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Supplementary Information

For

Fluorescent and electrochromic polyamides with pyrenylamine chromophore

By

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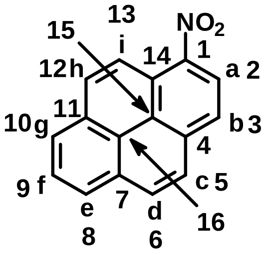
List of Contents for Supplementary Material:

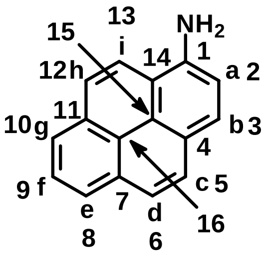
Materials. Pyrene (Acros), 4-fluoronitrobenzene (Acros), copper(II) nitrate trihydrate (Showa), 10% palladium on charcoal (Pd/C) (Lancaster), cesium fluoride (CsF) (Acros), acetic anhydride (Tedia), triphenyl phosphite (TPP) (Acros), and hydrazine monohydrate (TCI) were used without further purification. *N,N*-Dimethylacetamide (DMAc) (Tedia), *N,N*-dimethylformamide (DMF) (Tedia), pyridine (Py) (Wako), *N*-methyl-2-pyrrolidone (NMP) (Tedia), and acetonitrile (Tedia) were dried over calcium hydride for 24 h, distilled under reduced pressure, and stored over 4 Å molecular sieves in a sealed bottle. The aromatic dicarboxylic acids such as terephthalic acid (**5a**) (Wako), isophthalic acid (**5b**) (Wako), 4,4'-biphenyldicarboxylic acid (**5c**) (TCI), 4,4'-dicarboxydiphenyl ether (**5d**) (TCI), bis(4-carboxyphenyl) sulfone (**5e**) (New Japan Chemicals Co.), 2,2-bis(4-carboxyphenyl)hexafluoropropane (**5f**) (TCI), 1,4-naphthalenedicarboxylic acid (**5g**) (Wako), 2,6-naphthalenedicarboxylic acid (**5h**) (TCI), 1,4-dicarboxycyclohexane (**5i**) (TCI), and adipic acid (**5j**) (TCI) were used as received. Commercially obtained anhydrous calcium chloride ($CaCl_2$) was dried under vacuum at 180 ^oC for 8 h prior to use. Tetrabutylammonium perchlorate (TBAP) (TCI) was recrystallized twice by ethyl acetate under nitrogen atmosphere and then dried *in vacuo* prior to use. Poly(methyl methacrylate) (PMMA) (M_W 120,000) and propylene carbonate (PC) were used as received from Aldrich and Acros Organic, respectively.

Synthesis of 1-Nitropyrene (1): In a 500-mL three-neck round-bottomed flask equipped with a stirring bar under nitrogen atmosphere. To a mixture of pyrene (20.2 g, 100 mmol) and Ac_2O (26 mL, 277 mmol) in 200 mL of dried EtOAc was added $Cu(NO_3)_2$ (36 g, 150 mmol). The mixture was stirred at 55 ^oC for 24 hr and a thick yellow precipitate formed during nitration. The reaction was cooled to room temperature and inorganic materials were filtered off. The crude product obtained on evaporation of solvent was purified by recrystallized from amount of ethanol to afford 22.6 g (92 % in yield) of fluffy, amber, fine needles with a mp of 151-152 ^oC (by DSC 2 ^oC/ min). FT-IR (KBr): 1331, 1593 cm^{-1} (NO_2 stretch). ^1H NMR (500 MHz, DMSO-d_6, δ, ppm): 8.20 (t, J = 7.7 Hz, 1H, H_f), 8.26 (d, J = 8.9 Hz, 1H, H_h), 8.37 (d, J = 9.1 Hz, 1H, H_b), 8.39 (d, J = 9.3 Hz, 1H, H_i), 8.37 (d, J = 9.1 Hz, 1H, H_b), 8.39 (d, J = 9.3 Hz, 1H, H_i), 8.44 (d, J = 9.5 Hz, 1H, H_c), 8.45 (d, J = 7.5 Hz, 1H, H_e), 8.47 (d, J = 7.7

Hz, 1H, H_g) , 8.65 (d, *J* = 9.4 Hz, 1H, H_d) , 8.68 (d, *J* = 8.5 Hz, 1H, H_a). ^{13}C NMR (125 MHz, DMSO-d_6, δ, ppm): 120.83 (C^6), 122.62 (C^2), 123.58 (C^{14}), 123.71 (C^1), 124.69 (C^3), 126.90 (C^{12}), 127.30 (C^8), 127.44 (C^9), 127.96 (C^{10}), 129.45 (C^{16}), 130.36 (C^{15}), 130.78 (C^{13}), 131.59 (C^5), 134.56 (C^7+C^{11}), 142.25 (C^{16}).



Synthesis of 1-Aminopyrene (2): In a 250-mL three-neck round-bottomed flask equipped with a stirring bar under nitrogen atmosphere, 12.4 g (50 mmol) of nitro compound **1** and 0.15 g of 10 % Pd/C were dissolved/suspended in 80 mL of ethanol and 40 mL of THF. The suspension solution was heated to reflux, and 6.5 mL of hydrazine monohydrate was added slowly to the mixture, then the solution was stirred at reflux temperature. After a further 12 h of reflux, the solution was filtered to remove Pd/C, and the filtrate was evaporated under reduced pressure to dryness. The crude product was recrystallized by ethanol/water and dried *in vacuo* at 80 °C to give 9.23 g (85 % in yield) of greenish yellow crystals with a mp of 115-116 °C (by DSC 2 °C/ min). FT-IR (KBr): 3200-3400 cm^{-1} (N-H stretch). ^{1}H NMR (500 MHz, DMSO-d_6, δ, ppm): 6.34 (s, 2H, -NH_2), 7.40 (d, *J* = 8.3 Hz, 1H, H_a), 7.71 (d, *J* = 8.8 Hz, 1H, H_d), 7.86 (t, *J* = 7.7 Hz, 1H, H_f), 7.88 (d, *J* = 8.8 Hz, 1H, H_c), 7.92 (d, *J* = 9.3 Hz, 1H, H_i), 7.97 (d, *J* = 8.4 Hz, 1H, H_b), 7.98 (d, 1H, H_e), 7.99 (d, 1H, H_g), 8.29 (d, J = 9.2 Hz, 1H, H_h). ^{13}C NMR (125 MHz, DMSO-d_6, δ, ppm): 113.13 (C^2), 114.72 (C^4), 121.39 (C^{14}), 121.76 (C^6), 122.13 (C^{12}), 122.37 (C^8), 122.91 (C^{10}), 124.14 (C^{13}), 125.14 (C^{15}), 125.70 (C^{16}), 125.85 (C^9), 126.52 (C^3), 127.70 (C^5), 131.67 (C^{11}), 132.02 (C^7), 144.36 (C^1).



