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Electrochromic films with high optical contrast prepared by oxidative electropolymerization of a novel multi-functionalized cyclometalating ligand and its neutral-charged Pt(II) complexes

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ABSTRACT

A novel multi-functionalized cyclometalating ligand (HL) and its two neutral-charged Pt(II) complexes, i.e., [(L)PtCI] (C1) and [(L)Pt(C \equiv CC₆H₅)] (C2) (HL = 4-{*p*-[N-(4-(9-carbazole))butyl-N-phenyl]anilino}-6-phenyl-2,2'-bipyridine), have been successfully synthesized and verified by ¹H NMR, ¹³C NMR, elemental analysis and/or X-ray crystallography. The introduction of the electron-donating arylamino unit at the 4-position of the electron-withdrawing 6-phenyl-2,2'-bipyridine ligand forms the D–A system, resulting in the enhanced ¹MLCT bands in the absorption spectra and intense orange emissions in the PL spectra of C1 and C2. The carbazole units grafted through alkyl chain in HL, C1 and C2 electrochemically trigger the efficient cross-linking reaction to form polymer films, which have been characterized by AC impedance, SEM and spectroelectrochemistry. Each of the poly-HL and poly-C1 film and 67.3% for poly-C1 film), a reasonable coloration response time (6.3 s for poly-HL film and 3.1 s for poly-C1 film) and a comparable coloration efficiency (158 C⁻¹ cm² for poly-HL film and 132 C⁻¹ cm² for poly-C1 film) that can be switched by modulation of the applied potential.

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1. Introduction

Electrochromic materials with high optical contrast and coloration efficiency, long cycle life and appropriate response time have attracted a great deal of attention due to their potential applications in anti-glare mirrors, protective eyewear, smart windows, re-usable price labels and controllable light-reflective or light-transmissive display devices. A number of chemical species including metal oxides, viologens, metal coordination complexes and conducting polymers have been widely studied in solution and/or as film [1].

Hybrid metallopolymers electrogenerated from transition metal polypyridyl complexes, that consist of conjugated polymers with transition metals linked to or directly in the π -conjugated polymer backbone, is a promising group of electrochromic materials. Because their chromophoric properties, resulting from low-energy metal-to-ligand charge transfer (MLCT), intervalence charge transfer (IVCT), intraligand charge transfer (ILCT) and related visible region electronic transitions, can be tuned *via* the molecular design of ligands and complexes, and their multi-redox

natures of the ligand-based and metal-based processes can be switched with color changes in the regular potential window, these polymeric systems have greatly expected to use in all-solid-state electrochromic devices [2]. Iron(II), ruthenium(II) and osmium(II) complexes containing bromomethyl- [3], vinyl- [4], amino- [5] and pendant aniline- [6] substituted 2,2'-bipyridyl (NÑ) ligand, and amino- and hydroxyl-substituted 2,2':6',2"-terpyridinyl (NÑÑ) ligand [7] have been reductively or oxidatively electropolymerized to form electrochromic films. Among them, only the Ru(II)-based polymer film containing hydroxyl-substituted 2,2':6',2"-terpyridinyl ligand shows the anodic coloration from brown to dark yellow, the others exhibit the anodic de-coloration behavior associated with the M(II)/M(III) interconversion.

Recently, the cyclometalated Pt(II) complexes with tridentate phenyl-substituted bipyridine $(C\hat{NN})$ ligands [8–12] have been found numerous applications in organic light-emitting diodes (OLEDs) [13–16], optical limiting devices [17], DNA and protein binding [18], sensor [19–21] and self-assembled nanostructure [22]. However, to our best knowledge, using them as electrochromic film materials has so far never been reported yet. With the objective of obtaining a system having highly anodic coloration, enhanced optoelectronic properties and facile electropolymerization, we designed a novel multi-functionalized cyclometalating ligand (HL) and its two neutral-charged Pt(II)

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(i) Pd(OAc)₂/DPEphos/⁴BuONa/Toluene, 80°C, 12h;
(ii) NaH/THF, reflux overnight;
(iii) HAc, reflux 24h;
(iv) Cul/Et₃N/CH₂Cl₂, room temperature, stirred 12h.

