Supplementary Information

A comparative study of redox-active and ambipolar electrochromic triphenylamine- based polyimides prepared by electrochemical polymerization and conventional polycondensation methods†

Sheng-Huei Hsiao,*a Wei-Kai Liaoa and Guey-Sheng Lioub

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a Department of Chemical Engineering and Biotechnology, National Taipei University of Technology, Taipei, Taiwan 10608. E-mail: shhsiao@ntut.edu.tw
b Institute of Polymer Science and Engineering, National Taiwan University, Taipei, Taiwan 10617. E-mail: gqliou@ntu.edu.tw

Monomer Synthesis

N,N′-Bis(4-diphenylaminophenyl)pyromellitimide (TPA-PMDI)

A mixture of 2.86 g (11 mmol) of TPA-NH₂ and 1.09 g (5 mmol) of PMDA was dissolved in 30 mL of anhydrous DMAc in a 50 mL round-bottom flask. The reaction mixture was stirred at room temperature for 4 h, and then into which 6.73 mL of acetic anhydride and 5.22 mL of pyridine were added. After 2 h further stirring at 120°C, the solution was poured into 150 mL of methanol. The precipitated red product was collected by filtration and dried to give 3.34 g (95 % yield) of the desired monomer TPA-PMDI as red crystals with a melting point of 343.9−344.9 °C (DSC endotherm peak temperature), measured by DSC at 10 °C/min.

IR (KBr): 1769 and 1715 cm⁻¹ (imide ring C=O stretching). ¹H NMR (600 MHz, CDCl₃, δ, ppm): 7.11 (t, J = 7.4 Hz, 4H, H₄), 7.19 (d, J = 8.7 Hz, 12H, H₄ + H₆), 7.31 (d, J = 8.7 Hz, 4H, H₆), 7.32 (t, J = 7.5 Hz, 8H, H₃), 8.49 (s, 2H, H₇). TOF MS ES⁺: Calcd for [C₄₆H₃₀N₄O₄]⁺: m/z 702.2253; Found: m/z 703.2335 (M + H)⁺.
**N,N'-Bis(4-nitrophenyl)-N,N'-diphenyl-4,4'-biphenyldiamine (2)**

In a 250 mL three-neck flask equipped with a stirring bar and nitrogen gas inlet were placed 0.61 g (24 mmol) of sodium hydride and 60 ml dimethyl sulfoxide (DMSO). To the stirred mixture were added successively 3.36 g (10 mmol) of \(N,N'\)-diphenyl-4,4'-biphenyldiamine and 3.39 g (24 mmol) of \(p\)-fluoronitrobenzene at room temperature. Then the mixture was heated with stirring at 120 °C for 24 h under nitrogen atmosphere. After that, the solution was poured into 300 mL of methanol. The precipitated red product was collected by filtration and dried to give 4.45 g (77 % yield) of the desired dinitro compound 2 as yellow crystals with a melting point of 202.2–204.1 °C (DSC endotherm peak temperature) (lit., 2201 °C), measured by DSC at 10°C/min.

IR (KBr): 1580 and 1320 cm\(^{-1}\) (−NO\(_2\) stretching). \(^1\)H NMR (600 MHz, DMSO-d\(_6\), δ, ppm): 6.89 (d, \(J = 9.3\) Hz, 4H, \(H_f\)), 7.29–7.33 (m, 10H, \(H_b+H_c+H_e\)), 7.48 (t, \(J = 8.2\) Hz, 4H, \(H_d\)), 7.75 (d, \(J = 8.5\) Hz, 4H, \(H_a\)), 8.10 (d, \(J = 9.3\) Hz, 4H, \(H_g\)). \(^{13}\)C NMR (150 MHz, DMSO-d\(_6\), δ, ppm): 117.42 (C\(_{10}\)), 125.64 (C\(_{11}\)), 126.34 (C\(_8\)), 126.77 (C\(_3\)), 126.95 (C\(_6\)), 128.17 (C\(_2\)), 130.28 (C\(_7\)), 136.58 (C\(_1\)), 139.27 (C\(_{12}\)), 144.37 (C\(_9\)), 144.88 (C\(_4\)), 153.10 (C\(_5\)). TOF MS ES\(^{+}\): Calcd for \((C_{36}H_{26}N_4O_4)^+\): m/z 578.1957; Found: m/z 579.2032 (M + H)^+.