Synthesis of Model Compound, *N,N*-Di(4-benzamidophenyl)-1-aminopyrene (M1): A 50 mL round-bottom flask with a magnetic stirrer was charged with 0.400 g (1.0 mmol) of diamine monomer **4**, 0.244 g (2.0 mmol) of benzoic acid, 0.5 mL of triphenyl phosphite (TPP), 0.4 mL of NMP, and 0.3 mL of pyridine. The reaction mixture was heated with stirring at 120 °C for 3 hr. The reaction solution was poured into 150 mL of stirring cold methanol giving rise to a greenish precipitate that was collected by filtration, washed thoroughly with hot water and methanol, and dried *in vacuo* at 80 °C. Yield = 0.595 g (98%). IR (KBr): 3282 (amide N-H stretch), 1647 cm^{-1} (amide C=O stretch). ^{1}H NMR (500 MHz, DMSO-d_6, δ, ppm): 6.99 (d, J = 9.0 Hz, 4H, H_j), 7.51 (t, J = 7.1 Hz, 4H, H_m), 7.57 (t, J = 7.4 Hz, 2H, H_n), 7.68 (d, J = 9.0 Hz, 4H, H_k), 7.86 (d, J = 8.2 Hz, 1H, H_a), 7.94 (d, J = 7.2 Hz, 4H, H_l), 8.07 (t, J = 7.7 Hz, 1H, H_f), 8.12 (d, J = 9.3 Hz, 1H, H_d), 8.17 (d, J = 9.2 Hz, 1H, H_h), 8.19 (d, J = 9.2 Hz, 1H, H_i), 8.23 (d, J = 7.5 Hz, 1H, H_e), 8.30 (d, J = 7.8 Hz, 1H, H_g), 8.34 (d, J = 8.2 Hz, 1H, H_b) 10.19 (s, 2H, amide N-H). ^{13}C NMR (125 MHz, DMSO-d_6, δ, ppm): 121.73 (C^{18}), 121.89 (C^{19}), 122.85 (C^{6}), 124.01 (C^{4}), 125.13 (C^{8}), 125.37 (C^{10}), 125.58 (C^{14}), 126.35 (C^{3}), 126.57 (C^{9}), 126.88 (C^{15}), 127.03 (C^{13}), 127.20 (C^{2}), 127.23 (C^{12}), 127.53 (C^{22}), 127.76 (C^{5}), 128.31 (C^{23}), 128.86 (C^{16}), 130.46 (C^{11}), 130.78 (C^{7}), 131.39 (C^{21}), 133.49 (C^{24}), 134.97 (C^{20}), 140.69 (C^{1}), 144.31 (C^{17}), 165.15 (amide, C=O).

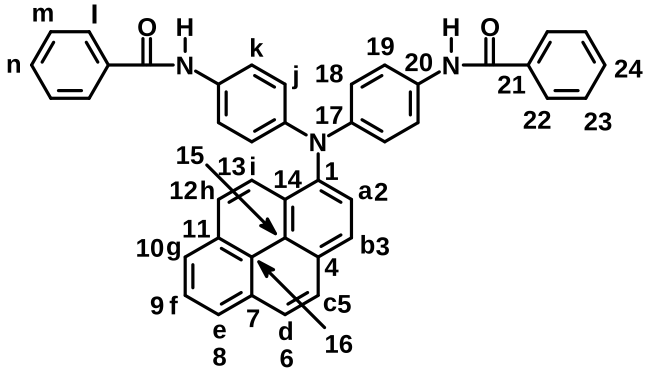
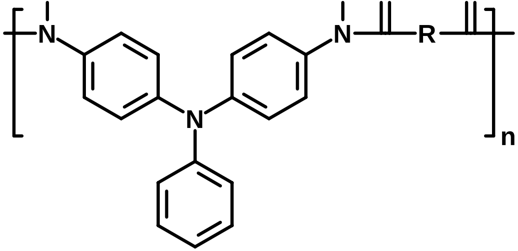


Table S1 Inherent viscosity[a] and solubility behavior[b] of polyamides

Polymer	η_{inh}	Various Solvent [c]					
Code	(dL/g)	NMP	DMAc	DMF	DMSO	*m*-Cresol	THF
6a	1.08	++ (++)	++ (++)	++ (+)	++ (+)	++ (+)	- (-)
6b	0.54	++ (++)	++ (++)	++ (+)	++ (+)	++ (+)	- (-)
6c	1.23	++ (++)	++ (++)	++ (+)	++ (+)	++ (+)	- (-)
6d	0.95	++ (++)	++ (++)	++ (++)	++ (++)	++ (+)	- (-)
6e	1.02	++ (++)	++ (++)	++ (++)	++ (++)	++ (+)	- (-)
6f	0.95	++ (++)	++ (++)	++ (++)	++ (++)	++ (+)	++ (-)
6g	0.76	++ (++)	++ (++)	++ (+)	++ (+)	++ (++)	- (-)
6h	1.13	++ (++)	++ (++)	++ (+)	++ (+)	++ (+)	- (-)
6i	0.73	++ (++)	++ (++)	++ (++)	++ (++)	++ (+)	- (-)
6j	0.70	++ (++)	++ (++)	++ (++)	++ (++)	++ (+)	- (-)

[a] Inherent viscosity measured at a concentration of 0.5 dL/g in DMAc – 5 wt % LiCl at 30 °C. [b] Solubility: ++: soluble at room temperature; + - : partially soluble; +: soluble on heating; - : insoluble even on heating. [c] Solvent: NMP: *N*-methyl-2-pyrrolidone; DMAc: *N*,*N*-dimethylacetamide; DMF: *N*,*N*-dimethylformamide; DMSO: dimethyl sulfoxide; THF: tetrahydrofuran. Values in parentheses are data of analogous polyamides **6’** having the corresponding diacid residue as in the **6** series.



6'

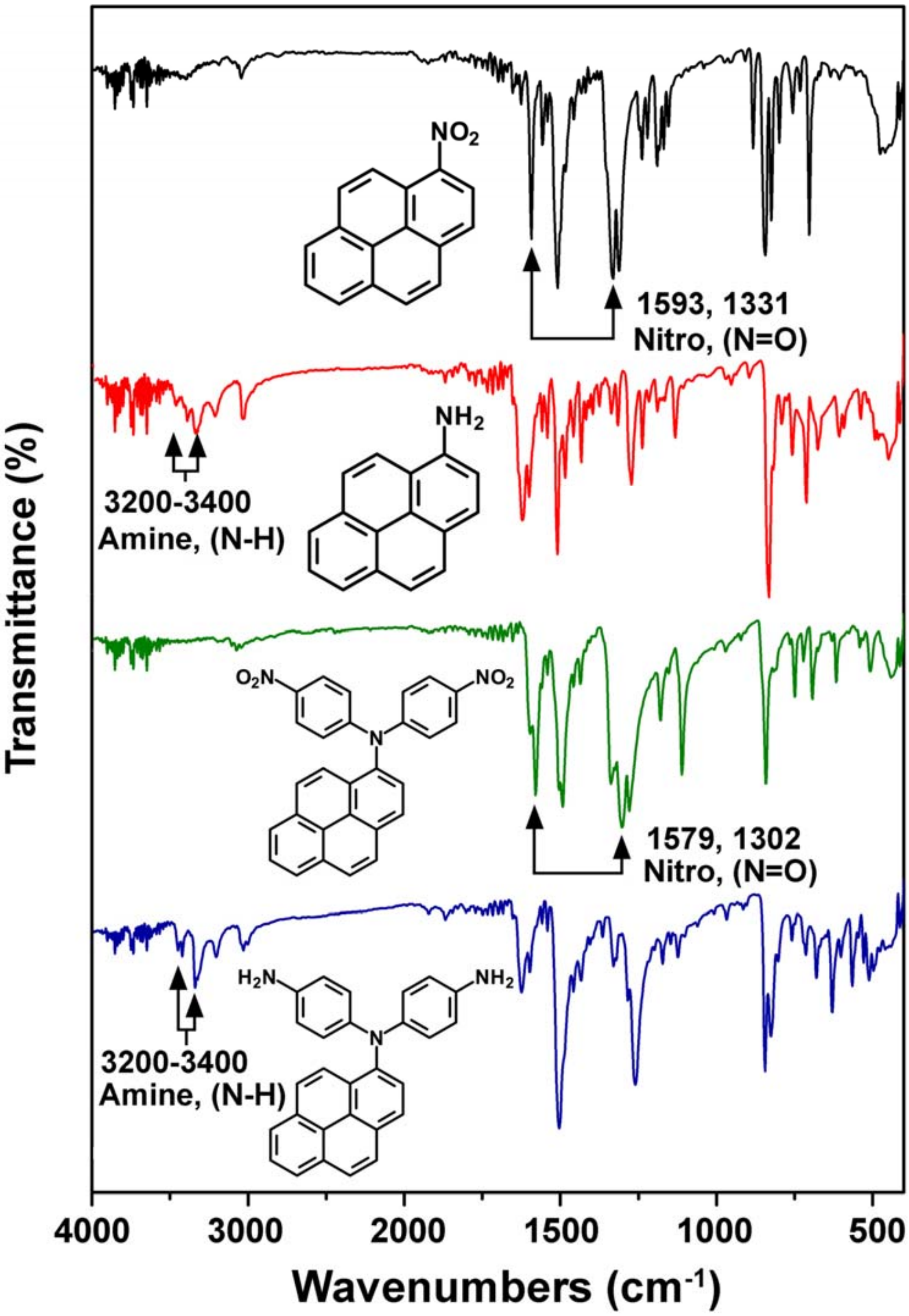


Fig. S1 IR spectra of compounds **1-4**.

