzene – CH=N–), 7.33–7.0 (m, aromatic ring of triphenylamie).

The other polymers were prepared by an analogous procedure and named as Scheme 2.

For comparison, we also prepared the series of polymers using HMPA as solvent according to the method of the literature [18] described in Supporting information.

2.3.1. Synthesis of Pla

Yield: 0.3547 g, 53.18%, reddish.

FTIR spectrum (KBr pellet): 3434 (N-H stretching), 1700 (H-C=O), 1622 (CH=N), 1595, 1498, (aromatic ring of benzene), 1300, 1279 (C–N), 1167 (C–C), 835 (p-substituted benzene).

¹H NMR(400 MHz, CDCl₃, ppm): 8.58 (d, –CH=N–), 8.07–7.63 (m, aromatic ring of benzene –CH=N–), 7.51–7.09 (m, aromatic ring of triphenylamie).

2.3.2. Synthesis of PIb

Yield: 0.2843 g, 42.62%, yellow.

FTIR spectrum (KBr pellet): 3433 (N-H stretching), 1700 (H-C=O), 1625 (CH=N), 1595, 1498, (aromatic ring of benzene), 1306, 1278 (C-N), 1171 (C-C), 832 (p-substituted benzene), 687 (single substituted benzene).

¹H NMR (400 MHz, CDCl₃, ppm): 8.39 (d, –CH=N–), 7.78–7.57 (m, aromatic ring of benzene – CH=N–),7.50–7.09 (m, aromatic ring of triphenylamie).

2.3.3. Synthesis of PIc

Yield: 0.1517 g, 22.74%, grey.

FTIR spectrum (KBr pellet): 3419 (N-H stretching), 1715 (H-C=O), 1627 (CH=N), 1595, 1499, (aromatic ring of benzene), 1359, 1270 (C-N), 1159 (C-C), 831 (p-substituted benzene), 685 (single substituted benzene).

¹H NMR (400 MHz, CDCl₃, ppm): 7.94 (d, –CH=N–), 7.76–7.56 (m, aromatic ring of benzene –CH=N–), 7.38–6.94 (m, aromatic ring of triphenylamie).

2.3.4. Synthesis of Ple

Yield: 0.3691 g, 54.28%, deep red.

FTIR spectrum (KBr pellet): 3428 (N-H stretching), 1669 (H-C=O), 1627 (CH=N), 1596, 1497, (aromatic ring of benzene), 1311, 1278 (C–N), 1189 (C–C), 8.13 (p-substituted benzene), 719 (single substituted benzene).



Scheme 1. Synthesis of monomers.





¹H NMR (400 MHz, CDCl₃, ppm): 8.65 (d, –CH=N–), 7.84–7.52 (m, aromatic ring of benzene –CH=N–), 7.43–7.0 (m, aromatic ring of triphenylamie).

2.3.5. Synthesis of PIId

Yield: 0.7114 g, 83.99%, yellow.

FTIR spectrum (KBr pellet): 3428 (N–H stretching), 1698 (H–C=O), 1625 (CH=N), 1594, 1505, 1492, (aromatic ring of benzene), 1313, 1285, (C–N), 1168 (C–C), 821 (p-substituted benzene), 697 (single substituted benzene).

¹H NMR (400 MHz, CDCl₃, ppm):8.39 (d, -CH=N-), 7.98–7.70 (m, aromatic ring of benzene -CH=N-), 7.48–7.0 (m, aromatic ring of triphenylamie).

2.3.6. Synthesis of PIIa

Yield: 0.2811 g, 37.38%, red.

FTIR spectrum (KBr pellet): 3434 (N–H stretching), 1701 (H–C=O), 1610 (CH=N), 1589, 1492, (aromatic ring of benzene), 1308, 1265 (C–N), 1156 (C–C), 824 (p-substituted benzene), 695 (single substituted benzene).

¹H NMR (400 MHz, CDCl₃, ppm): 8.52 (d, –CH=N–), 8.0–7.79 (m, aromatic ring of benzene –CH=N–), 7.49–7.08 (m, aromatic ring of triphenylamie).

2.3.7. Synthesis of PIIb

Yield: 0.5450 g, 72.47%, yellow.

FTIR spectrum (KBr pellet): 3434 (N–H stretching), 1702 (H–C=O), 1623 (CH=N), 1593, 1492, (aromatic ring of benzene),

1311, 1289 (C–N), 1169 (C–C), 822 (p-substituted benzene), 688 (single substituted benzene).

¹H NMR (400 MHz, CDCl₃, ppm): 8.52 (d, –CH=N–), 7.98–7.78 (m, aromatic ring of benzene –CH=N–), 7.48–7.08 (m, aromatic ring of triphenylamie).

2.3.8. Synthesis of PIIc

Yield: 0.4922 g, 75.49%, red.