**N,N'-Bis(4-aminophenyl)-N,N'-diphenyl-4,4'-biphenyldiamine (3)**

\(\text{O}_2\text{N}\)

(12)

(11)

(10)

(9)

(8)

(7)

(6)

(5)

(4)

(3)

(2)

(1)

\(\text{NO}_2\)

\(\text{g}\)

\(\text{f}\)

\(\text{e}\)

\(\text{d}\)

\(\text{c}\)

\(\text{b}\)

\(\text{a}\)
In the 100 mL three-neck round-bottomed flask equipped with a stirring bar, 3.6 g (6.2 mmol) of the dinitro compound 2, and 0.08 g of 10 % Pd/C were dissolved/suspended in 36 mL DMF. The suspension solution was heated to 60 °C under hydrogen atmosphere. After a further 48 h further stirring at 60 °C, the solution was filtered to remove Pd/C, and the filtrate poured into 300 mL of water. The product was collected by filtration and dried in vacuo at 30 °C to give 3.19 g of 3 as white powder in 89 % yield; m.p. = 285.4–287.4 °C (DSC endotherm peak temperature) (lit., 22 289 °C), measured by DSC at 10 °C/min

FT-IR (KBr): 3460, 3370 cm⁻¹ (−NH₂ stretch). ¹H NMR (600 MHz, DMSO-d₆, δ, ppm): 5.08 (s, 4H, H₃), 6.59 (d, J = 8.6 Hz, 4H, H₄), 6.83 (d, J = 8.6 Hz, 4H, H₅), 6.89-6.96 (m, 10H, H₆ + H₇ + H₈), 7.21 (t, J = 8.2 Hz, 4H, H₉), 7.45 (d, J = 8.5 Hz, 4H, H₁₀). ¹³C NMR (150 MHz, DMSO-d₆, δ, ppm): 114.90 (C₁₁), 121.20 (C₄), 121.26 (C₅), 121.64 (C₆), 126.53 (C₇), 128.04 (C₁₀), 129.02 (C₈), 132.30 (C₁), 134.96 (C₉), 146.24 (C₃), 146.62 (C₁₂), 147.65 (C₁₃). EI MS: Calcd for (C₃₆H₂₅N₄)⁺: m/z 518.2; Found: m/z 518.2.

**N-(4-Diphenylaminophenyl)phthalimide (M₁)**

A mixture of 2.86 g (11 mmol) TPA-NH₂ and 1.48 g (10 mmol) phthalic anhydride was dissolved in 5 mL of anhydrous DMAc in a 50 mL round-bottom flask. The reaction mixture was stirred at room temperature for 4 h, and then 6.73 mL of acetic anhydride and 5.22 mL of pyridine were added. After 2 h further stirring at 120 °C, the solution was poured into 200 mL of methanol. The precipitated yellow product was collected by filtration and dried to give 3.36 g (86 % yield) of the desired model compound M₁ as yellow crystals with a melting point of 205.3–206.2 °C (DSC endotherm peak
temperature), measured by DSC at 10 °C/min.

IR (KBr): 1742 and 1711 cm\(^{-1}\) (imide ring C=O stretching). \(^1\)H NMR (600 MHz, DMSO-\(d_6\), \(\delta\), ppm):

7.05–7.11 (m, 8H, H\(a\) + H\(c\) + H\(d\)), 7.32–7.36 (m, 6H, H\(b\) + H\(e\)), 7.88–7.91 (m, 2H, H\(f\)), 7.94–7.97 (m, 2H, H\(g\)).

\(N,N'\)-Bis(phthalimide)-\(N,N'\)-bis(4-aminophenyl)-\(N,N'\)-diphenyl-4,4'-Biphenyldiamine (\(M_2\))

A mixture of 0.65 g (1.3 mmol) of diamine 3 and 0.44 g (3.0 mmol) of phthalic anhydride was dissolved in 5 mL of anhydrous DMAc in a 50 mL round-bottom flask. The reaction mixture was stirred at room temperature for 4 h, and then 1.7 mL of acetic anhydride and 1.3 mL of pyridine were added. After 2 h further stirring at 120 °C, the solution was poured into 200 mL of methanol. The precipitated yellow product was collected by filtration and dried to give 0.8 g (79 % yield) of the desired model compound \(M_2\) as yellow crystals with a melting point of 367.2–368.7 °C (DSC endotherm peak temperature), measured by DSC at 10 °C/min.

