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Introduction

The bottom-up approach of assembling molecules and nanoparticles upon a surface is of fundamental importance for constructing novel materials or devices.1 Due to the recent advances of synthetic methodologies, large varieties of organic or polymeric nanoparticles can be synthesized and used as building blocks for construction of three-dimensional structures.2 Therefore, developments of assembling techniques for organizing organic molecules or nanoparticles are of primary interests in modern sciences and technologies. Despite their noncovalent and reversible nature, molecular self-assembly techniques have proven to be useful tools for the construction of nano-scale structures. Many examples are known nowadays, which contain strong (self-) complementary and unidirectional intermolecular interactions to facilitate the self-assembled architectures. Monolayers and Langmuir-Blodgett films are typical examples of nano-structures that could be achieved by self-assembly.

Organic nanoparticles are another kind of interesting structure that have attracted a lot of attention during the last decades. Organic nanoparticles can usually be prepared either

Benzenetricarboxamide-cored triphenylamine dendrimer: nanoparticle film formation by an electrochemical method[†]

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By dropwise addition of a solution of tricarboxamide-cored triphenylamine dendrimer **G1** in THF into water (5 \times 10⁻⁶ M), nanoparticles with average diameters of 80 \pm 20 nm were formed and collected by centrifugation. The particles show aggregation induced emission and emit green light under photoluminescence conditions. The particles can be fused together by applying a concept of electrochemical curing; the **G1** particles are coupled through electrochemical oxidation to form a film. This method provides a fast assembling process for constructing films in a few seconds. Fabrication of electrochromic and fluorescence switching devices was demonstrated.

by chemical methods or by physical methods. When organic molecules are dispersed in highly polar solvents, in particular in aqueous media, the organic molecules tend to aggregate due to the advantages of hydrophobic interactions.³ In the solid state, strong intermolecular electronic interactions such as dipolar interactions, hydrogen bond interactions and aromatic π - π interactions would also lead to molecular aggregation. The growth of the aggregates sometimes leads to nano-scale particles. Currently, a major challenge is the implementation of physical functions into nano-materials, such as luminescence ability, switching and electronic or photovoltaic properties. However, the aggregation of organic molecules strongly affects, or sometimes even alters the molecular properties. For example, aggregate formation usually leads to quenching of light emission with red-shifting of the emission spectrum, which has been a big challenge for the development of light-emitting devices,⁴ such as biological sensors or organic light emitting diodes. Recently, Tang reported observations of aggregationinduced emission (AIE) for siloles and diphenyldibenzofulvenes, which brought in a new dimension of research for organic materials.5 The AIE phenomenon poses a challenge to the current understanding of the luminescence process in the solid state.

Carefully reviewing the features of nano-materials reveals that their sizes are quite different, ranging from Ångströms (Å) to hundreds of nanometers (nm). For example, self-assembled monolayers usually have a film thickness on the nm scale.⁶ Layer by layer approaches could provide thin films with thicknesses on the 10 nm scale.⁷ Electropolymerization could give rise to relatively thick films, provided that the morphologies and homogeneity of the films could be well controlled.⁸ Nanoparticles, on the other hand, are relatively large species, with

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including hydrogen bonding, π - π stacking, and solvophobic interactions, are formed.

Our recent interest is to develop techniques that could help to integrate self-assembled mono-layers, layer-by-layer electrochemical deposited films, and nanoparticles to form optoelectronic devices. To achieve this purpose, we first have to select appropriate organic molecules that could help to finish the assembling.

diameters up to the hundred nm scale. These particles can be used as building blocks to construct three-dimensional arrays.⁹

Dendritic molecules have attracted much research interest for a variety of high-tech applications such as dye-sensitized solar cells,¹⁰ organic memory devices,¹¹ light harvesting materials,¹² and as components in drug or gene delivery systems.¹³ Among the family of dendritic molecules, dendrimers have well defined and unique macromolecular structures. Their highly branched and globular structures lead to a number of important physical and chemical properties that contrast to the linear polymers of analogous molecular weight.^{14,15} For example, dendrimers demonstrate significantly increased solubility that can be readily tuned by derivatizing the periphery and they also exhibit very low intrinsic viscosities when compared with their linear analogues.

Dendrimers containing triphenylamine (TPA) moieties are well reported in the literature.^{16–18} It is known that TPA-cored organic compounds are excellent hole-transport materials for optoelectronic applications. This family of dendrimers intrigues us because they have high branching numbers and are supposed to be more sensitive to electro-polymerization than the linear family, from a statistical point of view.