FTIR spectrum (KBr pellet): 3410 (N–H stretching), 1715 (H–C=O), 1605 (CH=N), 1571, 1507, 1492 (aromatic ring of benzene), 1312, 1287 (C–N), 1180 (C–C), 821 (p-substituted benzene), 703 (single substituted benzene).

¹H NMR(400 MHz, CDCl₃, ppm): 8.03 (d, –CH=N–), 7.9–7.64 (m, aromatic ring of benzene –CH=N–), 7.48–7.28 (m, aromatic ring of triphenylamie).

2.3.9. Synthesis of PIIe

Yield: 0.7241 g, 95.52%, deep-red.

FTIR spectrum (KBr pellet): 3433 (N–H stretching), 1641 (H–C=O), 1604(CH=N), 1570, 1491, (aromatic ring of benzene), 1311, 1290 (C–N), 1167 (C–C), 822 (p-substituted benzene), 713 (single substituted benzene).

¹H NMR(400 MHz, CDCl₃, ppm): 8.55 (d, –CH=N–), 7.9–7.73 (m, aromatic ring of benzene –CH=N–), 7.48–7.0 (m, aromatic ring of triphenylamie).

2.4. Measurements

Fourier transform infrared (FT-IR) spectra were recorded on a PerkinElmer Spectrum 100 Model FT-IR spectrometer. ¹H NMR spectra were measured on a Bruker AC-400 MHz spectrometer in CDCl₃, using tetramethylsilane as an internal reference. Gel permeation chromatographic (GPC) analysis was performed on a Waters instrument connected with one refractive index detector. All GPC analyses were performed using a polymer/THF solution at a flow rate of 1 ml/min at 70 °C and calibrated with polystyrene standards. Thermogravimetric analysis (TGA) was conducted with a PerkinElmer Pyris 6 TGA. Experiments were carried out on approximately 6-8 mg powder samples heated in flowing nitrogen or air (flow rate = 20 cm³/min) at a heating rate of 10 °C/min. DSC analyses were performed on a PerkinElmer Pyris diamond DSC at a scan rate of 10°C/min in flowing nitrogen (20 cm³/min). X-ray diffraction patterns were recorded using powder samples on a wide-angle $D/max-\gamma B$ diffractometer working in typical Bragg geometry with CuK α radiation (λ = 0.154 nm). UV-vis absorption spectra were recorded using a SHIMADZU UV-3600 spectrophotometer whereas the photoluminescence solution spectra were registered on a Jasco FP-6200 spectrometer with 450 W xenon lamp as the light source. The emission spectra of polyazomethines were taken at λ_{exc} being equal to about the wavelength of the absorption maximum.

Cyclic voltammetry (CV) measurements were conducted on a CH Instruments 660A electrochemical analyzer at a scan rate of 50 mV s^{-1} with a 0.1 M solution of LiClO₄ as an electrolyte under nitrogen atmosphere in dry acetonitrile (CH₃CN). The oxidation and reduction potentials of polymer film coated on a ITO disk were measured using a Pt wire and a Ag/AgCl electrode as a counter electrode and a quasi reference electrode, respectively. Under these conditions, the onset of oxidation and reduction potentials of the polymer thin films against the Ag/AgCl quasi reference electrode were measured and calibrated against the ferrocene/ferrocenium (Fc/Fc⁺) redox couple. The HOMO and LUMO levels of the polymers were calculated by assuming the absolute energy level of Fc/Fc⁺ as -4.80 eV to vacuum.

The morphology observation of the samples was carried out on AFM (Nanoscope Ia digital instrument, VECCO Co.) equipped with a silicon cantilever (typical spring constant $40 \, \text{Nm}^{-1}$) in tapping

mode under ambient conditions. Photographs of the polymer films were taken by using a Panisonic (DMC-LZ2) digital camera.

Density-functional theory (DFT) calculations were performed on a computer. Geometry optimizations were carried out using the B3LYP functional as implemented in Gaussian 98 program [29].

2.4.1. Synthesis of iodine-doped polyazomethine

A solution (CHCl₃) cast film of the polymers on a quartz slide was put into chamber filled with iodine crystals and stored for 36 h. The original orange film turned to black.

2.4.2. Synthesis of HCl-doped polyazomethines

The powders of the polymers were kept a closed chamber filled with HCl vapor at ambient temperature for 36 h. The original orange or red film all turned to dark red.

2.4.3. Synthesis of FeCl₃ doped polyazomethines

Some FeCl₃ powders were put into the solution (CHCl₃) of polymers and shaken for several minutes.

2.4.4. Synthesis of UV doped polyazomethines

The solution of polyazomethines (in $CHCl_3$) was exposed under the UV lamp with the power of 15 W at the exciting wavelength of 365 nm.

2.5. Device fabrication and test

The solutions of polymers in CHCl₃ were spin-coated onto indium tin oxide (ITO) electrodes laminated on ITO-coated glass substrate (15–25 Ω /square, ShenZhen Nanbo Technologies Ltd.) to form electrochromic layers. The electrolyte was prepared by adding LiClO₄ in dry acetonitrile. Electrochromic devices with a sandwich structure of ITO/electrochromic polymer/electrolyte/ITO were then fabricated under atmospheric conditions.

