Supplementary Information

for

Novel luminescent and electrochromic polyhydrazides and polyoxadiazoles bearing pyrenylamine moieties

by

Yi-Chun Kung\textsuperscript{a} and Sheng-Huei Hsiao\textsuperscript{a,b}

\textsuperscript{a} Department of Chemical Engineering, Tatung University, Taipei, 10452, Taiwan
\textsuperscript{b} Department of Chemical Engineering and Biotechnology, National Taipei University of Technology, Taipei, 10608, Taiwan

Table of Contents

Synthetic details for \textit{N,N}-di(4-cyanophenyl)-1-aminopyrene and \textit{N,N}-di(4-carboxyphenyl)-1-aminopyrene ...............................2

\textbf{Fig. S1} (a) \textsuperscript{1}H, (b) \textsuperscript{13}C, (c) H-H COSY and (d) C-H HMQC NMR spectra of \textit{N,N}-di(4-cyanophenyl)-1-aminopyrene in DMSO-\textit{d}_6........................................3

\textbf{Fig. S2} (a) \textsuperscript{1}H and (b) \textsuperscript{13}C, (c) H-H COSY and (d) C-H HMQC NMR spectra of \textit{N,N}-di(4-carboxyphenyl)-1-aminopyrene in DMSO-\textit{d}_6.............................4

\textbf{Fig. S3} IR spectra of polyhydrazide I-IPH and poly(1,3,4-oxadiazole) II-IPH...........4

\textbf{Fig. S4} DSC traces of polyhydrazide I-TPH and poly(1,3,4-oxadiazole) II-TPH with a heating rate of 20 °C/ min in nitrogen.........................................................5

\textbf{Fig. S5} TGA curves of polyhydrazide I-TPH and poly(1,3,4-oxadiazole) II-TPH with a heating rate of 20 °C/ min in nitrogen.................................5

\textbf{Fig. S6} Cyclic voltammograms of individual reacting compounds (~10^{-3} M) in CH\textsubscript{3}CN (for oxidation) and DMF (for reduction) solutions containing 0.1 M Bu\textsubscript{4}NClO\textsubscript{4} at a Pt coil electrode, scan rate = 50 mV/s.............................6

\textbf{Table S1} Elemental analysis of the polyoxadiazoles.................................6

Synthesis of \textit{N,N}-Di(4-cyanophenyl)-1-aminopyrene. To a solution of 15.20 g (70 mmol) of
1-aminopyrene and 17.56 g (145 mmol) of 4-fluorobenzonitrile in 100 mL of dried dimethyl sulfoxide (DMSO), 22.79 g (150 mmol) of dried CsF was added with stirring all at once, and the mixture was heated at 170 °C for 18 h under nitrogen atmosphere. The mixture was poured into 1 L of water/methanol (1:1). The precipitated compound was collected by filtration and washed thoroughly by methanol and hot water. The crude product was filtered and recrystallized from acetic acid/water to afford 20.55 g (70 % in yield) of pale brown needles with an mp of 241-242 °C (by DSC at a heating rate of 5 °C/min). FT-IR (KBr): 2218 cm⁻¹ (C≡N stretch). ¹H NMR (500 MHz, DMSO-d₆, δ, ppm): 7.16 (d, J = 8.8 Hz, 4H, H₉), 7.70 (d, J = 8.8 Hz, 4H, H₈), 7.82 (d, J = 9.2 Hz, 1H, H₆), 7.98 (d, J = 8.2 Hz, 1H, H₅), 8.13 (t, J = 7.7 Hz, 1H, H₄), 8.18 (d, J = 9.3 Hz, 1H, H₇), 8.27 (d, J = 9.0 Hz, 1H, H₄), 8.30 (d, J = 9.0 Hz, 1H, H₃), 8.31 (d, J = 7.2 Hz, 1H, H₂), 8.39 (d, J = 7.6 Hz, 1H, H₇), 8.44 (d, J = 8.2 Hz, 1H, H₆). ¹³C NMR (125 MHz, DMSO-d₆, δ, ppm): 104.19 (C²⁰), 118.94 (C≡N), 121.57 (C¹⁸ + C²), 123.72 (C⁹), 125.41 (C¹⁴), 125.84 (C⁸), 126.12 (C¹⁰), 126.71 (C⁵), 126.90 (C⁶), 127.13 (C¹³), 127.75 (C¹⁵), 127.90 (C⁷), 128.08 (C¹²), 129.22 (C¹), 130.28 (C¹⁶), 130.54 (C¹¹), 130.57 (C⁷), 133.81 (C¹⁹), 137.19 (C¹), 150.13 (C¹⁷). Anal. Calcd (%) for C₃₀H₁₇N₃ (419.48): C, 85.90 %; H, 4.08 %; N, 10.02 %. Found: C, 85.77 %; H, 4.12%; N, 10.11 %.