During the past decades, we have put effort into understanding how to control the electrochemical behaviors of TPA derivatives. The TPA core exhibits excellent coplanarity of the central nitrogen and the three coordinating carbons. The nitrogen lone-pair electrons can maintain uninterrupted conjugation with the aromatic arms. Therefore, the TPA core usually functions as a strong electron donor to conjugated systems.^{19,20} In addition, TPA derivatives possess high chargecarrier mobility and low ionization potential; their hole transporting rates are about 1×10^{-3} to 10^{-4} cm V s⁻¹.²¹ These properties make TPA derivatives very promising hole-transport materials in organic light emitting device applications. Reynolds reported the use of TPA containing hyperbranched conjugated polyelectrolyte bilayers for solar cell applications.²² TPA-cored dendrimers afford enhanced two-photon absorption performance with locked molecule planarity.23-25 TPA-cored nonconjugated polymers demonstrate a new approach for electropolymerization that provides good hole injection and transport performance in PLED, including low turn-on voltage and high brightness.6d

Besides the electrochemical properties, our target compound has to demonstrate self-assembly capability. Among the systems we searched, hydrogen bonded C_3 -symmetrical molecules that associate into supramolecular stacks through hydrogen bonds and π - π interactions have caught our attention.²⁶⁻²⁹ Many interesting properties such as fiber and organic gel formation from discotic tricarboxamides and trisureas have been recently investigated. In the organogels, three-dimensional entangled networks of fibers, held by noncovalent forces

By combining all the features we have mentioned before, the C_3 -symmetrical dendritic 1,3,5-benzenetricarboxylamides (BTCAs) G0 and G1, as shown in Scheme 1 and 2, were designed because they could show a combination of hydrogen bond interactions as well as aromatic π - π interactions, with an integration of photoluminescence, electroluminescence, and electrochemical activities. First, the central core contains a C_3 -symmetrical tricarboxamide unit, which provides the opportunity for aggregate formation through hydrogen bond interactions. The presence of the electron-withdrawing carboxyamide groups on the benzene ring makes the central domain electron-deficient. Therefore, when the electron-donating triarylamine dendrons are introduced as the outer sphere, an electronic-gradient would be established. In addition, the highly aromatic exterior would provide strong aromatic π - π interactions, which will be beneficial for the intermolecular aggregation. The electron-rich triarylamino dendrons are electrochemically active and could be electrochemically polymerized under appropriate conditions.

Our team is interested in electrochemical techniques for thin film deposition. Herein we demonstrate the use of electrochemical curing of nanoparticles of **G1** as a fast assembling technique for optoelectronic device fabrication. The fabrication strategies involve self-assembly layer formation, layer-by-layer electrochemical deposition, and electrochemical cross-linking of nanoparticles of **G1** on an indium tin oxide (ITO) surface. The performances of novel electrofluorescence devices (EFDs),³⁰ with fluorescence-switching and electrochromic properties, have also been studied.

Results and discussion

Synthesis of G0 and G1

While **1** was known in literature,³¹ **2** was prepared through a three-step synthetic sequence (Scheme 1). Goldberg condensation³² was adopted to facilitate the mono C–N coupling of **3** and **4**, using CuI (30 mol%)–*N*,*N'*-dimethyl-1,2-diamine (DMDA, 60 mol%)–K₃PO₄ (1.5 equiv.) as catalyst at 140 °C for 24 h to give **5**. A Suzuki coupling reaction would then proceed smoothly to give **6**, followed by deprotection of the phthalimide with NH₂NH₂ to give **2**. Dendrimers **G0** and **G1** were prepared from **8** and the corresponding arylamines **1** and **2** in the presence of DMAP–Et₃N. Compound **9** was prepared from **7** and **8** as reference for comparison.