3. Results and discussion

3.1. Synthesis of monomers

All monomers were synthesized using modified literature procedures. In general, many series of dinitrotriphenylamines are synthesized by the nucleophilic amination of aromatic amine and 4-fluoro-1-nitrobenzene under nucleophilic displacement conditions using a base CsF. But the CsF is expensive, and the yields with K_2CO_3 as base are low and the work-up need long time. So we substituted CsF by NaH, which gave high yields of dinitrotriphenylamine and less mono-substituted side product. Reduction of the dinitro intermediates was carried using 10% Pd/C in DMF in autoclave with high pressure H₂ and resulted in a near quantitative yield of diaminotriphenylamine derivatives without producing toxicity to atmosphere by using hydrazine as reductor and needing tedious process by using SnCl₂. Especially, the high pressure H₂ can convert the little raw materials to be soluble in the solution to be got rid of easily.

IR and ¹H NMR spectroscopic techniques were used to identify the structures of the intermediate compounds and the diamine monomers. The transformation of nitro to amino group could be revealed by the change of IR spectra. The nitro groups of intermediate compounds gave two bands at about 1587 and 1316 cm⁻¹ (-NO₂ characteristic symmetric and symmetric stretching vibration). After reduction, the typical absorptions of the nitro group disappeared and the amino group displayed the typical two N–H stretching absorption peaks in the region of 3300–3500 cm⁻¹. The ¹H NMR spectra confirm that the nitro groups have been completely



Fig. 1. FT-IR spectra of PIa-PIe.

transformed into amino groups by the resonance signals at around 3.6 ppm corresponding to the amino protons.

3.2. Synthesis of polymers

The TPA-based PAMs were prepared from dialdehyde and diamines using a simple one-step high-temperature solution polycondensation condensation procedure without catalysts and under N₂ atmosphere conditions. No attempts were undertaken to endcap the polymer chain ends or optimize the polymerization conditions with anhydrous LiCl or CaCl₂ as a water scavenger. The bulk TPA reduced the rigid-rod conformation to improve the processability of PAMs. The yield of the polymers was in the range of 37.38-95.52% (except PIc). All the PAMs could afford transparent films with good optical quality via solution casting. Structures of the PAMs were confirmed by FTIR and ¹H NMR (shown in Figs. 1 and 2 and Fig. S2). The strong absorption peaks at 1627 cm⁻¹ are attributed to the vibration of bond of C=N, while the chemical shifts in the range of 7.49-8.65 are ascribed to the proton at the H–C=N. When the PAMs were doped with electrochemical oxidation or I_2 , the C=N vibration shifted to 1618 cm^{-1} , with the vibration energy decreasing. The lower wavenumber of the imine group absorption indicates the better conjugation of π -electrons which suggested that the quinoid structure have formed. However, when the PAM was doped with HCl, the stretching vibration of C=N shifted to 1629 cm⁻¹, high energy area, which was assigned to the formation of C=NH⁺ (see Fig. S5).



Fig. 2. ¹H NMR spectra of PIa-PIe.

We also tried to use hexamethylphosphoramide (HMPA) as catalyst in according to the literatures [18], but found that the optical properties of products were different from the ones prepared without HMPA, therefore we did not select HMPA as catalyst. The result maybe was responsible for the complex forming from PAMs doped with HMPA.

3.3. Polymer solubility and morphology

The X-ray diffraction studies of the TPA-containing PAMs indicated that all the polymers were essentially amorphous. The solubility behavior of the PAMs depended on their chain packing ability and intermolecular interactions which was affected by the rigidity, symmetry, and regularity of the molecular backbone. The introduction of TPA group increases solubility of the polymers. So, the resulting PAMs showed good solubility in common organic solvents, such as CHCl₃, DMSO, NMP, DMAC, DMF, THF.

The film morphology of the active layer is very important to the performance of polymer solar cells and OLEDs. Thus, the film morphology of PAMs was studied. In common, the rate limiting step in the electrochromic switching process involves diffusion of dopant counterions into the polymer structure. So, the polymer morphology plays an important role in determining velocity of the electrochromic switching. In order to achieve sufficient speed, the morphology should be controlled to minimize the diffusion distance in PAMs. Films on the glass substrate were obtained by dissolving at room temperature the compound in chloroform to form a homogenous solution. Residual solvent was removed by heating the film. How the chemical structure of PAMs influence the surface morphologies were determined by atomic fore microscopy AFM. Fig. 3 showed a amorphous structure, depression of PIa, PId, PIIa and PIId on a Si wafer. The films of PAMs exhibit distinct phase separation into islands. All the samples show ordered linear structures and terraces-like structures oriented with different angles to each other, without preferred direction. Small grains about 30 nm diameter homogenously distributed can be noted on topography. Roughness and root-mean-square roughness (Ra, Rms) are determined to be 0.553-2.700 nm and 0.690-3.117 nm, respectively. This surface morphology suggests the presence of channels or pinholes in the film which be favor to transport counterions. These results were in accordance to UV-vis spectra and XRD measurements. The results suggest that the morphologies were dependent on the molecular structures, and convolution of molecules assembled during the vaporization of solvents. The molecular configuration was also optimized by method of molecular simulation which will be depicted in the following section