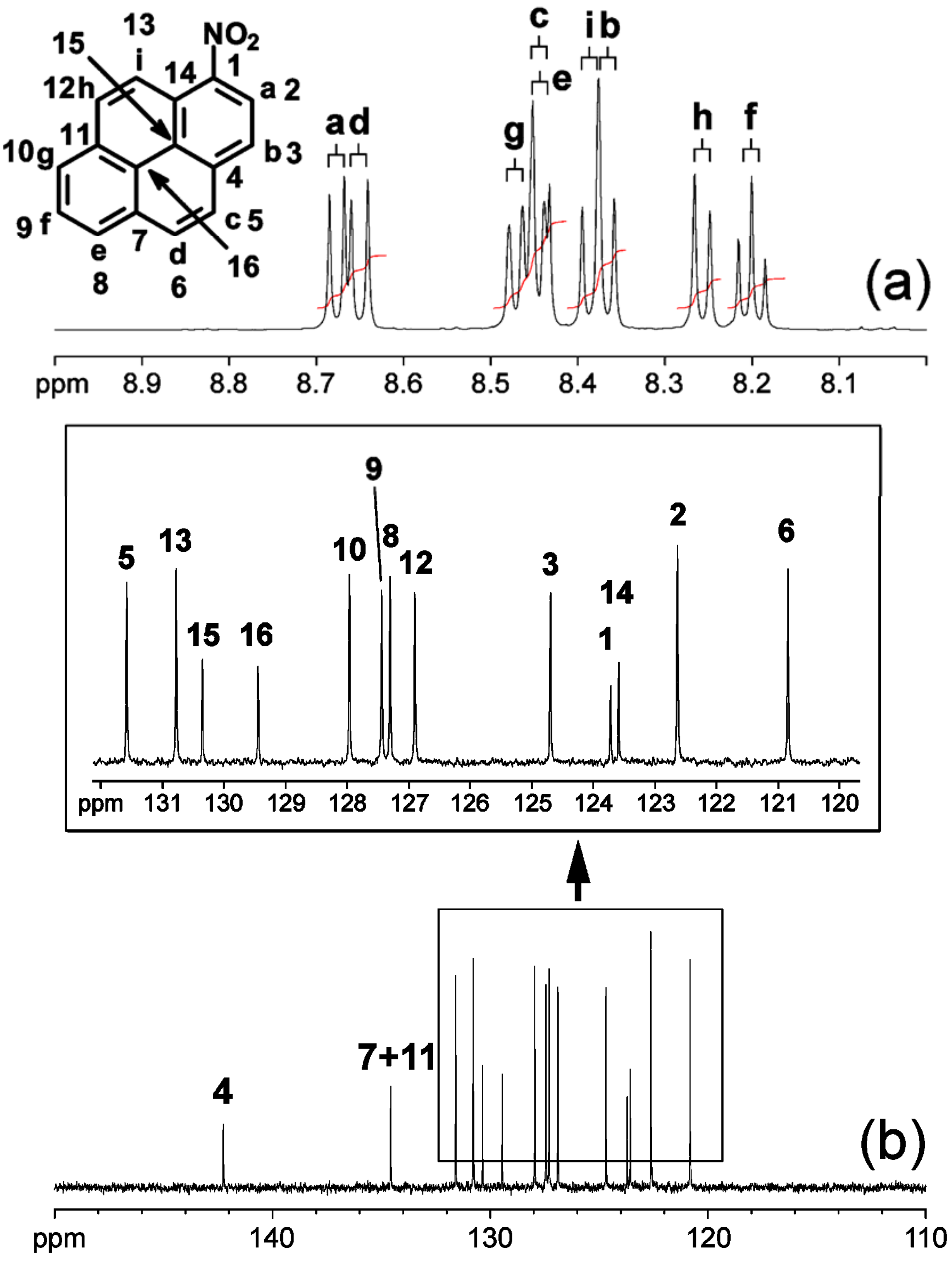


Fig. S2 (a) ^{1}H and (b) ^{13}C NMR spectra of 1-nitropyrene (**1**) in DMSO-d_6.

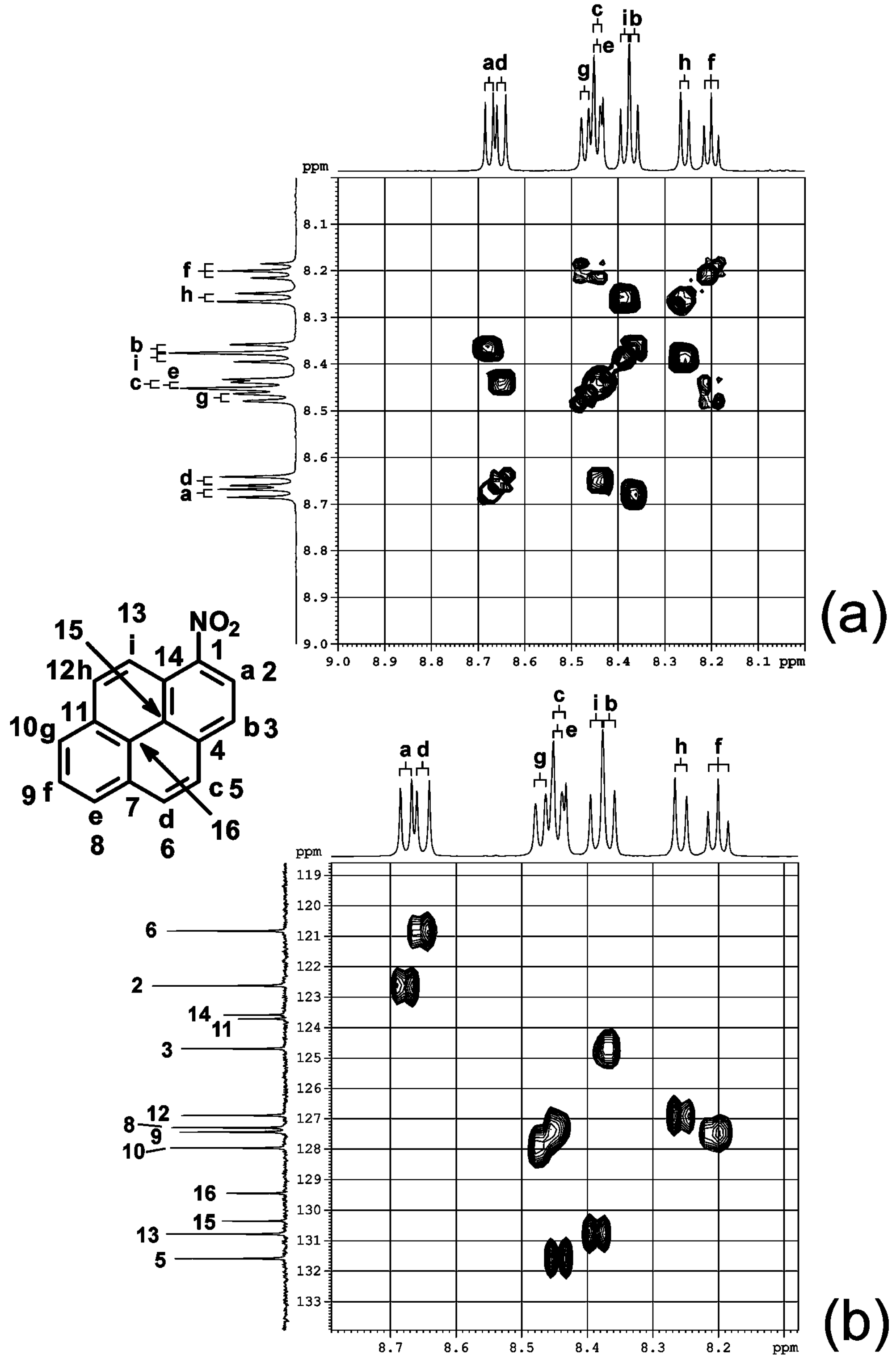


Fig. S3 (a) H-H COSY and (b) C-H HMQC NMR spectra of 1-nitropyrene (**1**) in DMSO-d_6.

