Supplementary Information

for

Novel luminescent and electrochromic polyhydrazides and polyoxadiazoles bearing pyrenylamine moieties

by

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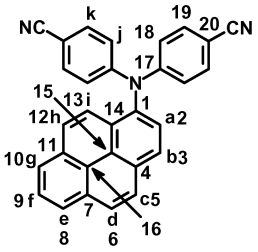
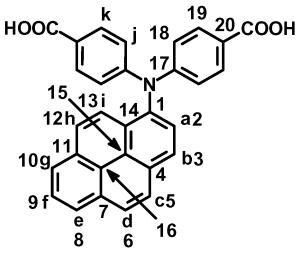
Synthesis of *N*,*N*-Di(4-cyanophenyl)-1-aminopyrene. To a solution of 15.20 g (70 mmol) of

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 ^{o}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 recrystalized from acetic acid/water to afford 20.55 g (70 % in yield) of pale brown needles with an mp of 241-242 ^{o}C (by DSC at a heating rate of 5 ^{o}C/min). FT-IR (KBr): 2218 cm^{-1} (C≡N stretch). ^{1}H NMR (500 MHz, DMSO-d_6, δ, ppm): 7.16 (d, J = 8.8 Hz, 4H, H_j), 7.70 (d, J = 8.8 Hz, 4H, H_k), 7.82 (d, J = 9.2 Hz, 1H, H_a), 7.98 (d, J = 8.2 Hz, 1H, H_d), 8.13 (t, J = 7.7 Hz, 1H, H_f), 8.18 (d, J = 9.3 Hz, 1H, H_b), 8.27 (d, J = 9.0 Hz, 1H, H_i), 8.30 (d, J = 9.0 Hz, 1H, H_h), 8.31 (d, J = 7.2 Hz, 1H, H_e), 8.39 (d, J = 7.6 Hz, 1H, H_g), 8.44 (d, J = 8.2 Hz, 1H, H_c). ^{13}C NMR (125 MHz, DMSO-d_6, δ, ppm): 104.19 (C^{20}), 118.94 (C≡N), 121.57 (C^{18} + C^{2}), 123.72 (C^{4}), 125.41 (C^{14}), 125.84 (C^{8}), 126.12 (C^{10}), 126.71 (C^{5}), 126.90 (C^{9}), 127.13 (C^{13}), 127.75 (C^{15}), 127.90 (C^{6}), 128.08 (C^{12}), 129.22 (C^{3}), 130.28 (C^{16}), 130.54 (C^{11}), 130.57 (C^{7}), 133.81 (C^{19}), 137.19 (C^{1}), 150.13 (C^{17}). Anal. Calcd (%) for $C_{30}H_{17}N_3$ (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 distillated water was stirred at 110 ^{o}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 ^{o}C (by DSC at 5 ^{o}C/min). FT-IR (KBr): 2700-3200 cm^{-1} (O-H stretch), 1682 cm^{-1} (C=O stretch). ^{1}H NMR (500 MHz, DMSO-d_6, δ, ppm): 7.11 (d, J = 8.8 Hz, 4H, H_j), 7.86 (d, J = 8.8 Hz, 4H, H_k), 7.96 (d, J = 8.1 Hz, 1H, H_a), 7.99 (d, J = 9.3 Hz, 1H, H_d), 8.11 (t, J = 7.6 Hz, 1H, H_f), 8.15 (d, J = 9.3 Hz, 1H, H_c), 8.25 (d, J = 9.1 Hz, 1H, H_i), 8.27 (d, J = 9.1 Hz, 1H, H_h), 8.28 (d, J = 7.5 Hz, 1H, H_e), 8.37 (d, J = 7.6 Hz, 1H, H_g),

8.43 (d, J = 8.2 Hz, 1H, H_b). ^{13}C NMR (125 MHz, DMSO-d_6, δ, ppm): 120.82 (C^{18}), 121.96 (C^{6}), 123.82 (C^{4}), 124.20 (C^{20}), 125.47 (C^{14}), 125.64 (C^{8}), 125.91 (C^{10}), 126.64 (C^{3}), 126.80 (C^{9}), 127.18 (C^{13}), 127.74 (C^{12}), 127.76 (C^{15}), 127.92 (C^{2}), 128.80 (C^{5}), 130.13 (C^{16}), 130.34 (C^{11}), 130.63 (C^{7}), 131.06 (C^{19}), 138.41 (C^{1}), 150.73 (C^{17}), 166.79 (C=O). Anal. Calcd (%) for $C_{30}H_{19}NO_4$ (457.48): C, 78.76 %; H, 4.19 %; N, 3.06 %. Found: C, 77.82 %; H, 4.23 %; N, 3.09 %.