The study of the hydrogen bond interactions

1,3,5-Tricarboxylamide derivatives favor the formation of hydrogen bond networks through intermolecular hydrogen bond interactions. In the NMR study, extremely broadened ¹H NMR signals for **G0** and **G1** were observed in CDCl₃, indicating that the free rotation of the amido side-chains is restricted by intermolecular hydrogen bond interactions. This is probably due to the self-assembly of **G0** and **G1** into columnar stacks at NMR concentration. However, in a mixed solvent of



CDCl₃–DMSO- d_6 (0.5 ml : 0.2 ml), the hydrogen bonding network was broken-up. Dissolution of the stacks and dissociation of the hydrogen bond aggregates led to well-resolved ¹H NMR spectra with sharpened signals: a broad singlet at δ 10.19 (3H, –NH–), a multiplet at 8.62–8.64 (3H_c of the central benzene ring), a multiplet at 7.69–7.71 (6H_a aromatic), a multiplet at 7.35–7.41 (22H aromatic), a multiplet at 7.06–7.18 (24H aromatic) and a multiplet at 6.90–7.04 (68H aromatic). The observation of the downfield shift of the amido protons above 9 ppm indicates that the amido protons are hydrogen bonded to DMSO- d_6 .

To further explore the hydrogen bond character of the dendrimers, a proton-NMR titration was carried out using the tricarboxamide **9** as the titrant (Fig. 1). With the amido protons substituted for methyl substituents, **9** could only act as the hydrogen bond acceptor. On addition of **9** to the NMR sample of **G1** (1×10^{-3} M), downfield shifts of the amido protons were clearly observed. As shown in Fig. 1, the trends of the ¹H NMR shifting pattern fit well with the equation³³

$$\frac{\Delta}{L]} = (-K_{\rm SL} \times \Delta) + (K_{\rm SL} \times \Delta_{\rm SL})$$

where $\Delta = \delta - \delta_0$ and $\Delta_{SL} = \delta_{SL} - \delta_0$. The formation constant (K_{SL}) for 1 : 1 complex formation (S + L = SL) was therefore measured as 665 ± 25 M⁻¹. These observations are consistent with the assumption of hydrogen bond network formation of tricarboxamide derivatives proposed in literature.



Scheme 2



The strong hydrogen bond interactions are also reflected in their high thermal stability. **G0** and **G1** form amorphous organic glass in the solid state with very high glassy transition temperatures of 153 °C and 185 °C, and decomposition (5% weight loss) temperatures of 431 °C and 510 °C, respectively.

In addition, other hydrogen bond related self-assembly properties of **G0** and **G1**, including the physical sorption on the ITO surface as well as nanoparticle formation will be discussed in later sections.

The photophysical properties of G0 and G1

Pertinent spectral data for G0, G1, 9, 1, and 2 are summarized in Table 1 and Fig. 2. G0 shows a characteristic absorption peaking at 300 nm along with a broad-shoulder at 340 nm. Perhaps due to the three-fold C₃ concentric symmetry, solvatochromic effects on the absorption are small.³⁴ The major absorption of G0 at 300 nm overlaps with that of 1, indicating that this absorption mainly arises from the dendritic side-arms. The extinction coefficient (ε) of G0 (5.8 × 10⁴ M⁻¹ cm⁻¹) is about 2.6 times the ε value of 1 (2.2 \times 10⁴ M⁻¹ cm⁻¹), suggesting that electronic perturbations from the BTCA unit are limited. On the other hand, the shoulder band is due to the charge transfer (CT) absorption from the dendritic triarylamine (TAA) branches to the BTCA core. G1 shows split absorption peaks at 300-400 nm, which covers the spectral region of 2. G1 has the first band at 310 nm, which is well overlayed with that of 2, and has an ε value of $12.2 \times 10^5 \text{ M}^{-1} \text{ cm}^{-1}$, which is about 2.5 times larger than that of 2 ($\epsilon = 4.9 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$). On the other hand, due to the contributions from the CT band, G1 shows stronger



Fig. 2 Comparison of UV-vis spectra: (a) G0, 1, and 9 in $\mathsf{CH}_2\mathsf{Cl}_2;$ (b) G1 and 2 in $\mathsf{CH}_2\mathsf{Cl}_2.$



Fig. 3 $\,$ Pictorial diagrams of the HOMO and LUMO of G1 calculated by PM5 methods.

Table 1	Photophysical data of ${\bf G0}$	tophysical data of G0 and G1							
	$\lambda_{\max}^{\text{abs }a}$ (nm)	ε^{b}	Fluorescence λ_{\max}^{FL} (nm) (QY) ^e						
			Solution ^c	Stokes shift	THF glass	Nanoparticle ^d			
G0	300	5.8	513 (0.0011)	215	495 (0.11)	515 (0.026)			
G1	310, 365	12.0, 19.9	520 (0.0027)	155	500 (0.14)	520 (0.048)			

^{*a*} Measured in CH₂Cl₂. ^{*b*} 10⁴ M⁻¹ cm⁻¹. ^{*c*} Measured in THF. ^{*d*} Measured in THF/H₂O = 1 : 9. ^{*e*} QY (quantum yield) is quantified in THF against coumarin 1 (0.85) as standard.³⁵



Fig. 4 AIE was observed for G0 (a) and G1 (b). The critical water fractions in THF are 50% and 30%, respectively.