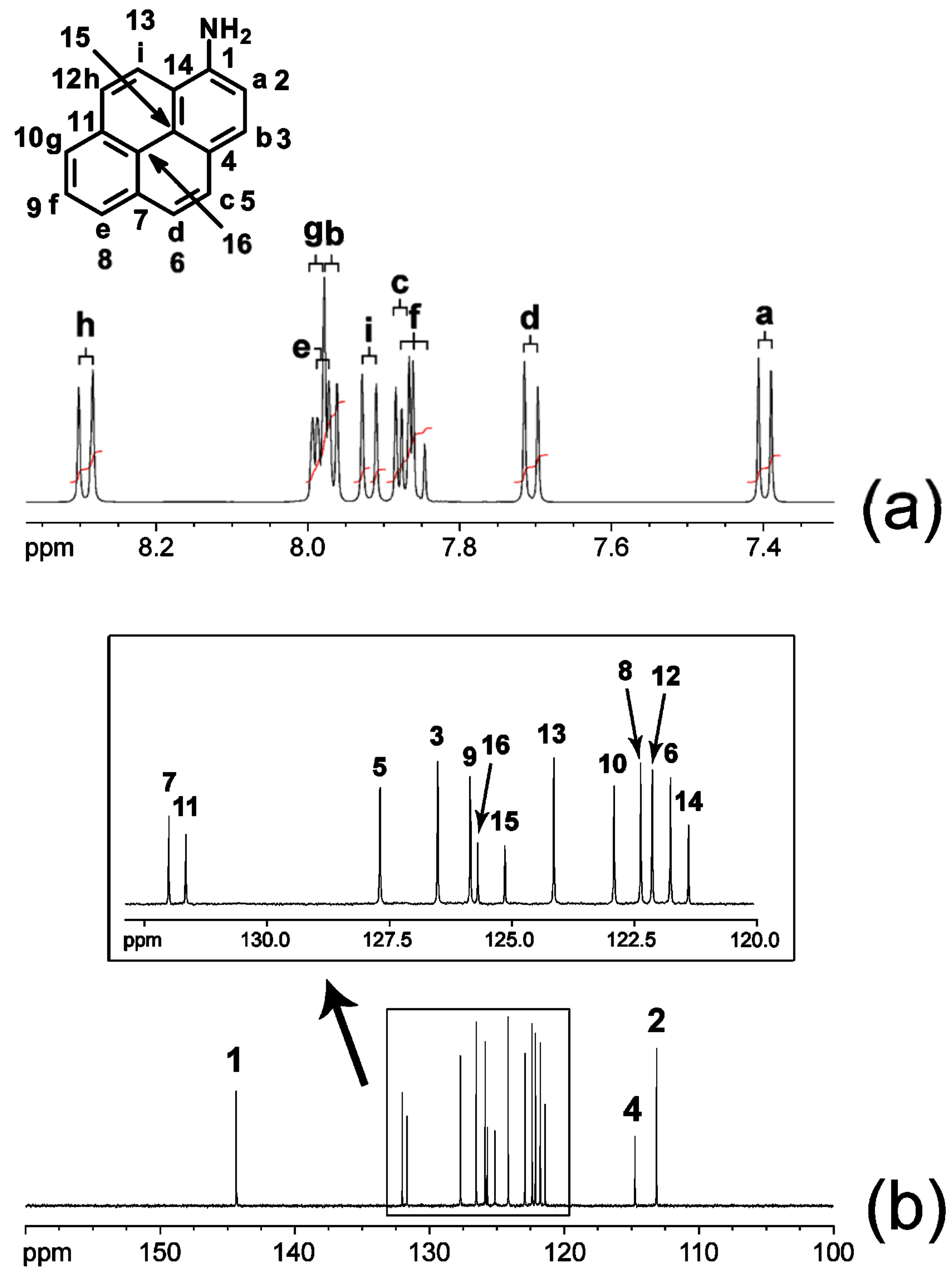


Fig. S4 (a) ^{1}H and (b) ^{13}C NMR spectra of 1-aminopyrene (**2**) in DMSO-d_6.

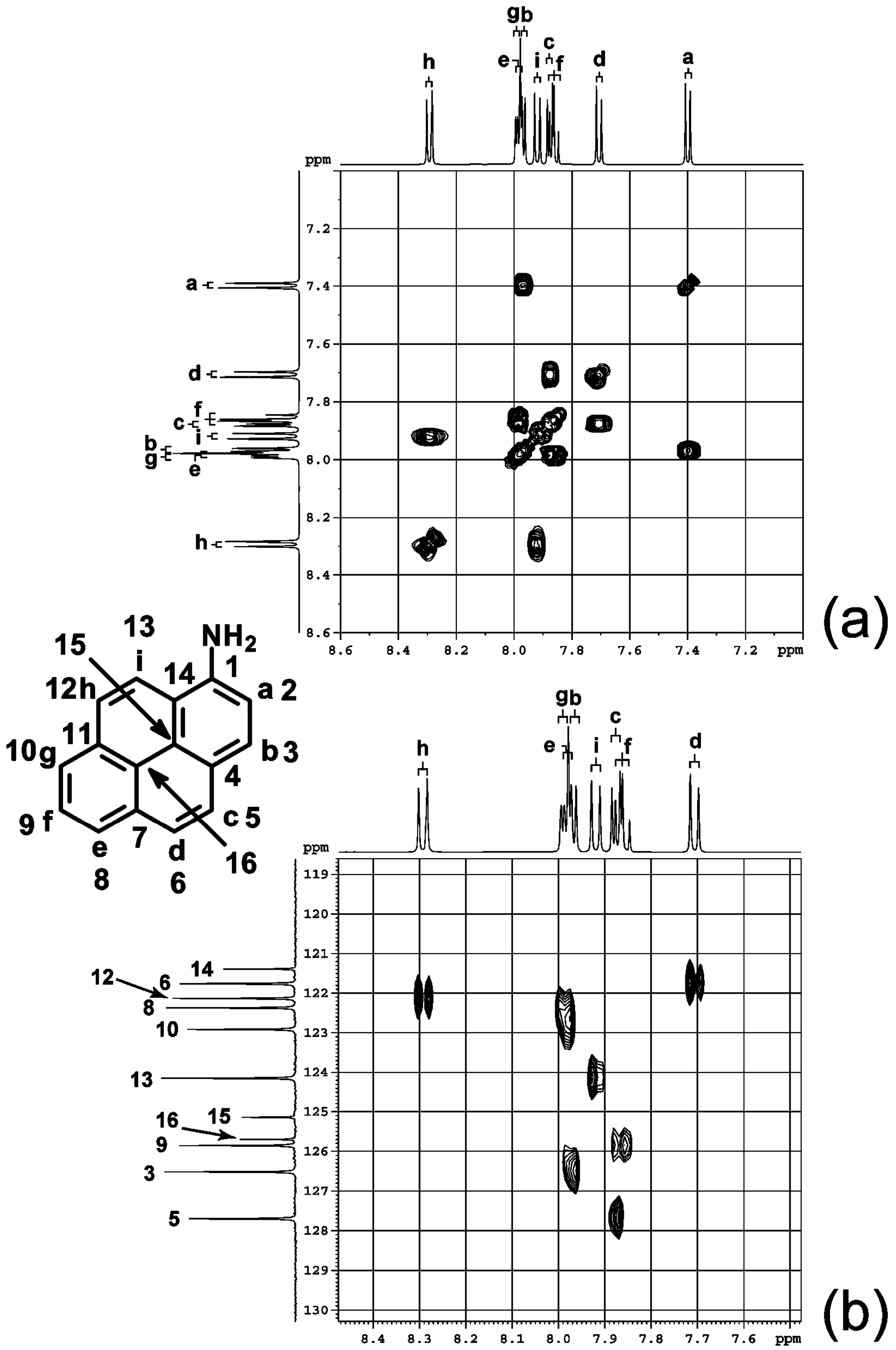


Fig. S5 (a) H-H COSY and (b) C-H HMQC NMR spectra of 1-aminopyrene (**2**) in DMSO-d_6.