Scheme 1. Synthetic route of HL, C1 and C2.

complexes (**C1** and **C2**) (Scheme 1). Incorporating an electrondonating diphenylamine (DPA) moiety at the 4-position of the electron-withdrawing 6-phenyl-2,2'-bipyridine ($C\hat{N}\hat{N}$) ligand aimed to form a donor–acceptor (D–A) system with the appearance of an intense n– π^* transition in UV region and a bathochromically shifted and much increased ¹MLCT transition of its corresponding Pt(II) complex in visible region [23]. A carbazole (CBZ) unit was introduced through alkyl chain to independently serve as an electropolymerizable site [24–27], which was expected to induce the efficient cross-linkage reaction to form CBZ polymers with high electrical conductivity and good optical quality.

2. Experimental

9-Butyl-carbazole [28], 4-[p-(N-butyl-N-phenyl)anilino]-6-phenyl-2,2'-bipyridine (HL²) [23] were synthesized according to the literature methods for parallel studies.

2.1. Synthesis of 9-(4-bromobutane)carbazole (3)

To a mixture of KOH (11.2 g) and ${}^{n}Bu_{4}NBr$ in H₂O (20 mL) was added dropwise a solution of carbazole (6.68 g, 40.0 mmol) and 1,4dibromobutane (20 mL, 160 mmol) in THF (80 mL), and the mixture was refluxed for 18 h. After the mixture was cooled to room temperature, the product was extracted with dichloromethane, washed with distilled water, and dried over anhydrous sodium sulfate and concentrated. The product mixture was purified by column chromatography (silica gel, petroleum ether: $CH_2Cl_2 = 2:1 (v/v)$). Compound **3** was obtained as a white needle crystal by recrystallizing from MeOH/ethyl acetate solution: 9.5 g (yield: 78.5%). ¹H NMR (300 MHz, CDCl_3): δ 8.10 (d, *J* = 7.8 Hz, 2H), 7.49–7.38 (m, 4H), 7.26–7.12 (m, 2H, *Ar*), 4.38 (t, *J* = 6.9 Hz, 2H), 3.38 (t, *J* = 6.4 Hz, 2H), 2.07 (m, 2H), 1.92 (m, 2H, $-CH_2$ –). ¹³C NMR (75 MHz, CDCl_3): δ 140.2, 125.7, 122.9, 120.4, 118.9, 108.5 (*Ar*), 42.1, 33.1, 30.2, 27.6 ($-CH_2$ –). Anal. Calcd for C₁₆H₁₆BrN: C, 63.59; H, 5.34; N, 4.63. Found: C, 63.38; H, 5.25; N, 4.43%.

2.2. Synthesis of 4-{p-[N-(4-(9-carbazole)butyl)-N-phenyl] anilino}-6-phenyl-2,2'-bipyridine (HL)

4-(*p*-Bromophenyl)-6-phenyl-2,2'-bipyridine (1) (1.94 g, 5.0 mmol), palladium acetate (13.0 mg, 0.06 mmol) and DPEphos (45.0 mg, 0.08 mmol) were charged into a flask and purged with argon. Aniline (1.0 mL, 10.7 mmol) was added via syringe, followed by toluene (20 mL), NaOBu^t (0.81 g, 8.5 mmol) was added in one portion. The reaction mixture was heated to 80 °C under stirring for 12 h. The solvent was removed by rotary evaporation. The residue was dissolved in dichloromethane, washed with distilled water, and dried over anhydrous sodium sulfate and concentrated. The crude product 2 was dissolved in THF (60 mL). NaH (2.5 g, >52%, in mineral oil) was added and purged with argon. The reaction mixture was stirred for 1 h at room temperature, and then 3(6.04 g)20.0 mmol) in THF (20 mL) was added dropwise via syringe. After the solution was refluxed until the conversion was complete (as monitored by thin layer chromatography), it was cooled to room temperature and poured into ice-water mixture slowly, extracted with CH₂Cl₂ until the water phase was colorless. The combined organic solution was washed with distilled water, dried over anhydrous sodium sulfate and concentrated. The crude product was purified by column chromatography (silica gel, petroleum ether: $CH_2Cl_2 = 2:1$ (v/v) containing 5% (v) triethylamine). Ligand HL was obtained as a pale yellow crystal by recrystallizing from MeOH/ethyl acetate solution: 1.7 g (yield: 54.8%). ¹H NMR (300 MHz, CDCl₃): δ 8.74–8.66 (m, 3H), 8.20 (d, *J*=7.2 Hz, 2H), 8.10 (d, J=7.8 Hz, 2H), 7.95 (s, 1H), 7.90 (t, J=7.5 Hz, 1H), 7.69 (d, *I*=8.7 Hz, 2H), 7.55–7.43 (m, 5H), 7.38–7.30 (m, 5H), 7.23 (t, *J*=6.9 Hz, 2H), 7.12–7.06 (m, 3H), 6.90 (d, *J*=8.7 Hz, 2H, *Ar*), 4.33 (t, *J*=7.0 Hz, 2H), 3.75 (t, *J*=7.3 Hz, 2H), 2.04–1.94 (m, 2H), 1.86–1.76 (m, 2H, -CH₂-). Anal. Calcd for C₄₄H₃₆N₄: C, 85.13; H, 5.85; N, 9.03. Found: C, 84.92; H, 5.67; N, 8.62%.