Fig. 5 SEM pictures of (left) nanoparticles of **G0** precipitated from THF–H₂O (1 : 9, 10⁻⁵ M) and (right) nanoparticles of **G1** precipitated from THF–H₂O (2 : 8, 5 \times 10⁻⁶ M).

absorption at 365 nm, with an ε value 3.2 times that of 2 ($\varepsilon = 6.3 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$).

G0 and **G1** show weak fluorescence (FL) in CH_2Cl_2 and THF at 25 °C. In THF, the quantum yields (QYs) are 0.0011 and 0.0027, respectively. The low QYs may be attributed to either intramolecular charge-transfer relaxation or rotational relaxation mechanisms. The possibility of rotational relaxation mechanisms being involved is supported by FL enhancement at 77 K in THF glass, in which **G0** and **G1** were flash-frozen. In this situation, the QYs were enhanced by almost 100 and 50 times to 11% and 14%, respectively. Restriction of the intramolecular rotation (RIR) by freezing the molecules in organic glass at 77 K could effectively reduce the bond-vibrational and rotational relaxation, leading to higher QYs. The Stokes shifts of 215 nm (13 900 cm⁻¹, 1.7 eV) and 155 nm (8160 cm⁻¹, 1.01 eV) for **G0** and **G1** are large, signifying the CT properties of the excited state.



Fig. 6 (a) Water droplet image on bare ITO glass; C/A = 20° . (b) Water droplet image on **G1** self-assembled ITO glass; C/A = 46° . (c) Cyclic voltammogram of the sorption layer of **G1** on the ITO. After the sorption process, the ITO plate was rinsed with CH₂Cl₂ before CV analysis. The presence of the characteristic CV wave pattern evidences the assembling of **G1** on the ITO surface.

To further understand the electronic structures of **G0** and **G1**. Semi-empirical calculations were carried out, using PM5 methods. The results clearly illustrate that the highest occupied molecular orbital (HOMO) locates at the triarylamino dendron while the lowest unoccupied molecular orbital (LUMO) is located at the central tricarboxyamide unit (Fig. 3). This result also implies that photoexcitation gives rise to a charge transfer state leading to charge separation properties in the excited state.

Aggregation induced emission enhancement and nanoparticle formation

AIE enhancement for **G0** and **G1** was observed by dropwise addition of the THF solutions into deionized water (Fig. 4). On the condition that the amounts of **G0** and **G1** were high enough, different from other BTCAs which form organo-gels, nanoparticles were collected (Fig. 5). Since the nanoparticles are soluble in most of the organic solvents and will aggregate and precipitate in water due to the lack of surface charges, particle size measurements by dynamic light scattering will be complicated. However, data and statistics on the particle size distribution could be collected based on SEM images, with average diameters of 60 \pm 20 nm and 80 \pm 20 nm being observed, respectively.

The arylamine-tricarboxamide cores are expected to be the archetypal AIE luminogen. The QY of **G0** increases to 2.6% in a THF-water (1 : 9) mixture in comparison to 0.11% in THF. The FL turns on at the critical water fraction of 50%. The final extent of emission enhancement (α^*_{AIE}) is about 24 times. Similarly, the FL turn-on for **G1** occurs at the critical water fraction of 30%. The QY increases from 0.27% to 4.8% and an α^*_{AIE} of 18 times is achieved. The AIE is consistent with the previous FL data at 77 K, which could be rationalized by restriction of the

Table 2 CV data of G0 and G1							
	$E_{\mathrm{ox}}{}^{a}\left(\mathrm{V}\right)$	$I_{\mathrm{pa}}{}^{a}$ (µA)	$HOMO^{b}$ (eV)	$E_{\rm g}^{\ c}$ (eV)	$LUMO^{d}$ (eV)		
G0	+0.91	13.5	-5.17	2.82	-2.35		
G1	+0.75, +0.99, +1.16	6.72, 6.2, 6.7	-5.01	2.73	-2.28		

^{*a*} Measured in CH₂Cl₂ with Bu₄NClO₄. ^{*b*} HOMO (Fc/Fc⁺) = $-e(E_{ox} - E_{ox,ferrocene}) + (-4.8) eV$, $E_{ox,ferrocene} = 0.536 V$. ^{*c*} E_g optical bandgap, determined from the absorption onset. ^{*d*} LUMO = $E_{HOMO} + E_g$.