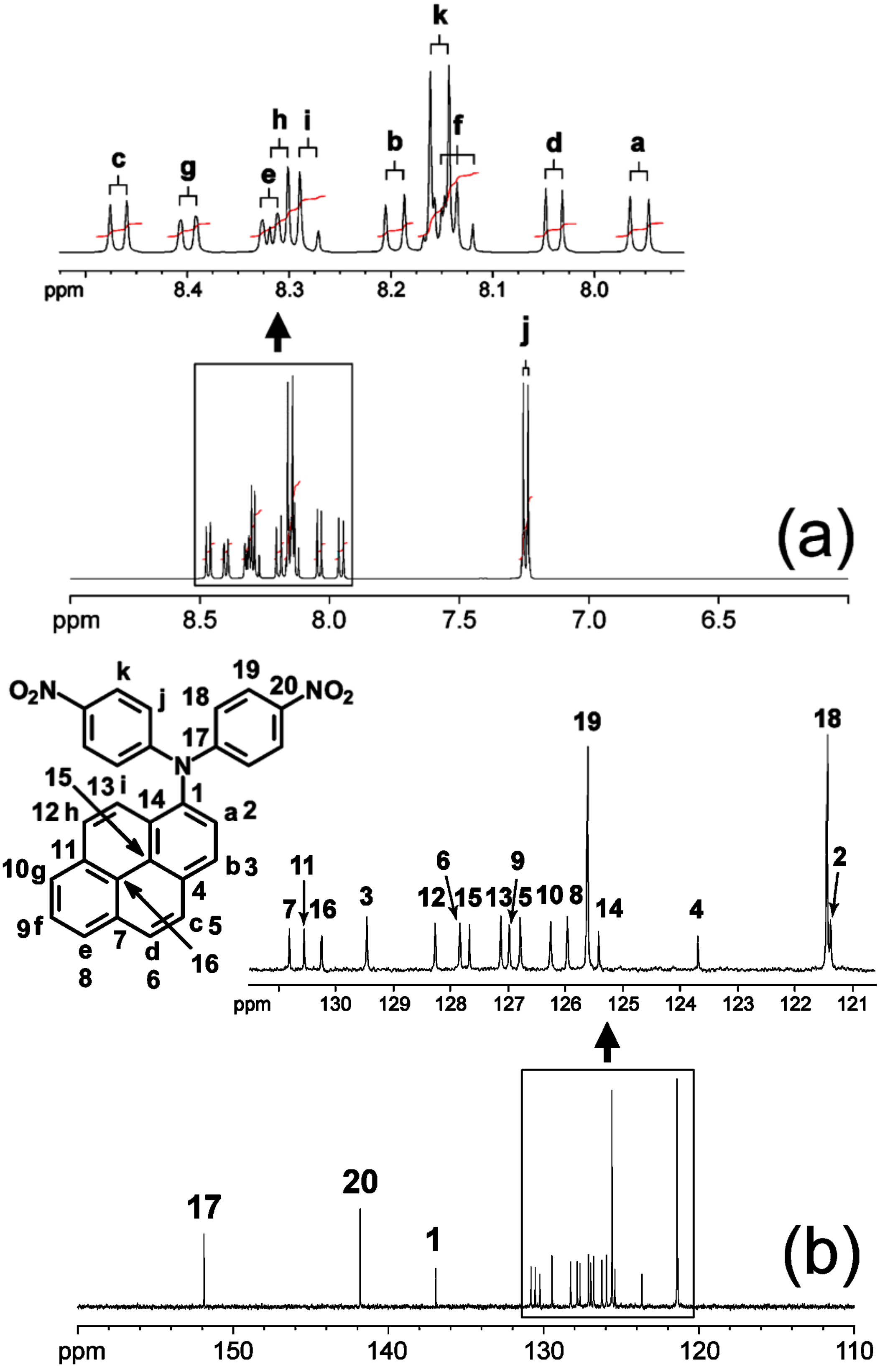


Fig. S6 (a) ^{1}H and (b) ^{13}C NMR spectra of dinitro compound **3** in DMSO-d_6.

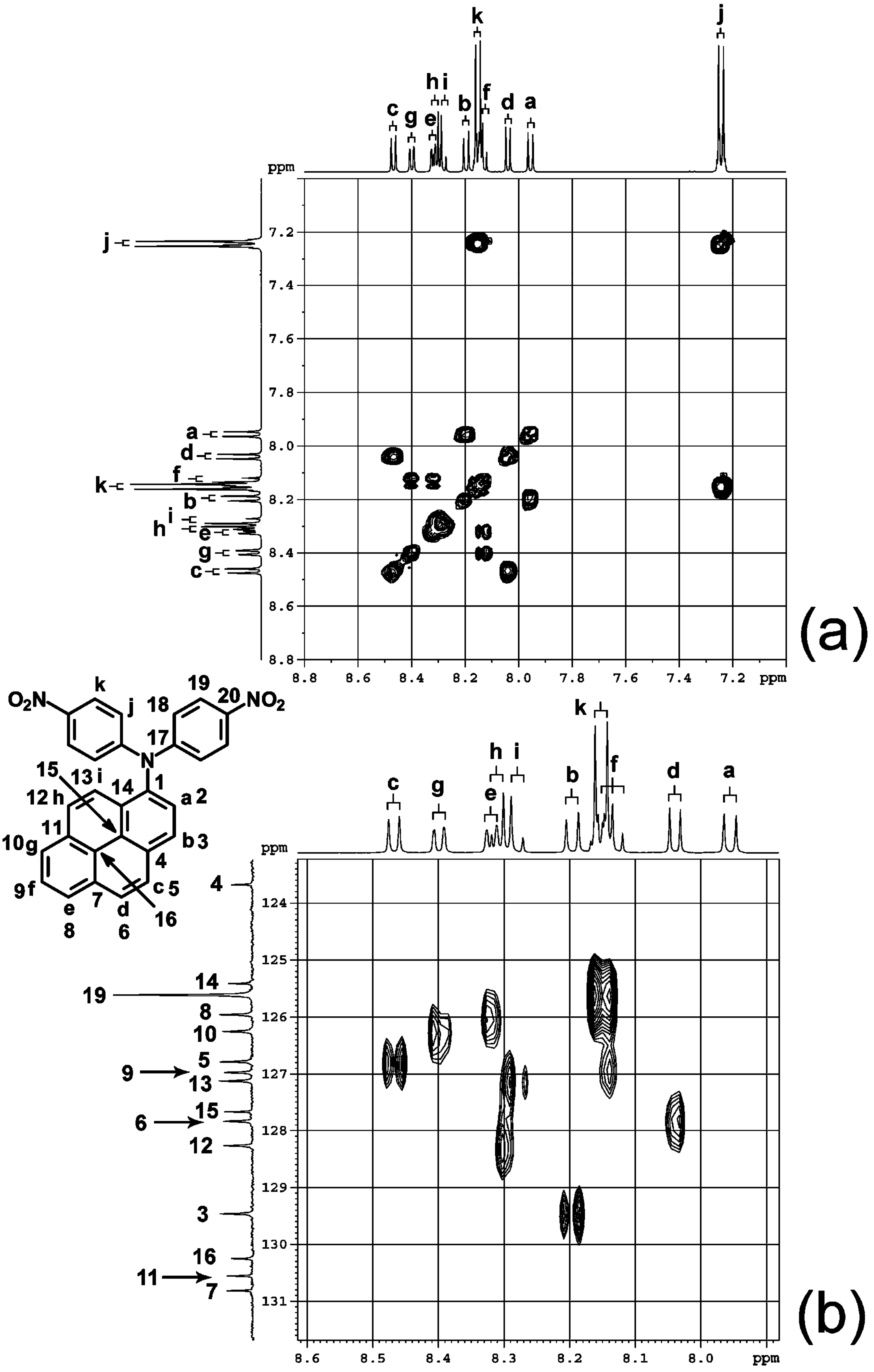


Fig. S7 (a) H-H COSY and (b) C-H HMQC NMR spectra of dinitro compound **3** in DMSO-d_6.