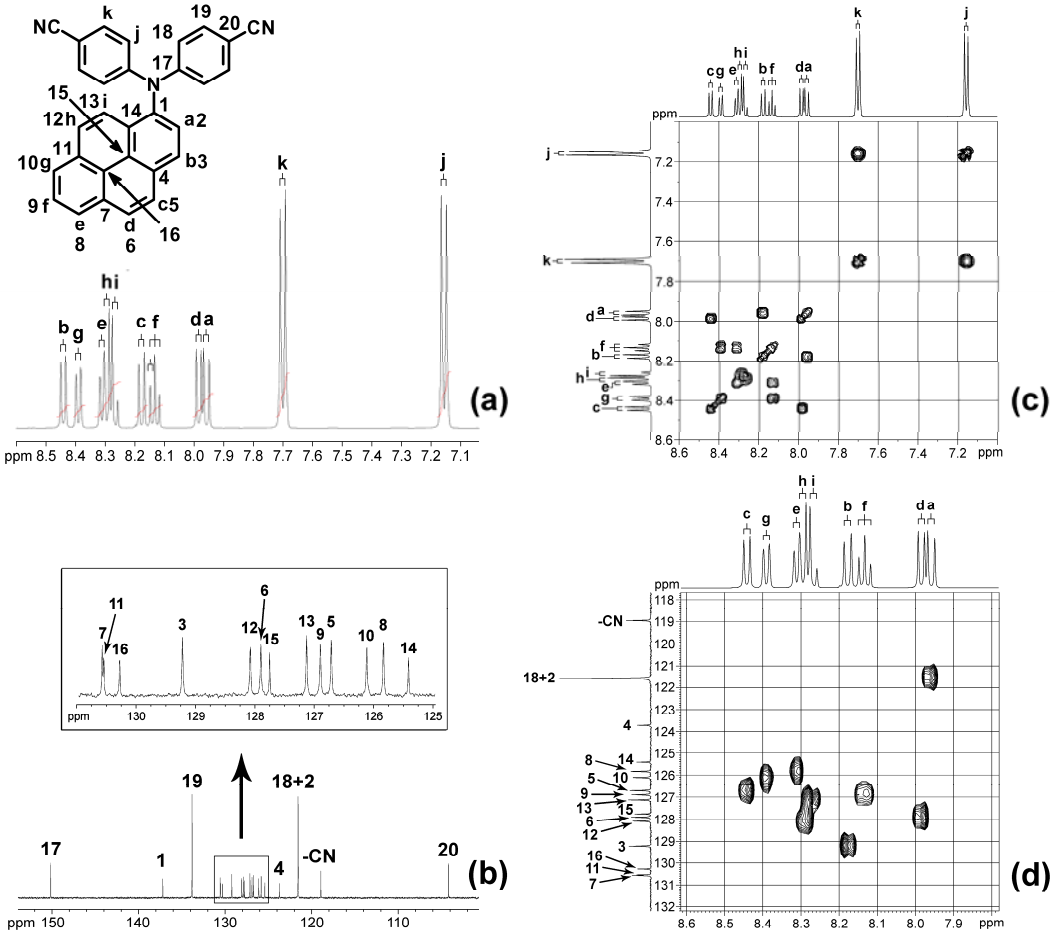


Fig. S1 (a) ^{1}H, (b) ^{13}C, (c) H-H COSY and (d) C-H HMQC NMR spectra of *N*,*N*-di(4-cyanophenyl)-1-aminopyrene in DMSO-d_6.