2.3. Synthesis of [(**L**)PtCl] (**C1**)

A mixture of HL (0.32 g, 0.5 mmol), K₂PtCl₄ (0.21 g, 0.5 mmol) and glacial acetic acid (30 mL) was refluxed for 24 h under a nitrogen atmosphere in the absence of light. The reaction mixture was then cooled to room temperature and filtered. The obtained solid was recrystallized from MeOH/CH₂Cl₂ solution twice to form the desired product as a red crystal: 0.35 g (yield: 82.4%). ¹H NMR (300 MHz, CDCl₃): δ 8.89 (d, *J* = 5.1 Hz, 1H), 8.68 (d, *J* = 8.1 Hz, 1H), 8.38 (s, 1H), 8.34 (t, *J* = 7.8 Hz, 1H), 8.14 (d, *J* = 7.8 Hz, 2H), 8.12 (d, *J* = 5.4 Hz, 1H), 7.92 (d, *J* = 8.7 Hz, 2H), 7.88 (t, *J* = 6.6 Hz, 1H), 7.75 (d, *J* = 7.5 Hz, 1H), 7.59 (d, *J* = 8.1 Hz, 1H), 7.50–7.36 (m, 5H), 7.21–7.04 (m, 8H), 6.85 (d, *J* = 8.7 Hz, 2H, *A*r), 4.42 (t, *J* = 6.9 Hz, 2H), 3.80 (t, *J* = 6.9 Hz, 2H), 1.88 (m, 2H), 1.72 (m, 2H, $-CH_2$ –). Anal. Calcd for C₄₄H₃₅ClN₄Pt: C, 62.15; H, 4.15; N, 6.59. Found: C, 61.67; H, 4.11; N, 6.28%.

2.4. Synthesis of $[(\mathbf{L})Pt(C \equiv CC_6H_5)](\mathbf{C2})$

A mixture of **C1** (0.30 mmol), $C_6H_5C=CH$ (1 mmol), Et_3N (5 mL) and CuI (5 mg) in degassed CH_2Cl_2 (50 mL) was stirred for 12 h under a nitrogen atmosphere at room temperature in the absence of

light. The reaction mixture was then evaporated to dryness under reduced pressure. The crude product was purified by flash chromatography (neutral Al₂O₃, CH₂Cl₂ as eluent) and recrystallized from CH₂Cl₂/MeOH solution. Complex **C2** was obtained as a red crystal in a yield of 87%. ¹H NMR (300 MHz, DMSO-*d*₆): δ 9.04 (d, *J* = 4.8 Hz, 1H), 8.69 (d, *J* = 8.1 Hz, 1H), 8.44 (s, 1H), 8.35 (t, *J* = 7.8 Hz, 1H), 8.18 (s, 1H), 8.14 (d, *J* = 7.8 Hz, 2H), 7.93 (d, *J* = 8.7 Hz, 2H), 7.86–7.75 (m, 3H), 7.60 (d, *J* = 8.1 Hz, 2H), 7.47–7.38 (m, 6H), 7.28 (t, *J* = 7.8 Hz, 2H), 7.22–7.04 (m, 8H), 6.87 (d, *J* = 9.0 Hz, 2H, Ar), 4.42 (t, *J* = 6.9 Hz, 2H), 3.81 (t, *J* = 6.9 Hz, 2H), 1.88 (m, 2H), 1.72 (m, 2H, –CH₂).