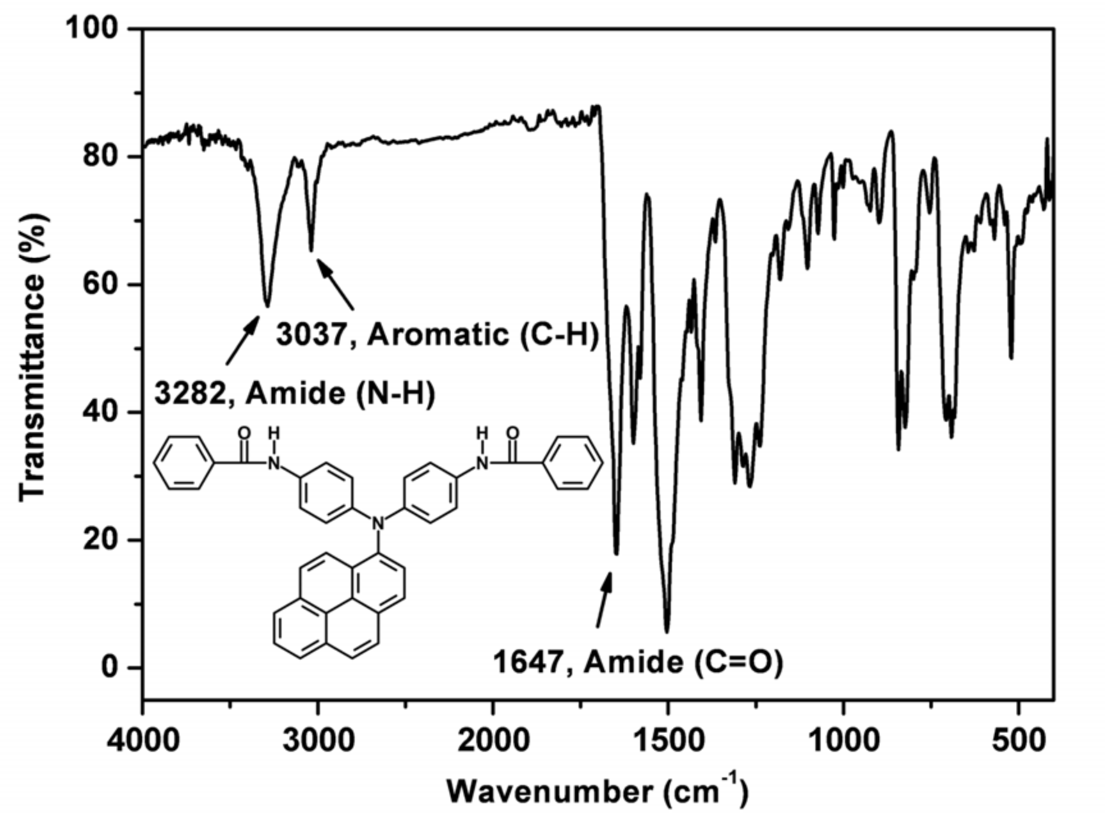


Fig. S8 IR spectra of amide-type model compound **M1**.

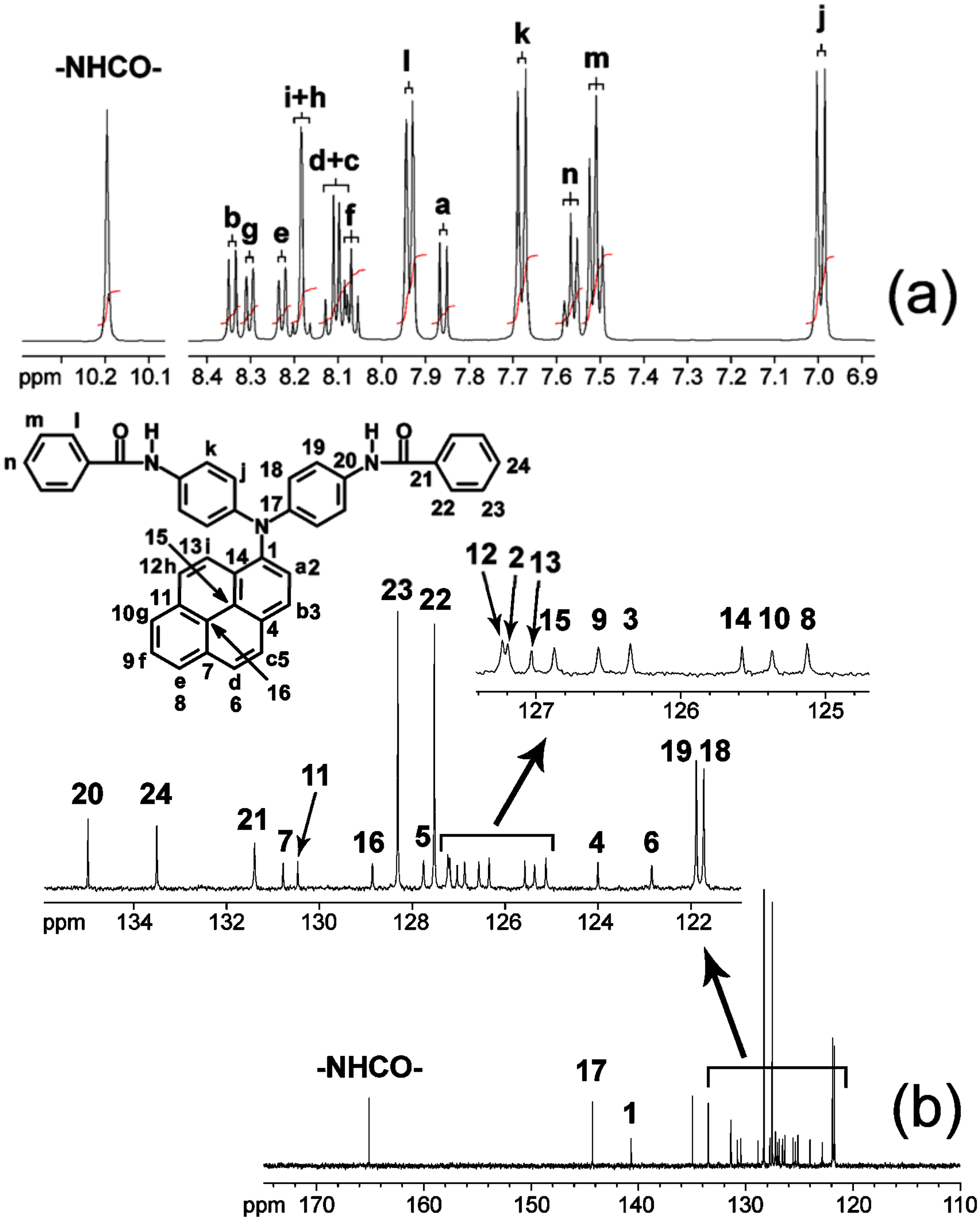


Fig. S9 (a) ^{1}H and (b) ^{13}C NMR spectra of model compound **M1** in DMSO-d_6.