**Synthesis of N,N-Di(4-carboxyphenyl)-1-aminopyrene.** A mixture of 5.35 g (95 mmol) of potassium hydroxide and 4.00 g (9.5 mmol) of the obtained dinitrile compound 1 in 30 mL of ethanol and 40 mL of distilled water was stirred at 110 °C until no further ammonia was generated. The time taken to reach this stage was about 4 days. The solution was filtered while hot and cooled to room temperature, and the pH value of filtrate was adjusted by 3 M hydrochloric acid (HCl) to near 3. The yellow precipitate was filtered, washed thoroughly with water and recrystallized from acetic acid/water to afford 3.86 g (88.5 % in yield) of pale yellow needles with a mp of 312-314 °C (by DSC at 5 °C/min). FT-IR (KBr): 2700-3200 cm⁻¹ (O-H stretch), 1682 cm⁻¹ (C=O stretch). ¹H NMR (500 MHz, DMSO-d₆, δ, ppm): 7.11 (d, J = 8.8 Hz, 4H, H₉), 7.86 (d, J = 8.8 Hz, 4H, H₈), 7.96 (d, J = 8.1 Hz, 1H, H₆), 7.99 (d, J = 9.3 Hz, 1H, H₅), 8.11 (t, J = 7.6 Hz, 1H, H₄), 8.15 (d, J = 9.3 Hz, 1H, H₇), 8.25 (d, J = 9.1 Hz, 1H, H₆), 8.27 (d, J = 9.1 Hz, 1H, H₅), 8.28 (d, J = 7.5 Hz, 1H, H₇), 8.37 (d, J = 7.6 Hz, 1H, H₈), 2
8.43 (d, J = 8.2 Hz, 1H, H₆). ¹³C NMR (125 MHz, DMSO-d₆, δ, ppm): 120.82 (C¹⁸), 121.96 (C⁶), 123.82 (C⁸), 124.20 (C²⁰), 125.47 (C¹⁴), 125.64 (C⁸), 125.91 (C¹⁰), 126.64 (C³), 126.80 (C⁶), 127.18 (C¹³), 127.74 (C¹²), 127.76 (C¹⁵), 127.92 (C²), 128.80 (C⁵), 130.13 (C¹⁶), 130.34 (C¹¹), 130.63 (C⁷), 131.06 (C¹⁹), 138.41 (C¹), 150.73 (C¹⁷), 166.79 (C=O). Anal. Calcd (%) for C₃₉H₁₉NO₄ (457.48): C, 78.76 %; H, 4.19 %; N, 3.06 %. Found: C, 77.82 %; H, 4.23 %; N, 3.09 %.

**Fig. S1** (a) ¹H, (b) ¹³C, (c) H-H COSY and (d) C-H HMQC NMR spectra of N,N-di(4-cyanophenyl)-1-aminopyrene in DMSO-d₆.
Fig. S2 (a) $^1$H and (b) $^{13}$C, (c) H-H COSY and (d) C-H HMQC NMR spectra of $N,N$-di(4-carboxyphenyl)-1-aminopyrene in DMSO-$d_6$.

Fig. S3 IR spectra of polyhydrazide I-IPH and poly(1,3,4-oxadiazole) II-IPH.
**Fig. S4** DSC traces of polyhydrazide I-TPH and poly(1,3,4-oxadiazole) II-TPH with a heating rate of 20 °C/ min in nitrogen.

**Fig. S5** TGA curves of polyhydrazide I-TPH and poly(1,3,4-oxadiazole) II-TPH with a heating rate of 20 °C/ min in nitrogen.
Fig. S6 Cyclic voltammograms of individual reacting compounds (~10^{-3} M) in CH$_3$CN (for oxidation) and DMF (for reduction) solutions containing 0.1 M Bu$_4$NClO$_4$ at a Pt coil electrode, scan rate = 50 mV/s.

Table S1 Elemental analysis of the polyoxadiazoles

<table>
<thead>
<tr>
<th>Polymer Code</th>
<th>Elemental Analyses of Polymers</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Formula Weight</td>
</tr>
<tr>
<td>II-TPH</td>
<td>(C$<em>{38}$H$</em>{21}$N$_5$O$_2$)$_n$</td>
</tr>
<tr>
<td></td>
<td>(579.63)$_n$</td>
</tr>
<tr>
<td>II-IPH</td>
<td>(C$<em>{38}$H$</em>{21}$N$_5$O$_2$)$_n$</td>
</tr>
<tr>
<td></td>
<td>(579.63)$_n$</td>
</tr>
</tbody>
</table>