Fig. 7 Electrochemical treatments of G1: (a) G1 on Pt in TBAP–CH₂Cl₂; (b) correlation plot of electropolymerized film thickness and the number of CV cycles; (c) SEM image of electropolymerized G1 on ITO in TBAP–EtCN.

intramolecular rotation (IMR) process of the luminogen. In the solution state, the molecules undergo an active IMR process that leads to quenching of the excited states and hence low QY. In the aggregate state, the IMR process is restricted probably through intermolecular hydrogen bond and π -stacking interactions. The RIR process blocks the non-radiative decays and enhances the QYs of **G0** and **G1**.

Electrochemical behavior of G0 and G1

The redox behavior of the dendrimers (10^{-3} M) was examined by cyclic voltammetry (CV). The data are summarized in Table 2. **G0** shows a redox couple at +0.91 V, which corresponds to the oxidation of the triphenylamino branches. On the other hand, the anodic wave of **G1** splits into two reversible and one irreversible redox couples with half-potentials at $E_{1/2}^{(1)} = +0.75 \text{ V}$, $E_{1/2}^{(2)} = +0.99$ V, and $E_{\rm p}^{(3)} = +1.19$ V. Almost identical anodic peak-currents ($I_{\rm pa}$) of 6.72 µA, 6.20 µA, and 6.70 µA were recorded, suggesting that the CV waves are composed of three sequential single-electron oxidation processes. The splitting of the waves of **G1** evidences that the electronic couplings among the amino cores are strong.

Sorption of G1 on ITO glass

The ITO surface is a polar surface. Therefore, water droplets would spread to give a small contact angle of 23° (Fig. 6a). However, the surface polarity could be altered by sorption of **G1** onto the surface through immersion of the plate into a CH_2Cl_2 solution of **G1**. An ITO plate with **G1** self-assembled on top shows a larger contact angle of 46° , indicating a relatively nonpolar surface in comparison to the bare ITO surface (Fig. 6b). The presence of the **G1** layer was also evidenced by CV. After the self-assembling of **G1** on the ITO, the ITO plate was rinsed with CH_2Cl_2 and subjected to CV analysis. The oxidation waves arising from the **G1** layer could be clearly observed (Fig. 6c), illustrating that a layer of electrochemically active **G1** was settled on the electrode surface. The presence of the layer as a primer would be beneficial for further electrochemical deposition.

Electropolymerization of G0 and G1

The electropolymerization of **G0** and **G1** was studied by repeated CV sweep methods. Although triarylamines have been used to cause electrochemical deposition through aryl-aryl coupling, the deposition of **G0** is ineffective; only a small extent





 Table 3
 Fluorophoric and electrochromic properties of the electrochemically deposited thin film of G1

	Potential sten			Response time		0		
Doping status	switching (V)	Opto-physical response	λ_{\max} (nm)	$t_{\mathrm{C}}\left(\mathrm{s}\right)$	$t_{\mathrm{B}}\left(\mathrm{s}\right)$	ΔOD	$\left(\mathrm{mC}\ \mathrm{cm}^{-2}\right)$	$(cm^2 C^{-1})$
Neutral state	0	Fluorescence	520	_	_	_		
1 st doping state	0/+0.90	Electrochromism	500	51	32	0.477	5.8	82.2
			1600	51	32	0.477	5.8	82.2
2 nd doping state	0/+1.20	Electrochromism	860	57	46	0.973	13.6	71.6



Fig. 8 Electrochemical cross-linking of nanoparticles of G1: (a) CV of nanoparticles on ITO in TBAP–EtCN. (b) SEM image of the film formed from electrochemically fused nanoparticles of G1.

of deposition was observed even at a slow sweep-rate of 10 mV s⁻¹. This is probably due to the π -resonance effect induced by the *para*-amido group that reduces the cation radical spindensity on the terminal phenyl units and hence reduces the probability of the radical coupling process between the **G0** molecules (Scheme 3).