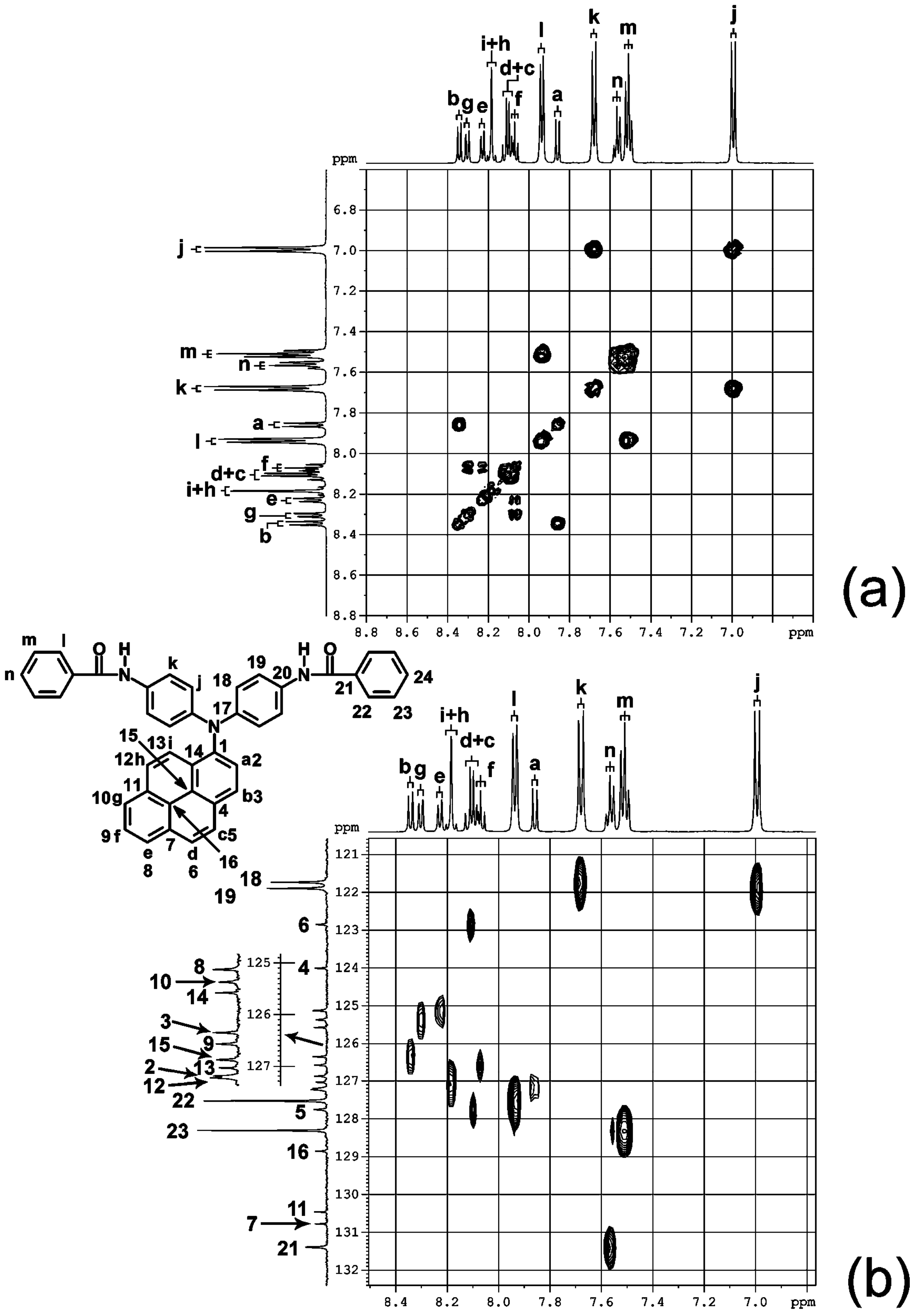


Fig. S10 (a) H-H COSY and (b) C-H HMQC NMR spectra of **M1** in DMSO-d_6.

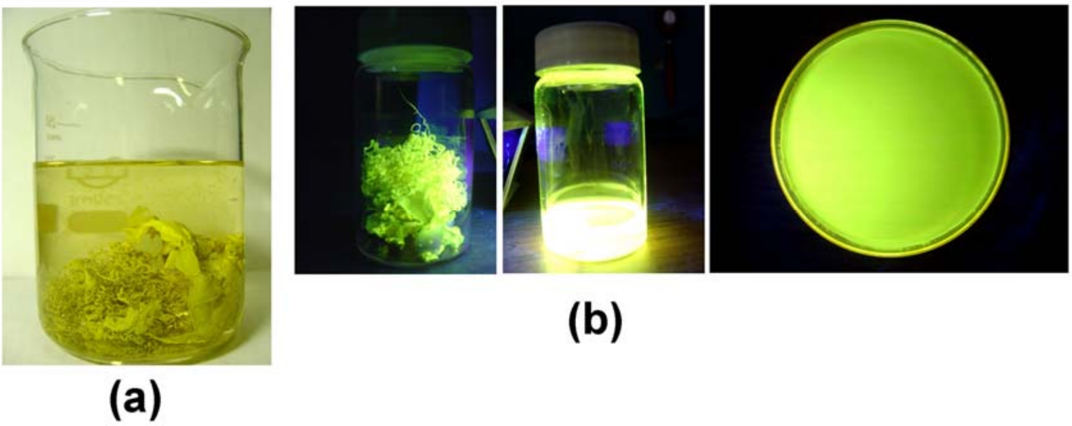


Fig. S11 (a) The as-prepared sample of polyamide **6i;** (b) Photoluminescence of the as-prepared sample, its DMAc solution, and its cast film irradiated by a laboratory UV lamp.

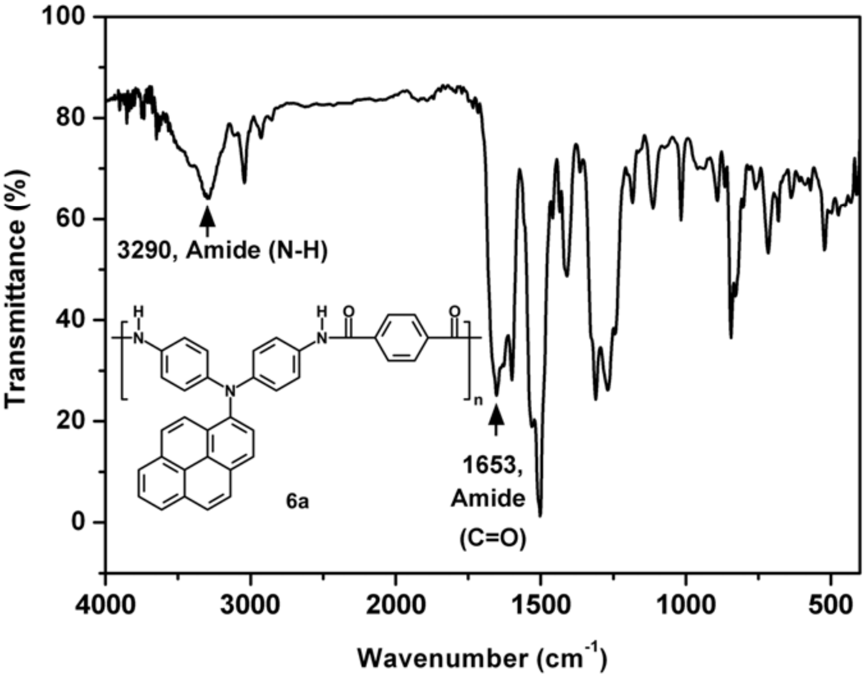


Fig. S12 IR spectra of polyamide **6a**.