3. Results and discussion

3.1. Synthesis of monomers

Scheme 1 illustrates the synthesis of ligand and complexes explored in this work. 4-(p-bromophenyl)-6-phenyl-2,2'bipyridine (1) was obtained using Kröhnke's method [29]. The powerful palladium-catalyzed Buchwald method and the efficient Pd(OAc)₂/DPEphos catalyst/ligand system [30] were adopted to facilitate the condensation of aniline with 4-(p-bromophenyl)-6-phenyl-2,2'-bipyridine (1). Then the arylamino-substituted intermediate (2) reacted with 9-(4-bromobutane)carbazole (3) to afford ligand HL. The cyclometalated Pt(II) chloride [(L)PtCl] (C1) was synthesized by refluxing the ligand HL and K_2PtCl_4 in glacial acetic acid for 12 h. The Pt(II) acetylide complex $[(L)Pt(C \equiv CC_6H_5)]$ (C2) was obtained by employing Sonogashira's conditions (CuI/Et₃N/CH₂Cl₂) and chromatography separation. All the compounds have good solubility in CH₂Cl₂ and were verified by ¹HNMR, ¹³CNMR and/or elementary analysis. Structure of complex C2 was revealed by X-ray crystallography.

3.2. Crystal structure of complex C2

The single crystal of $[(L)Pt(C \equiv CC_6H_5)](C2)$ was grown by slowly evaporating the solvent from its concentrated CH₂Cl₂/MeOH solution, whose crystal data and crystal structure parameters are listed in Table 1. Fig. 1 shows its perspective view and the dimensional packing diagram. The coordinate geometry of the Pt atom is a distorted square planar configuration with the C(1)-Pt(1)-N(1) and N(1)-Pt(1)-N(2) angles of $78.7(3)^{\circ}$ and $80.5(3)^{\circ}$. The bond distances of Pt-C(1), Pt-N(1) and Pt-N(2) are 2.097(10), 1.984 (7) and 2.016 (8)Å, respectively, which are comparable to those of previously reported analogous [31-34]. The configuration of $C\hat{N}\hat{N}$ ligand is basically a plane with the C(1)-C(6)-C(7)-N(1) and N(2)-C(12)-C(11)-N(1) torsion angles of 0.03° and 4.81°. The dihedral angle between the phenyl ring at 4-position of the CNN ligand and the plane of the $[(\hat{CNN})Pt]$ moiety is 23.22°. The geometry of the N(3) atom is a distorted tetrahedral configuration with the C(20)–N(3)–N(23), C(20)–N(3)–N(29) and C(23)–N(3)–N(29) angles of $120.6(9)^{\circ}$, $121.4(9)^{\circ}$ and $115.9(8)^{\circ}$. The peripheral CBZ unit is approximately a plane with the C(37)-C(38)-C(39)-C(40)torsion angle of 0.62°. The dihedral angle between the phenyl ring

Table 1

Crystal data and crystal structure parameters.

Complex	C2
Empirical formula	$C_{52}H_{40}N_4Pt$
Formula weight	915.96
Temperature (K)	293(2)
Wavelength (Å)	0.71073
Crystal system	Triclinic
Space group	P-1
a (Å)	9.994(6)
b (Å)	10.566(7)
<i>c</i> (Å)	23.245(13)
α(°)	96.802(12)
β(°)	96.313(11)
γ (°)	115.686(11)
Volume (Å ³)	2160(2)
Ζ	2
$D_c (mg m^{-3})$	1.408
Absorption coefficient (mm ⁻¹)	3.286
F(000)	916
Crystal size (mm)	$0.15 \times 0.13 \times 0.08$
heta range for data collection (°)	2.51-25.00
Limiting indices	$-11 \le h \le 11, -10 \le k \le 12, -22 \le l \le 27$
Completeness to θ = 25.00°	98.9%
Data/restraints/parameters	7526/248/514
Goodness-of-fit on F ²	1.029
Final R indices $[I > 2\sigma(I)]$	$R_1 = 0.0781, wR_2 = 0.1765$
R indices (all data)	$R_1 = 0.1249, wR_2 = 0.1979$
Largest diff. peak and hole (e Å ⁻³)	1.929 and -1.641