3.4. Thermal properties

The weight-average molecular weight (M_w) and polydispersity (PDI) were determined as 2678–11,435 and 1.35–1.89, respectively (Table 1). In general, the M_ws of polymers containing amine 3' are larger than the ones containing amine 3 unit which may be due to steric hindrance that makes the latter possessing high weight more insoluble than the former. From the M_n , the polymer has about average 5 units.

As shown in Table 1, the thermal properties compared with the analogous PAMs, the series of PAMs did not showed clear T_g but showed an enhanced thermal stability (Fig. 4). Because of the decreased conformational flexibility or free volume caused by the introduction of planar napthalene groups in the repeat unit. All the polymers indicated no clear melting endotherms up to the decomposition temperatures on the DSC thermograms.



Fig. 3. AFM images of Pla, Pla (upper), Pld, Pld (below) in tapping mode of PAMs coated on ITO (silicon substrates was cured at 120 °C).

Table 1
Thermal properties and molecular weights of the PAMs.

	5%	20%	50%	Mn	M _w	Mz	PDI polydispersity
PIa	452	551	>700	2250	3252	4309	1.44
PIb	399	526	>700	1900	3216	4881	1.69
PIc	426	525	>700	1731	2678	3604	1.55
PId	453	515	>664	4230	7982	12,450	1.89
PIe	419	557	>700	3447	4656	6286	1.35
PIIa	363	562	>700	3062	4387	6852	1.43
PIIb	244	542	>700	7233	10,212	14,621	1.41
PIIc	218	534	>700	3624	5015	6824	1.38
PIId	458	542	>665	5039	8024	12,400	1.59
PIIe	281	520	>700	6980	11,435	16,814	1.63



Fig. 4. TG diagrams of Pla-Ple.

In according to the literature [30], the weight loss below 400 $^{\circ}$ C could be attributed to out-gassing of residual monomer species such as TPA and H₂O. The latter is thought to be due to a post-polycondensation process, where amine and aldehyde end groups in the polymer continue to react and water is expelled.

Thermal stability of the PAMs was evaluated by TGA measurements in nitrogen atmospheres using 5 and 20 wt% loss values for comparison. Typical TGA curves for Pla–Ple are illustrated in Fig. 6. Almost all the PAMs did not show remarkable weight loss before 200 °C in nitrogen atmosphere. The $T_{\rm ds}$ (the decomposed temperature) at 20% weight loss of the (Pla–Ple) in nitrogen stayed in the range of 515–557 °C, respectively. They left more than 50% char yield at 700 °C in nitrogen. The TGA data indicated that these PAMs had fairly high thermal stability.

3.5. UV-vis absorption and photoluminescence

The optical properties of the PAMs were investigated by UV–vis absorption and PL spectroscopy. The results are summarized in Table 2.

3.5.1. UV-vis spectra and salvatochromism

UV-vis maximum peaks of PIa-PIe in CHCl₃ and in NMP in the range of 410-487 nm were shown in Fig. 5 and Fig. S6, respectively. For example, PIa showed the peak at 456 nm, assignable to the π - π ^{*} transition resulting from the conjugation between the aromatic rings and nitrogen atoms. The maximum absorption of PAMs indicated an obvious bathochromic shift compared to that of the corresponding monomers (such as 322 nm of N,N'-bis(4-aminophenyl)-N,N'-di-2-naphthalenyl-1,4benzenediamine or 383 nm of 4,4'-diformyltriphenylamine). It was clear that the polymerization of monomers resulted in the extension of the π system along the polymer backbone due to the π - π ^{*} transitions of the aromatic chromophores, naphthylamine and TPA units. The polymers solutions appeared yellow-orange to red whereas the monomers showed colorless. In the same monomer amine series (such as monomer 3 series), the absorption peaks presented in the order: $\lambda_{P_e} > \lambda_{P_c} > \lambda_{P_a} > \lambda_{P_d} > \lambda_{P_b}$, as the author expected, which indicating $P_{\rm b}$ (polymerization with 1,3isophthalaldehyde) has the lest conjugated structure and P_e with S donor atom owed the best conjugated form. It is worth to be noted that phthaldialdehyde was not generally used as monomer in polymerization, but the PIc showed interesting properties which have longer λ than even that of PIa, because the conjugated structure was prolonged.

The maximum absorption peaks of PI and PII series in solid film hyperchromically shifted by 0–20 nm with respect to that in solution which means that the PAMs are not apt to aggregation due to the propeller structure of triphenylamine.