IR (KBr): 1736 and 1714 cm\(^{-1}\) (imide ring C=O stretching). \(^1\)H NMR (600 MHz, CDCl\(_3\), \(\delta\), ppm): 7.09 (t, \(J = 7.4\) Hz, 2H, H\(b\)), 7.19–7.21 (m, 12H, H\(a\)+ H\(c\) + H\(e\)), 7.28–7.32 (m, 8H, H\(a\) + H\(d\)), 7.50 (d, \(J = 8.6\) Hz, 4H, H\(f\)), 7.80 (dd, 4H, H\(g\)), 7.96 (dd, 4H, H\(h\)).
Figure S1 IR spectra of (a) TPA-PMDI, (b) dinitro compound 2 and (c) diamine monomer 3.
Figure S2 Mass spectra of (a) TPA-PMDI, (b) dinitro compound 2 and (c) diamine monomer 3.
Figure S3. IR spectra of model compounds $M_1$ and $M_2$. 
Figure S4. (a) $^1$H NMR and (b) H-H COSY spectra of diimide compound TPA-PMDI in CDCl$_3$. 
Figure S5. (a) $^1$H NMR and (b) H-H COSY spectra of dinitro compound 2 in DMSO-$d_6$. 
Figure S6. (a) $^{13}$C NMR and (b) C-H HMQC spectra of dinitro compound 2 in DMSO-$d_6$. 
Figure S7. (a) $^1$H NMR and (b) H-H COSY spectra of diamine compound 3 in DMSO-$d_6$. 
Figure S8. (a) $^{13}$C NMR and (b) C-H HMQC spectra of diamine compound 3 in DMSO-$d_6$. 
Figure S9. (a) $^1$H NMR and (b) H-H COSY spectra of model compound M$_1$ in DMSO-$d_6$. 
Figure S10 (a) $^1$H NMR and (b) H-H COSY spectra of model compound $M_2$ in CDCl$_3$. 
Figure S11 Current monitored and optical transmittance changes of the film on the ITO-glass slide in 0.1 M Bu$_4$NClO$_4$/CH$_2$Cl$_2$ while the potential was switched: (a) PI-E film (thickness: 200 ± 100 nm) between 0.0 V and 1.0 V at 485 nm with a pulse time of 30 s and (b) PI-C film (thickness: 200 ± 30 nm) between 0.0 V and 1.0 V at 490 nm with a pulse time of 40 s.
Figure S12 Current monitored and optical transmittance changes of the film on the ITO-glass slide in 0.1 M Bu$_4$NClO$_4$/CH$_2$Cl$_2$ while the potential was switched: (a) PI-E film (thickness: 200 ± 100 nm) between 0.0 V and 1.3 V at 740 nm with a pulse time of 35 s and (b) PI-C film (thickness: 200 ± 30 nm) between 0.0 V and 1.3 V at 750 nm with a pulse time of 40 s.
<table>
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<th>Cycling times&lt;sup&gt;a&lt;/sup&gt;</th>
<th>ΔOD&lt;sub&gt;490&lt;/sub&gt;&lt;sup&gt;b&lt;/sup&gt;</th>
<th>Q&lt;sub&gt;d&lt;/sub&gt;&lt;sup&gt;c&lt;/sup&gt; (mC cm&lt;sup&gt;−2&lt;/sup&gt;)</th>
<th>CE&lt;sup&gt;d&lt;/sup&gt; (cm&lt;sup&gt;2&lt;/sup&gt; C&lt;sup&gt;−1&lt;/sup&gt;)</th>
<th>Decay (%)&lt;sup&gt;e&lt;/sup&gt;</th>
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<sup>a</sup> Switching between 0 and 1.0 V (vs. Ag/AgCl).

<sup>b</sup> Optical Density (ΔOD) = log[T<sub>bleached</sub> / T<sub>colored</sub>], where T<sub>colored</sub> and T<sub>bleached</sub> are the maximum transmittance in the oxidized and neutral states, respectively.

<sup>c</sup> Q<sub>d</sub> is ejected charge, determined from the in situ experiments.

<sup>d</sup> Coloration efficiency (CE) = ΔOD/Q<sub>d</sub>.

<sup>e</sup> Decay of coloration efficiency after cyclic scans.
Table S2 Coloration efficiency of polyimide PI-C

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<th>Q&lt;sub&gt;d&lt;/sub&gt;&lt;sup&gt;d&lt;/sup&gt; (mC cm&lt;sup&gt;−1&lt;/sup&gt;)</th>
<th>CE&lt;sup&gt;e&lt;/sup&gt; (cm&lt;sup&gt;2&lt;/sup&gt; C&lt;sup&gt;−1&lt;/sup&gt;)</th>
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<sup>a</sup> Switching between 0 V and 1.0 V (vs. Ag/AgCl).
<sup>b</sup> Optical Density (ΔOD) = log[T<sub>bleached</sub> / T<sub>colored</sub>], where T<sub>colored</sub> and T<sub>bleached</sub> are the maximum transmittance in the oxidized and neutral states, respectively.
<sup>c</sup> Q<sub>d</sub> is ejected charge, determined from the in situ experiments.
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<sup>e</sup> Decay of coloration efficiency after cyclic scans.