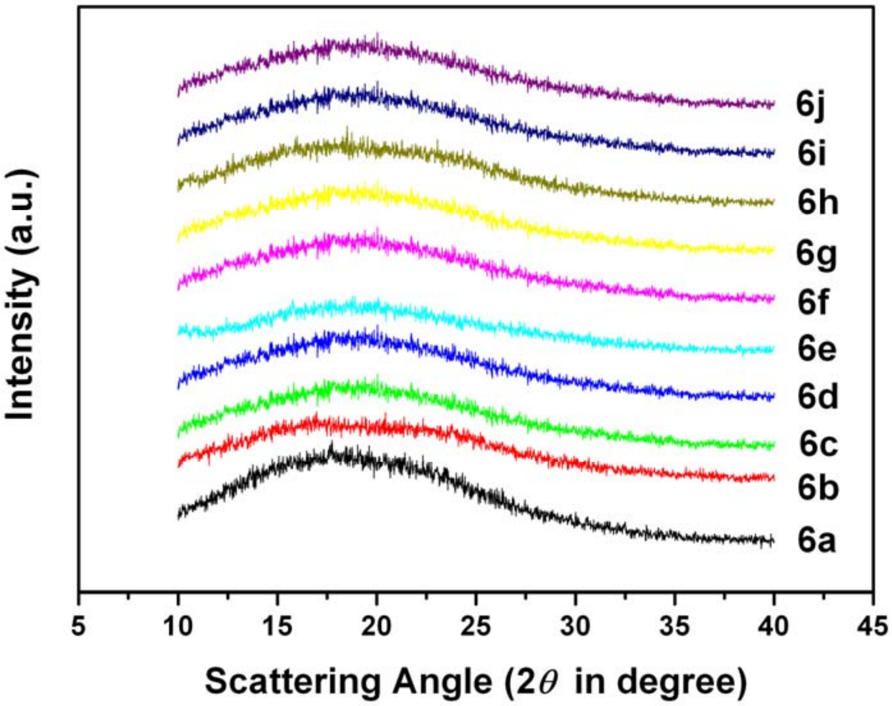


Fig. S13 WAXD patterns of polyamides **6a-6j**.

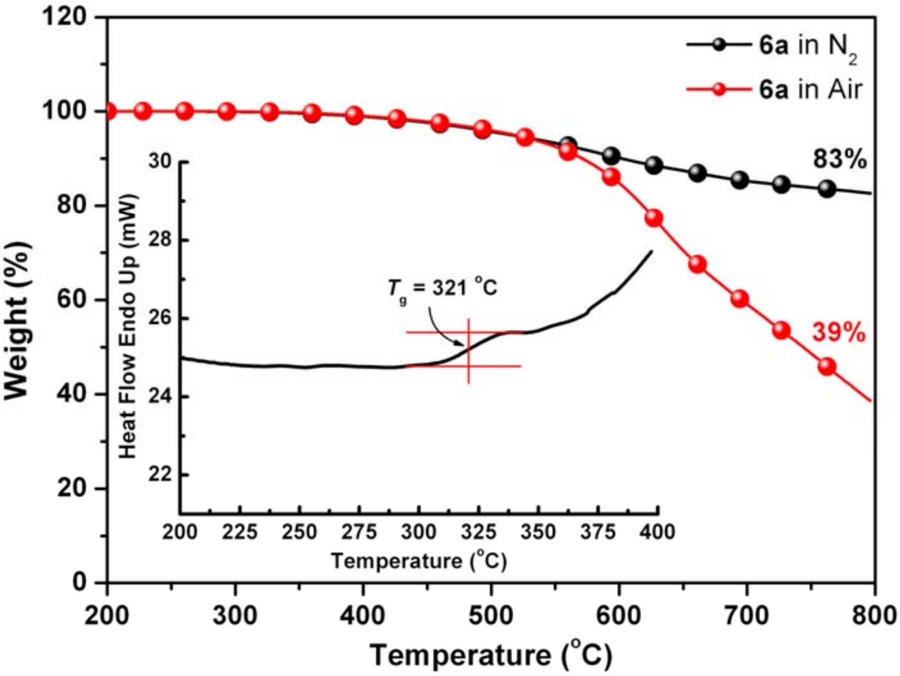


Fig. S14 TGA and DSC curve of polyamide **6a** with a heating rate of 20 °C/min.

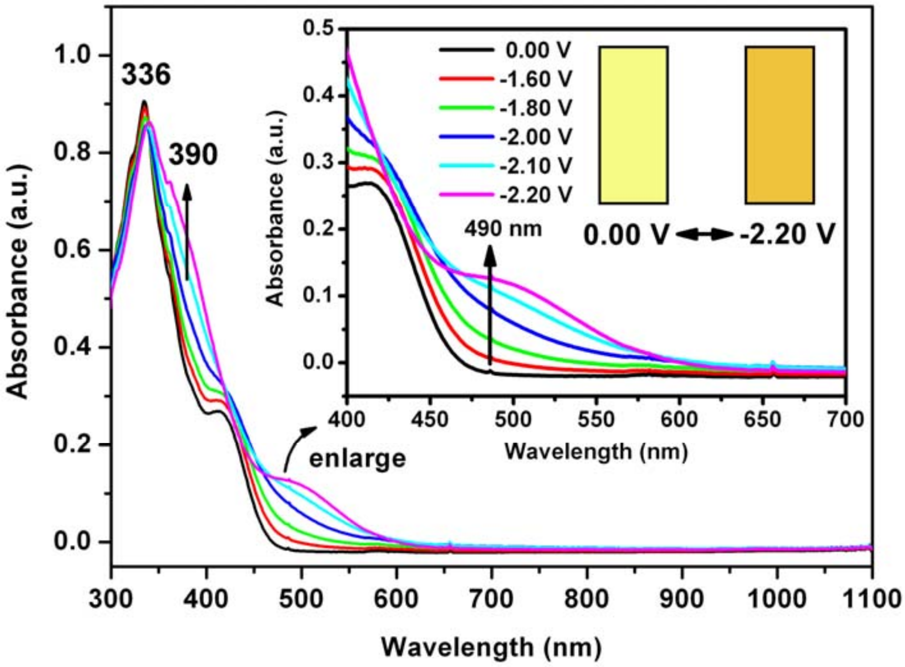


Fig. S15 Spectral changes of polyamide **6d** thin film on an ITO-coated glass substrate (in DMF with 0.1 M NBu_4ClO_4 as the supporting electrolyte) along with increasing of the applied voltage up to -2.20 V (vs. Ag/AgCl couple as reference). The inset shows the color changes between neutral and reductive states.

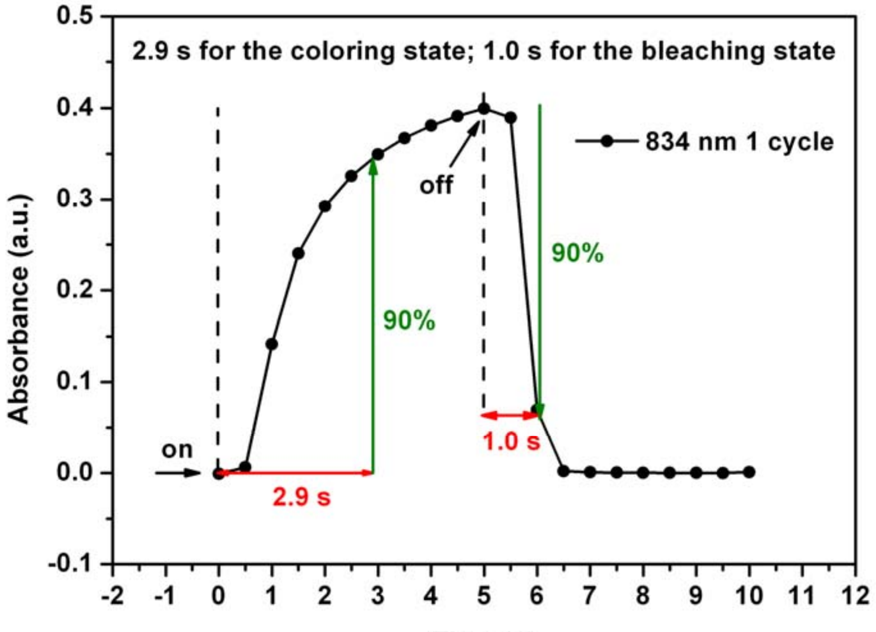


Fig. S16 Calculation of optical switching time for polyamide **6d** thin film at λ_{max} = 834 nm as the applied voltage was stepped between 0 and 1.00 V (vs. Ag/AgCl couple as reference) with cycle time = 10 s.