The UV–visible spectra of PII series are blue shifted to short wavelength, compared with the corresponding PI series, which is indicating that the introduction of a biphenyl unit between the imine groups in PIIa has great influence on absorption shift in UV–visible spectra. The observed changes of the optical absorption spectra when the backbone structure is varied can be attributed to the modification of the polymer chain planarity. The phenomena is identical to the result calculated and will be discussed in conformation section.

The solvatochromism and protonation of the PAMs in different solvents were examined to study the influence of the solvent polarity and the protonating agent on the absorption and emission wavelength of the 10 multi-bifunctional oligomers. The two results (solvatochorim and protonation) showed different as follows.

The maximum peak also depends on the polarity of solvent. For example, as shown in Fig. 5, Figs. S6 and S7, the PI series of polymers exhibited maximum UV-vis absorption at 403-479 nm in NMP solutions but showed maximum UV-vis absorption at 410–487 nm in CHCl₃ solutions which displayed obvious negative solvatochromism. With an increase in the solvents polarity from chloroform to NMP, and consequently with increase in the solvent of dipole moment (μ = 1.01D for CHCl₃, μ = 4.09D for NMP, μ = 1.61D for *m*-Cresol), the peak located at the long wavelength is blue shifted in NMP solution. The result is similar to the report of Sek [24], contrary to the positive solvatiochromism result of Jenekhe [25], which indicating that the charge-transfer nature of the absorption band and that the ground state is more stabilized than the excited state of PAM. We supposed that the interesting phenomena maybe was also induced by complexion of the acid H proton in the certain solvent such as CHCl₃, *m*-Cresol (see the curves in Fig. S7). Phenol is much more acidic than aliphatic



Fig. 5. UV-visible absorption spectra of PI series and PII series in CHCl₃.

alcohols (pKa < 10) and in some cases is capable of protonating polymer with basic centers.

3.5.2. PL spectra measurement

Fig. 6 also shows the PL spectra of PAMs measured in CHCl₃ (conc.: 10^{-6} mol/L). PL quantum yields φ of the samples in different solvents were measured by using quinine sulfate dissolved in 1 N sulfuric acids a reference standard (φ = 0.546). The quantum yields of these polymers after refractive index correction can be calculated according to the following equation [31]:

$$\phi_{\text{unk}} = \phi_{\text{std}} \left(\frac{I_{\text{unk}}}{I_{\text{std}}} \right) \left(\frac{A_{\text{std}}}{A_{\text{unk}}} \right) \left(\frac{\eta_{\text{unk}}}{\eta_{\text{std}}} \right)^2$$

where ϕ_{unk} , ϕ_{std} , I_{unk} , I_{std} , A_{unk} , A_{std} , η_{unk} , and η_{std} are the fluorescent quantum yield, integration of the emission intensity, absorbance at the excitation wavelength, and the refractive indices of the corresponding solutions for the samples and the standard, respectively. Here, we use the refractive indices of the pure solvents as those of the solutions. The aromatic PI series exhibited PL emission maxima around 600 nm in CHCl₃ solution with PL quantum yield relatively low φ below 1% compared to PPV. Obviously, the diamines 3 and 3' emitted faintly as soon as they copolymerized with corresponding dialdehydes, whereas the photoluminescence of the 3 and 3' is clearly seen by the naked eyes. This phenomenon can possibly be attributed to non-planar of the whole PAM molecules, a higher rate of radiationless decay, the strong acceptor characteristic of formed C=N structure, and the intramolecular photoinduced electron transfer (PET) from triphenylamine to aldehyde in both PI and PII [32].



Fig. 7. Cyclic voltammograms for polymers in CH₃CN/0.1 M LiClO₄ with ferrocene/ferrocenium (Fc/Fc⁺) as an internal standard, at 50 mV s⁻¹. Black are representing PI series; red are representing PI series. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article.)

3.6. Electrochemistry properties

To further understand the electronic structures of the polymers, and then provide key parameters for the design of devices, it is necessary to determine the energy levels of the HOMO and the lowest unoccupied molecular orbital (LUMO) of the conjugated polymers. Thus, the electrochemical characteristics of the polymers films on a Pt electrode were investigated by cyclicm voltammetry (CV) with Bu_4NPF_6 (0.1 M in acetonitrile) as the electrolyte and Ag/Ag⁺ electrode as reference electrode at a scan rate of 50 mV s⁻¹, and the results are summarized in Fig. 7 and Table 2. In the voltammograms, the redox peaks have been associated with reduction–oxidation process accompanying the double injection/extraction of Li⁺ ions and electrons. Both polymers exhibit two obvious oxidation peaks: the first reversible one corresponds to the oxidation of the TPA moiety, and the other is attributed to the formation of the TPA²⁺ radical ion. To obtain accurate redox potentials, the reference electrode was calibrated by the ferrocene/ferrocenium (Fc/Fc⁺),

Table 2
Optical and electrochemical properties for PAMs.