of the secondary ligand and the plane of the [(C $\hat{N}\hat{N})Pt$] moiety is 71.5°.

Instead of forming a continuous chain with Pt–Pt linkage in [(CÑÑ)PtCl] [33,34], the complex molecules are stacked in a head-to-tail fashion (Fig. 1) with a Pt–Pt distance of 5.62 Å, suggesting no metal–metal interaction. The neighboring [(CÑÑ)Pt] moieties are parallel with the least dihedral angle of 0.000°, and their interplanar separation of 3.64 Å indicates that they are likely to be held together by a weak π – π interaction between the CÑÑ ligands.

3.3. Photophysical properties of monomers

Table 2 summarizes the absorption maxima and extinction coefficients of their absorption bands. The intense absorption bands in the high-energy region are dominated by ¹IL transitions, while the low-energy band at $\lambda_{max} = 448 \text{ nm}$ in the absorption spectrum of C1 is assigned to the spin-allowed singlet $d\pi(Pt) \rightarrow \pi^*(L)$ metal-to-ligand charge transfer (¹MLCT) transition, which is bathochromically shifted and more intense when the Pt(II) halide (C1) changes to the Pt(II) acetylide (C2). Owing to the strong D-A interaction between the electrondonating aniline moieties and the electron-deficient $(C\hat{N}\hat{N})$ cyclometalating ligand [23], the molar extinction coefficients of the MLCT bands of complexes C1 and C2 are 2-3 times larger than those of the reported (CNN) cyclometalated Pt(II) complexes without the arylamine group [8–14]. Compared to those of the reported complexes $[(L^2)PtCl]$ and $[(L^2)Pt(C \equiv CC_6H_5)]$ $(HL^2 = 4-[p-(N-butyl-N-phenyl)anilino]-6-phenyl-2,2'-bipyridine)$

Table 2

Photophysical properties of the ligand and Pt(II) complexes.

Compound	UV, in fluid solution ^a , $\lambda_{max,abs}$ (nm) ($\epsilon \times 10^3 dm^3 mol^{-1} cm^{-1}$)	PL, $\lambda_{max,em}(nm)^{b}$ (Φ^{c})	
		In fluid solution ^a	In solid state
HL	346 (28.5), 294 (37.0), 262 (50.9)	462	446
C1	448 (19.8), 376 (20.6), 328 (27.2), 294 (55.3), 264 (75.3)	592(0.10)	612
C2	462 (sh,20.5), 448 (20.9), 378 (22.2), 332 (26.2), 286 (58.3), 264 (62.4)	598(0.24)	598, 623(sh)

 $^a\,$ Measured in degassed CH_2Cl_2 solutions at 298 K (concentration \sim 1 \times 10 $^{-5}\,mol\,dm^{-3}$).

^b Excited wavelength: 450 nm.

^c [Ru(bpy)₃](PF₆)₂ in degassed acetonitrile at 298 K (Φ_r = 0.062) as reference.



Fig. 1. Perspective view (top) and crystal packing (bottom) of C2 with the numbering scheme adopted (hydrogen atoms have been omitted for clarity).

[23], the long-wavelength absorption spectra of **C1** and **C2** have no apparent change, suggesting the introduction of CBZ unit through alkyl chain can not influence on the energy level of the $[(L^2)Pt]$ moiety.