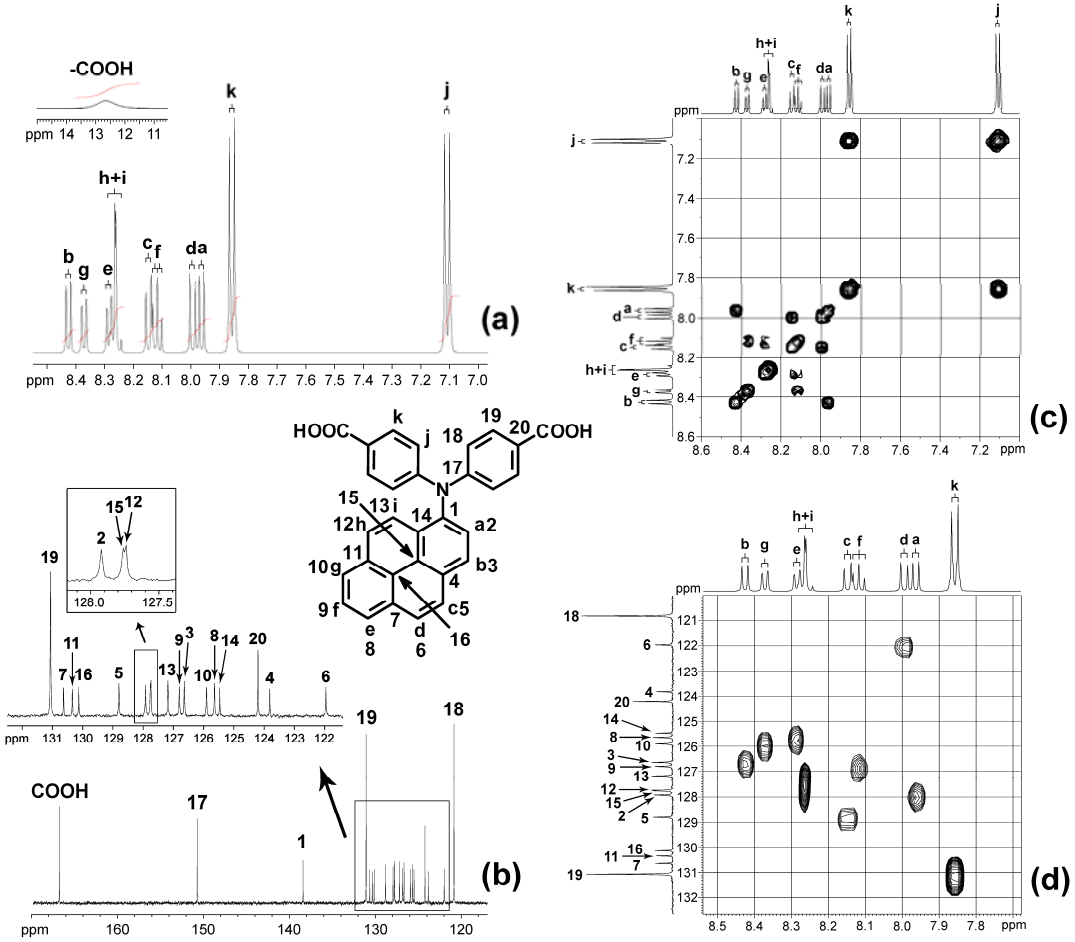


Fig. S2 (a) ^{1}H and (b) ^{13}C, (c) H-H COSY and (d) C-H HMQC NMR spectra of *N*,*N*-di(4-carboxyphenyl)-1-aminopyrene in DMSO-d_6.

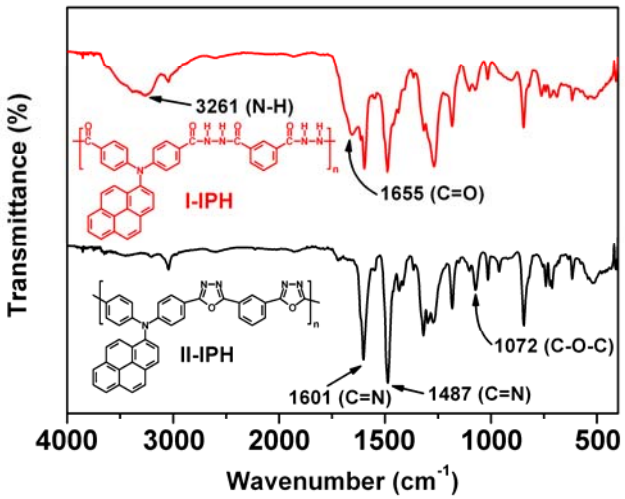


Fig. S3 IR spectra of polyhydrazide **I-IPH** and poly(1,3,4-oxadiazole) **II-IPH**.

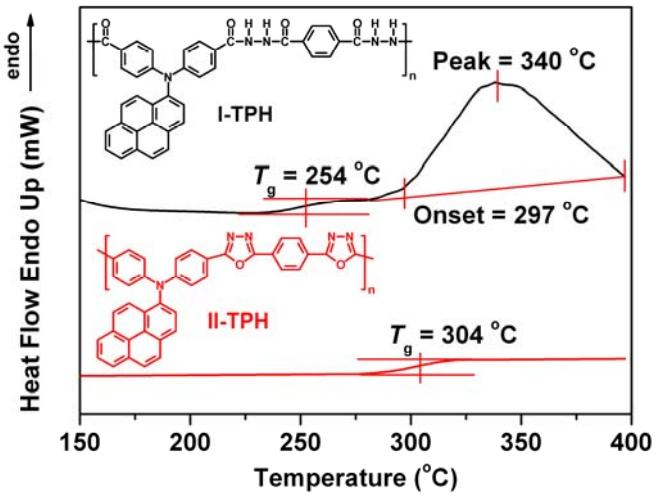


Fig. S4 DSC traces of polyhydrazide **I-TPH** and poly(1,3,4-oxadiazole) **II-TPH** with a heating rate of 20 °C/ min in nitrogen.