	$\lambda^{abs}_{solution}/\lambda^{abs}_{film}$	$\lambda^{PL}_{solution}$	λ_{onset}^{abs}	$\phi_{\rm (CHCl_3)}\%$	Epeak vs. Ag/AgC1	$E_{\text{onset}}^{\text{peak}}$ vs. Ag/AgC1	$E_{\rm HOMO}^{\rm electro}$	$E_{\rm LUMO}^{ m electro}$	$E_{\rm g}^{ m solution}$	$E_{\rm HOMO}^{\rm quntum}$	$E_{\rm LUMO}^{ m quntum}$	E_{g}^{quntum}
PI	a 456/455	610	528.3	0.011	1.139	0.449	-4.879	-2.579	2.35	-4.886	-2.227	2.659
PI	b 410/398	590	424.4	0.019	1.476	0.882	-5.312	-2.472	2.92	-4.859	-1.965	2.894
PI	c 462/462	459	542.6	0.010	1.484	0.892	-5.322	-2.362	2.29	-4.889	-2.264	2.625
PI	d 424/422	574	488.7	0.014	1.540	0.995	-5.425	-2.895	2.53	-4.759	-1.872	2.887
PI	e 485/482	612	578.8	0.062	0.496	0.286	-4.716	-2.566	2.15	-4.879	-2.519	2.360
PI	Ia 429/437	503	511.7	0.026	1.500	0.917	-5.347	-2.927	2.42	-4.708	-2.085	2.623
PI	Ib 392/402	495	468.5	0.033	1.224	0.779	-5.209	-2.529	2.65	-4.759	-1.789	2.97
PI	Ic 457/456	500	520.8	0.428	1.432	0.904	-5.334	-2.344	2.38	-4.779	-1.982	2.797
PI	Id 416/417	505	479.3	0.216	1.732	1.064	-5.494	-2.914	2.58	-4.577	-1.796	2.781
PI	le 479/471	598	555.7	0.007	0.652	0.261	-4.691	-2.461	2.23	-4.694	-2.115	2.579



Fig. 8. Electronic absorption spectra of PIe and PIIe in the process of electrochemical p-type doping between 0.0 and 1.2 V with 0.05 V potential intervals (insets are the pictures of doped PAMs).

whose redox potential is assumed to have an absolute energy level of -4.80 eV to vacuum. As a result, the HOMO energy values were calculated using the equation [33]

$$E_{\text{HOMO}} = -e(E_{\text{ox vs Ag/AgCl}} + 4.43) \text{ eV}$$

where $E_{\rm ox}$ is the onset oxidation potential vs. Ag/AgCl. The HOMO energy values of PIIe and PIId were calculated to be at in the range from -4.691 to -5.494 eV.

The LUMO energy levels of the polymers are estimated from the HOMO energy levels and E_g using the equation

$$E_{\rm LUMO} = E_{\rm HOMO} + E_{\rm g}^{\rm opt}$$

due to the reduction curves could hardly be obtained, which is at bewteen -2.344 (PIIc) to -2.927 (PIIa)eV.

$$E_{\rm g}$$
 (eV) = $\frac{1240}{\lambda_{\rm onset}}$ (nm)

In the PAM containing the same amine monomer, P_e showed the highest HOMO, and the P_d exhibited the lowest HOMO. The rule was the same as that of UV–visible absorption. The different site linked aldheyde played the key role in the electron structure and regulated the gaps of PAMs. The energy level predicted that the conjugated PAMs also can be suitable for different goal such as OLED or solar energy cell.

3.7. Electrochromic properties

The spectroelectrochemical properties of the polymer solution were monitored by a UV–vis spectrometer at different applied potentials. The absorption spectral changes of PIe and PIIe are shown in Fig. 8, which exhibit that λ_{max} value for the π – π * transitions of pristine PIe is centered at 485 and PIIe is centered at 470 nm, respectively. When the applied external potential was gradually raised from 0.6 to 1.2 V, the absorption intensity at 470 nm of PIIe slightly decreased, while two new peaks at about 311 nm and 619 nm appeared. The new spectrum was assigned to the cationic radical PAM^{+•} [22]. Meanwhile, the PIIe film color changed from yellow to red. When the applied potential was higher than 1.5 V, the film color was changed from red to purple which is different to which changed from green to dark blue in Ref. [22].

The purple film was not very stable and dissolved in solution. Stepwise oxidation of the polymer films by applied external potentials also resulted in a decrease in the π - π * transitions and their lower energy transitions intensified at 633 for Ple and 619 nm for Plle, respectively. Since neutral state absorptions for Ple and Plle were at 485 and 470 nm and lower energy transition emerged at 633 and 619 nm, partially oxidized polymer solution revealed

blue–green color for PIe and blue for PIIe. Further oxidation of PIe and PIIe films resulted in blue color due to diminished π – π * transition intensity, respectively. A similar spectral change was observed for other PAMs of PIa–PIe series and the corresponding PIIa–PIIe series.