The PL data of monomers are also listed in Table 2. Ligand HL shows a blue emission band at 462 nm in CH_2Cl_2 solution, which is blue-shifted to 446 nm in solid state due to the decrease of thermal vibration in fluid solution. Excited at 450 nm, which is into the Pt(II)-based MLCT absorption band, complex **C1** and **C2** display strong emissions at λ_{max} = 592 and 598 nm with relatively high



Fig. 2. First and second CV curves of HL (a), HL^2 (b), 9-butyl-carbazole (c), C1 (d) and C2 (e) on a Pt electrode.

quantum yield of 0.10 and 0.24 in CH₂Cl₂ solution at 298 K, respectively, originated from the spin-forbidden triplet excited states. In solid state, red-shifted emission bands at λ_{max} = 612 and 623 nm were observed for **C1** and **C2**, respectively, which are likely arise from the π - π interactions between neighboring [(CNN)Pt] moieties.



Fig. 3. Repetitive cyclic voltammograms of HL(a), C1 (b) and C2 (c) on a Pt electrode.



Fig. 4. Cyclic voltammograms of poly-HL (top), poly-**C1** (middle) and poly-**C2** (bottom) after 10 cycles on a Pt disk electrode in 0.1 mol L⁻¹ Bu₄NClO₄/CH₂Cl₂ solution at the potential scan rates of 20 mV s⁻¹ (**1**), 50 mV s⁻¹ (**2**), 100 mV s⁻¹ (**3**), 150 mV s⁻¹ (**4**), 200 mV s⁻¹ (**5**) and 250 mV s⁻¹ (**6**). (Inset: dependence of the anodic and cathodic currents on the potential scan rate.)

3.4. Electrochemical polymerization (EP)

Two anodic waves at E_p = +1.13 and +1.34 V (vs. SCE) and a combined cathodic wave at E_p = +0.65 V (vs. SCE) were observed in the first cycling scan of HL (Fig. 2(a)). It is known that arylamine and CBZ moieties can be oxidized to the respective mono radical cations and that CBZ is oxidized at a potential higher than that of the structurally related arylamine analogues [35]. And with reference to the



Fig. 5. Impedance spectra (-Z'' vs. Z') measured on poly-HL (top), poly-C1 (middle) and poly-C2 (bottom) modified Pt disk electrodes after potential sweeping cycles of 10, 20 and 30 in 0.1 mol L⁻¹ Bu₄NClO₄/CH₃CN solution containing 1.0×10^{-3} mol L⁻¹ ferrocene as a redox probe.

redox behaviors of HL^2 (Fig. 2(b)) and 9-butyl-carbazole (Fig. 2(c)), we propose that the DPA moiety of HL is involved in the first oxidation process and the CBZ group of HL is involved in the second oxidation process. In the second anodic scan, a broad wave at more negative potential clearly appeared, suggesting that new electroactive species were generated after the first CV scan. As the cyclic scan proceeded, intensity of anodic and cathodic currents gradually increased with the formation of a broad oxidation wave from overlapping of the three anodic waves and apparently negative shift of the cathodic wave (Fig. 3(a)), indicating the presence of a

Table 3

Solution resistance (R_s) , electron transfer resistance (R_{et}) and capacity (C) of the various modified Pt electrodes.

Electrode name	$R_s(\Omega)$	$R_{et}\left(\Omega ight)$	$C_{dl}(\mathrm{Fcm^{-2}})$
Poly-HL-10	178	4250	2.26×10^{-9}
Poly-HL-20	120	3550	5.50×10^{-8}
Poly-HL-30	178	2870	4.30×10^{-8}
Poly- C1 -10	160	3180	5.50×10^{-8}
Poly-C1-20	170	2820	$5.50 imes 10^{-8}$
Poly-C1-30	300	2310	8.80×10^{-8}
Poly- C2 -10	160	1590	$6.50 imes 10^{-9}$
Poly- C2 -20	130	1450	8.50×10^{-9}
Poly- C2 -30	30	1320	8.50×10^{-9}



Fig. 6. The equivalent circuit proposed for polymer films modified ITO electrodes.

conductive polymer on the electrode. With the fact that HL^2 can not be electropolymerized under the same condition, these results indicate that introduction of a CBZ unit in HL triggers the cross-linking reaction following an $E(CE)_n$ -type mechanism [36], and that the generated 3,6-polycarbazole moiety is more easily oxidized than the parent compound [37]. However, because the CBZ radical cation has coupling rate constants that are 4–5 orders of magnitude higher than those of the arylamine analogues [35], we cannot exclude the oxidative coupling of arylamine radical cations simultaneously involving in the electropolymerization process.