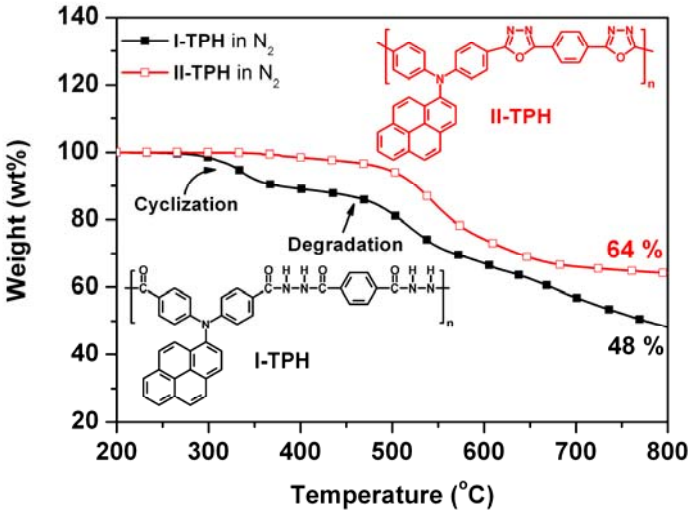


Fig. S5 TGA curves of polyhydrazide **I-TPH** and poly(1,3,4-oxadiazole) **II-TPH** with a heating rate of 20 °C/ min in nitrogen.

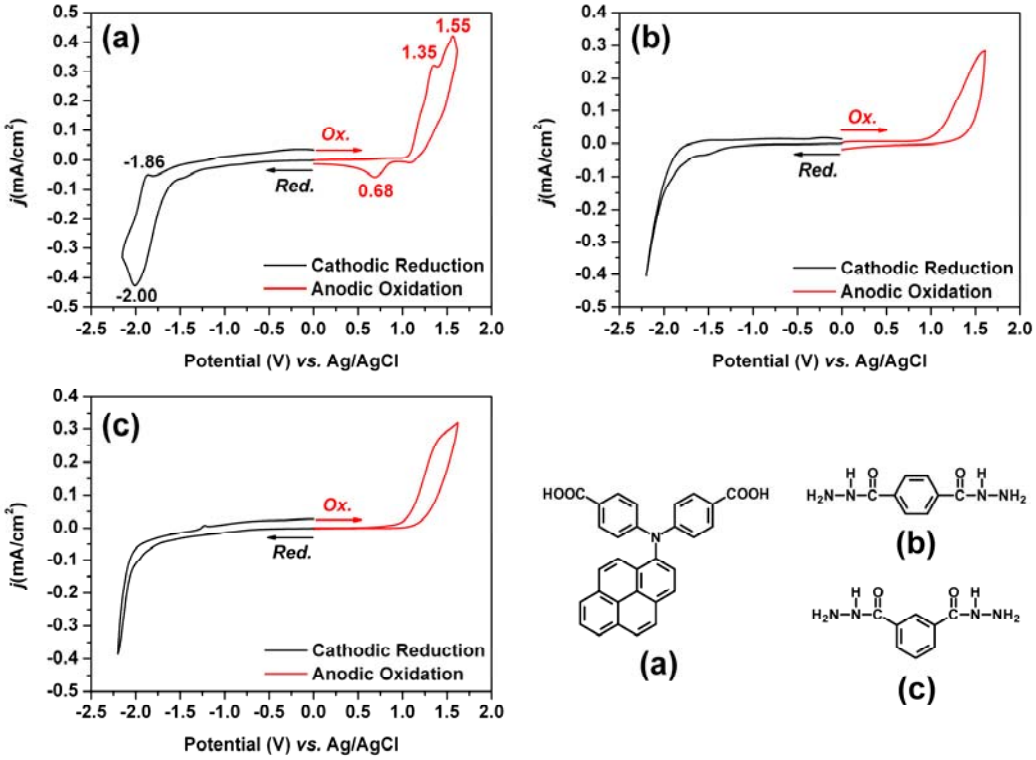


Fig. S6 Cyclic voltammograms of individual reacting compounds (~10^{-3} M) in CH_3CN (for oxidation) and DMF (for reduction) solutions containing 0.1 M Bu_4NClO_4 at a Pt coil electrode, scan rate = 50 mV/s.

Table S1 Elemental analysis of the polyoxadiazoles

Polymer Code	Elemental Analyses of Polymers				
	Formula Weight		C (%)	H (%)	N (%)
II-TPH	$(C_{38}H_{21}N_5O_2)_n$	Calcd.	78.74	3.65	12.08
	$(579.63)_n$	Found	78.61	3.57	11.89
II-IPH	$(C_{38}H_{21}N_5O_2)_n$	Calcd.	78.74	3.65	12.08
	$(579.63)_n$	Found	78.59	3.53	11.92