Electropolymerization of **G1** proceeds more effectively than that of **G0**. Although the CV sweep (Fig. 7a) between 0.00 and +1.10 V that covered the first two oxidations did not lead to any fruitful deposition, electrochemical deposition was triggered when the CV sweep was extended to +1.30 V, indicating that the third oxidation is crucial for initiating the polymerization (Scheme 4).

We tentatively explain the electrochemical behavior as follows: the first two reversible oxidations occurring at $E_{1/2}^{(1)} =$ +0.75 V and $E_{1/2}^{(2)} =$ +0.99 V would lead to a closed-shell benzidine dication resonance form, which is known to be relatively inert towards electropolymerization. However, the third oxidation would lead to terminal radical cations that are highly reactive for electropolymerization.

The electrochemical deposition rate of G1 was followed by monitoring the thickness of the deposited film versus the number of CV cycles being applied for the deposition. In Fig. 7b, one can see that the growth rate is almost linear proportional to the number of CV cycles. Thicknesses up to about 218 nm were observed, indicating that the electrochemical deposition is very effective. This result implies that migration of the triphenylamine radical cation from the ITO surface to the outmost area of the deposited layer proceeds very efficiently. The morphology of the electrochemically deposited thin films of G1 at an early stage (3 cycles) was directly observed through field-emission scanning electron microscopy (SEM). A selected representative SEM image is shown in Fig. 7c. The surface of the electropolymerized G1 was highly smooth with the ITO surface feature being maintained. This observation indicates that the growth of the polymeric film was initiated homogeneously on the ITO surface.

Electrochromism of the deposited film of G1

The properties of the migration of electrolytes inside the polymer matrix are of particular interest. One way to understand these properties is to follow the dynamics of the electrochromism of the deposited film. The electrochromism of the deposited film of G1 on ITO glass was studied by a potentialstep method from 0 V to 1.25 V, with increments of 0.05 V and a holding time of 5 min being employed. The data are summarized in Table 3. In the neutral state at 0 V, the film exhibits strong absorption peaking at 385 nm and is perceived as colorless due to the low absorbance in the visible region. Under UV irradiation, a green FL peak at 500 nm, which is about 30 nm hypsochromically shifted compared to that of G1 in the amorphous film state, was observed. Two oxidation steps are evidenced in the electrochromic (EC) studies: (1) the film turned red (λ_{max} at 500 nm) at 0.95 V with NIR absorption appearing at 1600 nm, which is due to the inter-valence charge transfer



Fig. 9 EC cell with nanoparticles of **G1** using Bu₄NClO₄ in CH₂Cl₂ as a supporting electrolyte: (a) schematic diagram of the device structure. (b) Green FL and (c) colorless properties of the device at 0 V. (d) Brown-red color at 0.9 V. (e) Deep blue color at 1.2 V.

absorption of the benzidine radical cation. (2) The film turned deep blue (λ_{max} at 860 nm) at 1.25 V with the duo absorption bands at 500 nm and 1600 nm fading away simultaneously. We tentatively propose the formation of the closed-shell benzidine dications at this stage.

Electrochromic switching studies for the thin-film were performed to monitor the percental transmittance changes as a function of time at their absorption maxima (λ_{max}). The response times, including the bleaching time ($t_{\rm B}$) and the coloring time ($t_{\rm C}$), were evaluated by stepping the potential repeatedly between the neutral and oxidized states. The response times were measured at 90% of the full transmittancechange. The optical density change Δ (OD) is defined as

$$\Delta(\text{OD}) = \log(t_{\text{B}}/t_{\text{C}})$$

The coloration efficiency is defined as

$$\eta = \Delta(\text{OD})/Q$$

where *Q* represents the charge required to cause the change in the coloring process.

Perhaps due to the strong intermolecular hydrogen bond networking interactions that retard the electrolyte migration in the polymer matrix, the rate of the coloring and bleaching processes are relatively slow in comparison to other electrochromic polymers reported in the literature. When the electrochromic test was manipulated, with the potential step switching between 0 and +0.9 V, the times required to attain 90% of complete coloring and bleaching at the first doping state are 51 and 31 seconds, respectively. It is known that in the electrochromic process the charge has to be kept balanced. When the polymer film is oxidized, more counter ions would migrate into the polymer matrix in order to keep the charge balanced. Therefore, strong intermolecular hydrogen bonding interactions that restrict the segmental motions of the polymer matrix would slow down the diffusion rates of the electrolytes, and hence prolong the coloring and bleaching processes. Since hydrogen bond networks could be restored when the polymer is reduced back to the neutral state, this provides a driving force to squeeze out the electrolyte and therefore the bleaching rate is much faster than that of the coloring process.