Similarly, orange poly-**1C** and poly-**2C** films were obtained by the oxidative electropolymerization of **1C** and **2C**, respectively. Compared with that of **HL**, the CV spectra of **1C** (Fig. 2(d)) and **2C** (Fig. 2(e)) also show the Pt(II)-based anodic waves at +0.99 V (vs. SCE). The single peak at +1.28 V in the first anodic scan of **1C** is attributed to the combination of the aniline-based wave and the negative-shifted CBZ-based wave, while the smaller negativeshifted potential of the CBZ-based wave was found and the DPA-based wave was observed as a shoulder peak in the first anodic scan of **2C**. The oxidation wave of generated 3,6-polycarbazole moiety at the range of 0.6–0.8 V [37] also appeared in the second scan of **1C** and **2C**. Due to the overlapping effect of multi-redox waves, the poor-defined CV spectra of **1C** (Fig. 3(b)) and **2C** (Fig. 3(c)) were finally obtained after 10 cycling scans.

Fully washed with CH_2Cl_2 and ethanol to remove the unreacted monomer and oligomeric species, each of the poly-HL and



Fig. 8. Spectroelectrochemical spectra of poly-HL (top), ploy-C1 (middle) and poly-C2 (bottom) films coated ITO.



Fig. 7. SEM images of poly-HL film modified ITO after potential sweeping cycles of 10 (left), 20 (middle) and 30 (right), respectively.



Fig. 9. Dynamic changes of the transmittance and current upon switching the potential between 0 and +1.8 V with a pulse width of 200 s applied to the poly-HL (left) and poly-C1 (right) films coated ITO in 0.1 mol L⁻¹ Bu₄NClO₄/CH₂Cl₂ solution.

poly-**1C** films showed the linear increase of anodic and cathodic currents with the scan rate in monomer-free electrolytic solution (Fig. 4(a) and (b)) and a good stability upon over hundreds of potential sweeping cycle, indicating that polymer films adhere well to Pt electrode. While poly-**C2** film displayed an ill-linear dependence of anodic and cathodic currents upon the scan rate (Fig. 4(c)).

Poly-HL, poly-C1 and poly-C2 films on Pt and ITO electrodes with different coverage were obtained by controlling the potential scan cycle, respectively. Fig. 5 shows the AC impedance spectra of polymer films modified Pt electrodes after 10, 20 and 30 potential sweeping cycles. The resulting circuit is shown in Fig. 6. Table 3 summarizes the values obtained for the typical elements of the equivalent circuit, including the solution resistance (R_s) , the electron transfer resistance (R_{et}) and the double layer capacitance (C_{dl}). For each of polymer films, every spectrum was fitted by a semicircle at high frequencies and the diameter of fitted semicircle decreased with the scan number. Because the diameter of the semicircle corresponds to the electron transfer resistance (R_{et}) , the results suggested that the more potential scan cycle, the easier charge transfer from the electrolyte to the polymer/ITO electrode surface. The inverse dependence of AC impedance on the potential scan cycle is probably related to the morphology of polymer film at different growth stage. In order to verify this proposal, poly-HL, poly-C1 and poly-C2 films on ITO electrodes prepared after 10, 20 and 30 potential sweeping cycles were captured by SEM, respectively. The same changes of the film morphology (Fig. 7), from the discontinuous island (left) to the dense layer (middle) and then to the island-on-layer morphology (right), were observed for each of polymer films during its growth process. The continuous and dense coverage likely benefits the electron transfer in the polymer film.

Meanwhile, comparison of the R_{et} values of poly-**C1**/ITO and poly-**C2**/ITO electrodes to poly-**HL**/ITO electrodes demonstrates a clear drop in impedance, which means that the introduction of Pt(II) complexes in organic poly-HL film improves the electron transfer to the electrolyte by reducing the impedance of the electrode. Such enhanced conductance is likely attributed to the conductivity of the metal centers, the reduced electron-localization effect of the electron-deficient (CNN) cyclometalating ligand and the planar configuration of [(CNN)Pt] moieties in the obtained hybrid metal-lopolymers.