The dynamic optical behavior of the device was measured. A wavelength of 424 nm was selected as the reference wavelength due to the maximum value of optical contrast. In potential-step experiments performed shown in Fig. 9a, the switching time is set every 5 s between neutral and oxidized states. The optical switch is fast and fully reversible. Examining a single transition more closely (Fig. 9b) shows that the switching time between these two extreme redox states is about 1 s. After over continuous 50 cyclic switches between 0.00 and 1.35 V, the polymer films still exhibited good stability of electrochromic characteristics.

3.8. Acidchromic properties

As seen from the spectra (Fig. 10), initially neutral PIa and PId in solution have the absorption maxima at 456 and 424 nm, respectively. Upon continual exposure of HCl vapor, new absorption bands emerged at 596 and 567 nm which were accompanied by a decrease in neutral state absorptions. Neutral solutions of two kinds of polymers were yellow and yellow-green, however upon the exposure of HCl vapor, the solution turned into blue and violet as is shown as inset pictures in Fig. 9 for PIa and PId, respectively. It is probably because the protonation on the nitrogen of the imine linkage by acid results in the backbone planarization, which leads to an increased π -electron delocalization. This also conforms the fact that the triphenylamine is a much stronger electron-donating moiety and protonation of the C=N in PAMs results in a much stronger electron-accepting group, thereby enhancing charge separation of π -electrons in the conjugated donor-acceptor structure is realized. Absorption spectra for PIa and PId revealed isosbestic point in solution form which confirms the coexistence of discrete chromophores. That also eased the detection of different colors for PIa and PId solutions upon HCl vapor or acid addition in solution.

Further exposure of the solution to ammonia vapor reversed the polymer to the initial absorption for the polymers (shown in inset of Fig. 10). The ammonium chloride formed during the deprotonation steps remained trapped in the solution which made the solution some opaque. This indicates the reversibility of solution doping process by adding HCl and pH responsive characters of polymers.

In camphorsulfonic organic acid solution, like HCl, due to doped with H⁺, the lowest-energy absorption maximum peak is red-shifted to longer wavelength at 546 nm (see the spectra in Fig. S7). The difference of absorption of PAM doped with from



Fig. 9. Double-potential-step chronoamperommetry (a) and a single transmittance at 424 nm (b) ($E_1 = -0.1$ V (the fully neutral state) and $E_2 = 1.5$ V (fully oxidized state)) of Pld in a 0.1 mol l⁻¹ LiClO₄/CH₃CN solution (a) 1st cycle and (b) 28th cycle. One cycle corresponds to one double-potential-step.

camphorsulfonic acid to HCl maybe is due to that camphorsulfonic acid which is more interacting agent, forming stronger force than inorganic acid, thus lowering chain conformational planarity being caused either by steric effects or by interactions with dopants, reduces this overlap and widens the band-gap.

3.9. Doped upon oxidation with FeCl₃ and UV exposure

The compounds were additionally oxidized chemically with $FeCl_3$ to confirm their stability. As seen in Fig. 11, the PIId



Fig. 11. UV-visible spectra of PAMs (PIId) doped with FeCl₃ for 0–15 min.



Fig. 12. Spectra of Pld recorded in anhydrous and deaerated $\rm CHCl_3$ under UV at 365 nm for 10, 20, 30, 40, 50 s.

undergoes significant color changes similar to those obtained anodically. The absorbance at 423 nm, corresponding to the neutral state of PIId, decreases concomitant with the formation of a new peak at 572 nm. It can be concluded that the oxidized species are stable since their color is persistent and does not dissipate with time, which otherwise is indicative of decomposition. The stability of PIId and its oxidized form is further epitomized by the reversible change in absorbance intensity with the addition of hydrazine. The same phenomena take place in PIa–PIe series and PIIa–PIIe series.

Fig. 12 shows the UV–vis absorption spectra of the Pld in CHCl₃ under UV irradiation, respectively. Yellow solution of pristine Pld



Fig. 10. UV-visible spectra changes upon PIa and PId doped with HCl vapor.



Fig. 13. Calculated optimum configuration of PIa and PIIa.

changed their color to reddish-violet under the UV irradiation of 365 nm light from 0 to 50 s at room temperature. The color change was dependence of the irradiation time. When the irradiation time increased from 0 to 50 s, the peak of the absorption at 424 nm of PId decreased gradually, whereas one new band grew at 537 nm and increase gradually and the polymer doped with photoirradiation can be recovered by adding the hydrate to the solution. However, the recovered absorption peak was hypsochromic shifted compared with pristine solution after being dedoped with hydrazine hydrate, suggesting there was some degradation in the process of being doped. We also determined the polymers in NMP solution and PMMA matrix in the same concentration, however, it was strange that no such phenomenon took place. The CHCl₃ seemed to decompose and emit Cl₂ under the UV irradiation. So the result was attributed to the reaction of Cl with the PId. The dramatic color changes can be explained by the different electronic states (proton tautomerism) and configuration rearrangement of the π electrons resulting from the photoirradiation [34]. The variation of the absorption spectra of the TPA-based PAMs with acidity, metal complex and Cl₂ suggests that these polymers may have potential applications for chemical sensors.