When the potential stepping was switched between 0 and +1.2 V, the second doping state could be accessed. However, similar time scales were observed for the coloring and bleaching times. The values of $t_{\rm C}$ and $t_{\rm B}$ were found to be 57 and 41 seconds, respectively. These numbers are close to those for the first doping process. It is noteworthy to emphasize that the rising of the absorption at 860 nm is due to closed-shell dication formation in the matrix. The observation of the similar time scale for both the radical cation and the closed-shell dication formation processes indicates that the first doping process is the rate determining step. After formation of the radical cations, further oxidation to the second doping state would proceed more effectively. It is noteworthy to point out that the color of the doping states is highly stable under ambient conditions; the film could be kept in the doped forms for weeks without decay.

EC cell of nanoparticles of G1

Although the layer-by-layer approach provides a means for fabrication of thin film devices, film-growth by electrochemistry is usually time-consuming. To speed up the fabrication process, we adopted nanoparticles of G1 as building-blocks for electrochromic (EC) cell fabrication. We introduce an idea of electrochemical curing, or electrochemical welding36 herein. The G1 particles are coupled by electrochemical oxidation to form an integrated film. Data and a schematic diagram of the idea are shown in Fig. 8 and 9. Fig. 9a shows the electrochemical curing tactics for film device assembly and fabrication: (1) a layer of the polymerized G1 was deposited electrochemically on the ITO surface by using a CV method for 5 cycles. The thickness of the layer was about 50 nm. The deposited film functioned as a primer^{6b} to increase the adhesion of the nanoparticles onto the ITO surface in the next step. (2) A G1 nanoparticle suspension in aqueous THF was applied to fill-up the cell. The cell depth was 65 µm. The plate was heated at 80 °C until the solvent was completely dried. A film from the nanoparticles could then be obtained. It is noteworthy to remember that the high glass-transition temperature of 158 °C for G1 helps to maintain the nanoparticles in a spherical shape. (3) Since the nanoparticles are insoluble in EtCN, electrochemical cross-linking of the nanoparticles was performed in a supporting electrolyte of Bu₄NClO₄ (TBAP) in EtCN to form a film.

Fig. 8a shows the CV traces of the electrochemical treatments. In the first anodic scan, three characteristic waves of **G1** could be clearly seen. However, the CV wave pattern was changed due to electrochemical cross-linking and reached a stable new pattern after several repeated CV cycles. The peak currents in each of the latter CV cycles remain almost the same, indicating that leaching of the **G1** based material from the film is minimal.

More interesting is the fact that the solubility of the electrochemically treated nanoparticle layer significantly drops and becomes insoluble in CH_2Cl_2 . This is due to the successful electrochemical cross-linking reaction that significantly reduces the solubility of the solid matrix. Fig. 9b shows an SEM image of the nanoparticle film after electrochemical treatment. Nanoparticles of **G1** are fused. However, variation of the particle diameter becomes more significant. This is probably due to the partial leaching of **G1** from the particles during the electrochemical crosslinking process. Nevertheless, the low solubility of the film allowed the latter electrochromic studies to be performed in CH_2Cl_2 .

Fig. 9b–e demonstrate the electrochromic properties of the device in TBAP–CH₂Cl₂. At the neutral state, the plate highly fluoresces with a green color. When the film was oxidized to the first doped state, the plate turned brown-red. The photo-luminescence was completely quenched in this state. Further oxidation turned the device a deep-blue color. The device is so robust that the opto-physical properties could be repeated by switching the applied electrical potentials between 0 and 1.25 V for many redox cycles without decay.

Conclusion

In summary, we demonstrated that it is possible to fuse G1 nanoparticles by electrochemical oxidation under appropriate

conditions to form a 3D matrix. The process involves the concept of self-assembly of **G1** on ITO to alter the surface polarity, electrochemical deposition of **G1** to form a primer layer that enhances nanoparticle adhesion, and electrochemical cross-linking of the particles to form an insoluble matrix. This tactic provides an efficient approach for fabrication of electrochromic and fluorescence switching devices with large contact surface areas with the supporting electrolyte.

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