3.5. Spectroelectrochemical characterization of the electrogenerated films in solution

The spectroelectrochemical properties of poly-HL, poly-C1 and poly-C2 films on ITO electrodes were performed at various applied potentials, respectively (Fig. 8). In the neutral form, at 0V, poly-HL film exhibited a red-shifted ¹IL transition at λ_{max} = 360 nm and a new wave at λ_{max} = 468 nm, which indicate that the formation of a large π -conjugated D-A system [38]. A broad wave having its maximum absorption wavelength at 620 nm was gradually formed and blue-shifted with positive increase of the applied potential (Fig. 8 (a)). This result is in agreement with that of the oxidized biscarbazole within the range of 500-800 nm [39,40], reconfirming that the dimerization of the CBZ moiety of HL is involved in the electropolymerization process. We note, however, that the oxidation of oligomeric arylamine analogues, such as N,N,N',N'-tetraphenyl-4,4'-diaminobiphenyl (TPB), produces radical dications that also exhibit a broad absorption band in this range [41,42]. Thus, the contribution from the absorption of oxidized arylamine oligomer, generated from simultaneously coupling of arylamine radical cations in the electropolymerization process, cannot be excluded.

The UV–vis spectrum of poly–**C1** (Fig. 8(b)) at 0.8 V shows an enhanced ¹IL transition in the high-energy region and a red-shifted ¹MLCT wave at λ_{max} = 460 nm. As the applied potential became more anodic, the ¹MLCT wave blue-shifted with decrease of its intensity, and a broad band at λ_{max} = 602 nm gradually increased in intensity. The clear isosbestic point at 502 nm suggested that the conversion between the neutral and oxidized states of poly-**C1** film. Poly-**C2** film showed similar changes of the UV–vis spectrum with the presence of an isosbestic point at 507 nm, but no apparent absorption peak at the low-energy region was observed (Fig. 8(c)). All of the polymer films underwent a clear color change from orange to bluish black after their full oxidation.

The dynamic electrochromic experiments of poly-HL, poly-C1 and poly-C2 films were carried out at 660, 615 and 650 nm, respectively, where the maximum transmittance differences between redox states were observed in the visible region. The potential was step-switched between 0 (the neutral state) and +1.8V (the oxidized state) at regular intervals of 200 s. Except for poly-C2 film, poly-HL and poly-C1 films showed good stability and reversibility in monomer-free electrolytic solution. As indicated in Fig. 9, the changes in the absorbance reflect the switch in current, and the kinetics of the charge transport process can be referenced to the coloration response time. The times required for 95% full transmittance changes of poly-HL film are 6.3 s for the coloration step and 24.1 s for the bleaching step, reflecting the ease of charge transport in its oxidized form of the conducting film. The optical contrast $(\Delta T, \%)$ is 81.8%, which is much higher than that in related materials [3-7,43], with the black coloration efficiency of $158 \,\mathrm{C}^{-1} \,\mathrm{cm}^2$. Poly-C1 film displays a faster coloration time of 3.1 s, which is consistent with its enhanced conductance, and a comparable bleaching time of 27.2 s with the optical contrast of 67.3% and the coloration efficiency of 132 C⁻¹ cm². Taken together, these results suggested that poly-HL and poly-C1 films exhibit promising electrochromic properties in solution.

4. Conclusions

Herein, we successfully synthesized and characterized a novel multi-functionalized cyclometalating ligand and its two neutralcharged Pt(II) complexes. The bathochromically shifted maxima in the absorption and emission spectra of **C1** and **C2** indicated that the incorporation of an electron-rich arylamino group into the electron-deficient $(C\hat{N}\hat{N})$ moiety can strengthen the donor-acceptor (D-A) interaction. The electrochemical studies suggested that the introduction of carbazole unit through alkyl chain in ligand and complexes can trigger the efficient cross-linking reaction to form polymer films, which were confirmed by the spectroelectrochemical properties of as-formed polymer films. Poly-HL and poly-**C1** films with good stability and significantly anodic coloration exhibited great potential in electrochromic applications.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.electacta.2011.11.083.

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