3.10. Quantum chemistry calculation

In order to obtain deeper insight into the polymer structure–property relationships, ground-state geometry

optimizations and energy levels of oligomer of PI and PII series, were carried out using density functional theory at the B3LYP/6-31G level.

The average C–C bond lengths (C4–C5) between the N3=C4 linkage and phenylene ring of PIa-PIe are in the range 1.449-1.466Å and of PIIa-PIIe are in the range 1.386-1.540 Å, respectively, while the C=N bond lengths (N3=C4) are in the range of 1.244–1.386 Å (shown in Fig. 13). The bonds in PII series are more average than those of PI series. The torsional angles (φ_2) between the C=N linkage and adjacent phenylene or thiophene ring (with aldehyde group) are in the range of 179.0-180.0, which suggest that monomer (with aldehyde group) unit part has a planar conformation which is same to the part of monomer (N-phenylene ring) unit. The replacement of the phenylene ring (with aldhyde group) by thiophene and triphenylamine or alternation of the site of substitution of group, has no influence on the dihedral angle φ_1 and φ_2 . It is contrary to the results in our previous work [23] that the conformation was dependence on the phenylene ring (with aldhyde) intensely. This may be explained by that the diamine played the key role in the conformation of PAMs.

To better understand the evolution of the oxidation and reduction potentials, the electronic structures of the polymer series (as isolated oligomers) were evaluated by using DFT at the B3LYP/6-31G level of theory; the highest-occupied molecular orbital (HOMO) and lowest-unoccupied molecular orbital (LUMO) energies and HOMO–LUMO energy gaps (E_g) are given in Table 2.



Fig. 14. Pictorial representations of the electron density in the frontier molecular orbitals of repetition units for PIa–PIe and PIIa–PIIe in the order.

Pictorial representations of the frontier molecular orbitals of PI and PII series are shown in Fig. 14, which illustrate that the electron density distribution of the HOMO state of the basic unit (ground state) was mainly located on diamine moiety for electronic state of the first oxidation state, and that of the LUMO state of the basic unit was mainly located on dialdhyde and extended to the C=N moiety. Seen from Fig. 14, it is obvious that the electronic density contours show that the electron lone pair of the nitrogen atoms have strong coupling with π electrons. This leads to an intramolecular charge transfer with significant distribution of the electronic density over the entire molecule. The large conjugated area provides an extended region across which the excited state can be efficiently dissipated. The quantum calculation suggests that the fluorescence is efficiently quenched by intramolecular photoinduced electron transfer (PET) that occurs from the amine HOMO to the LUMO of both the CH-aryl and azomethine moiety.

The dialdehydes play key role in LUMO and HOMO energy levels in the similar manner. In the same serials of PAMs, the different aldehydes with different degree of conjugation can tune the gap. The trend of E_g for the oligomer series follows in the order: $P_{e(thiophene)} < P_{a(terephthalaldehyde)} \approx P_{c(phthaldialdehyde)} < P_{d(triphenylamine)} < P_{b(1,3-isophthalaldehyde)}$, which basically corresponds with the experimental data in the order: $P_e < P_c < P_a < P_d < P_b$ (Table 2). The bias may be due to the adjacent ring which plays extra interaction on the energies. It should be noted that the calculated results are based on monomer unit and cis form, in fact, the experiments data are obtained from oligomer of polymer and more complicated. The thiophene-based PAMs revealed the narrowest

gaps, best conjugation and electron transport which illustrate that heteroatom S influence predominantly on the gaps. On the other hand, PAM with 1,3-isophthalaldehyde having the worst conjugated structure showed the broadest gaps.

In general, the energy gaps of the PAMs containing biphenhyldiamine are broader than the corresponding ones of PAMs containing 1,4-benzenediamine, which is indicating the latter one owned the more conjugated structure. The theory results revealed basically consistence to the experimental data.

4. Conclusion

In summary, two new series of triphenylamine-based conjugated polymers PI and PII containing naphthalenyl groups have been successfully synthesized. Both of them exhibit good solubility in common organic solvents and excellent thermal stability. The energy levels and band gap of the polymers could be effectively tuned by changing the dialdehyde unit in the main chains. The calculated HOMO and LUMO energy levels of these polymers by theory method are in the range of -4.879 to -5.494 and -2.344to -2.927 eV vs. the vacuum level, respectively, which are similar to the experiment result that indicated the PAMs would be used in organic layer electroluminescent diode (OLED) and Photovoltagic cell as hole transporting materials or functional dyes. All obtained PAMs revealed excellent stability of electrochromic characteristics, changing color from original yellowish to red or blue.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j. electacta.2012.04.117.

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