Supporting Information

Substituents and Resonance Effects on the Electrochemical Stability of Polyelectrochromic Triarylamine-based Polymers

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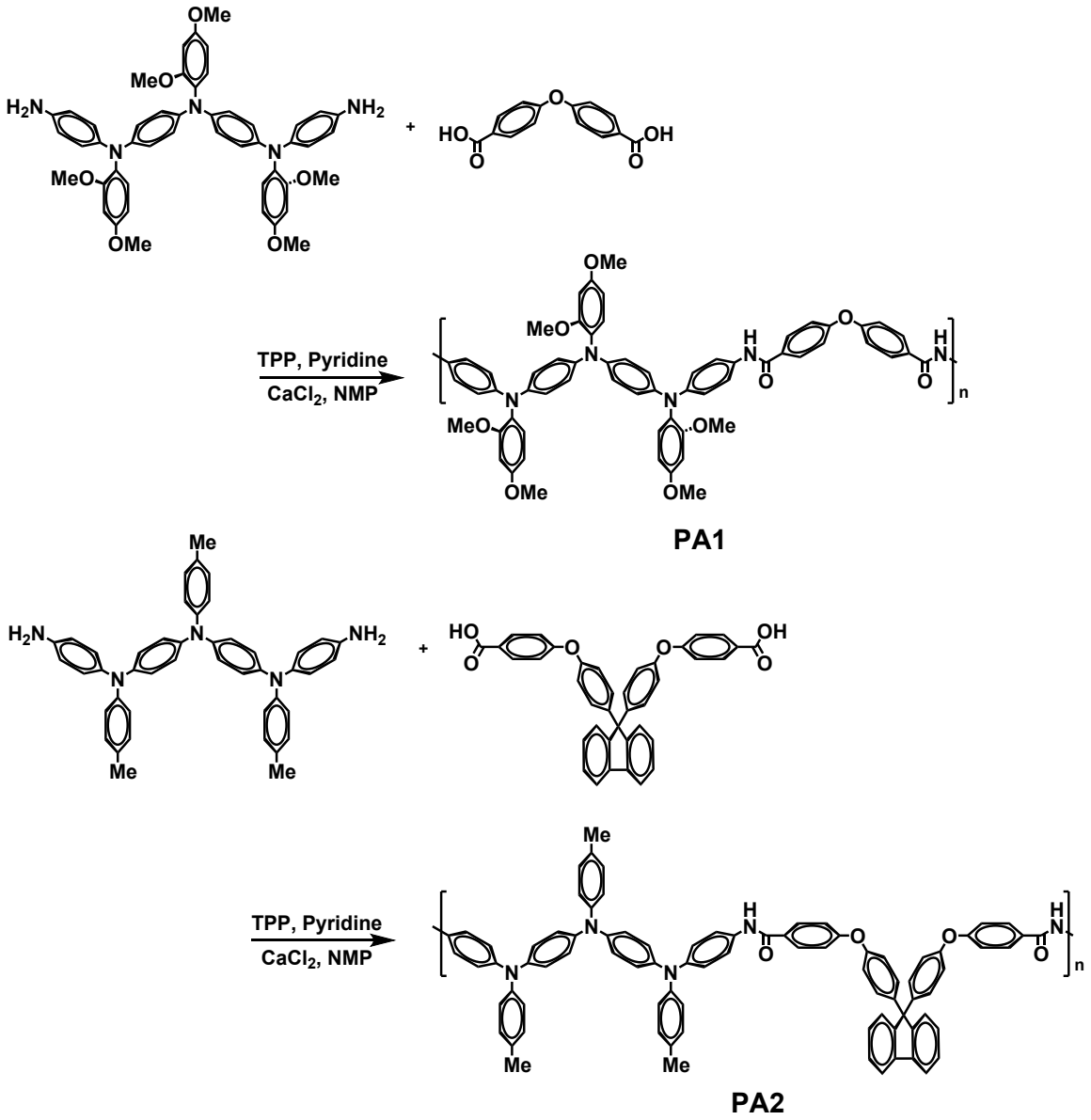

Scheme S1. Synthesis of the studied polyamides, **PA1** and **PA2**.

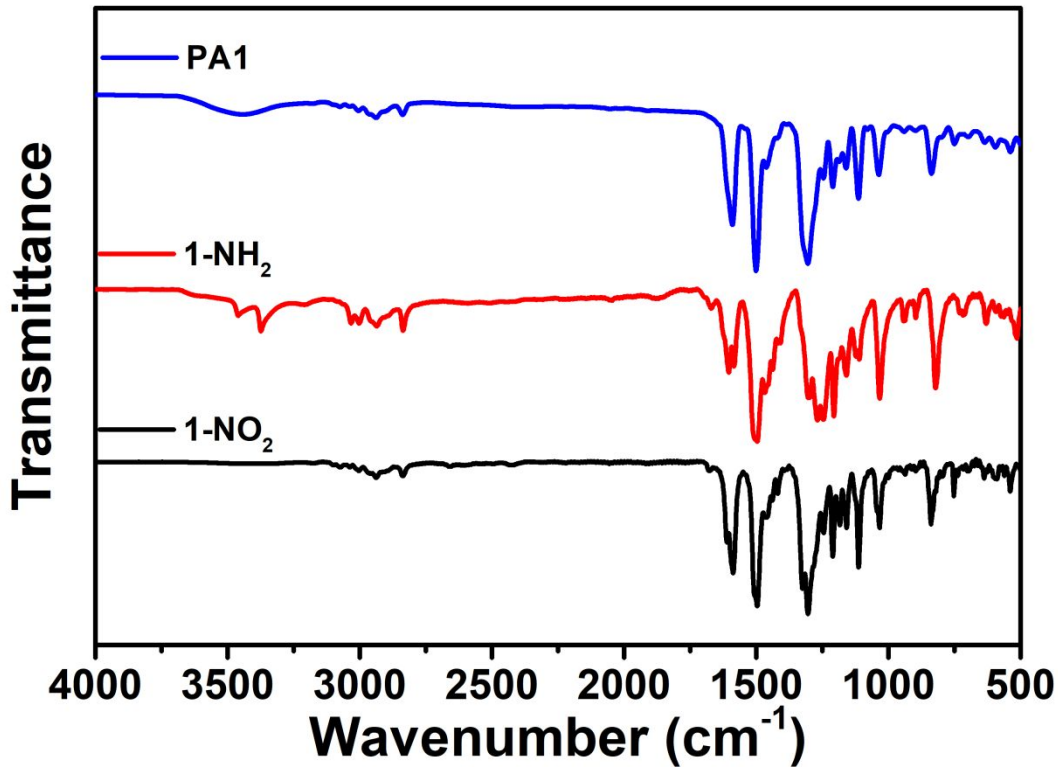

Figure S1. FT-IR spectra of **1-NO_2**, **1-NH_2**, and **PA1**.

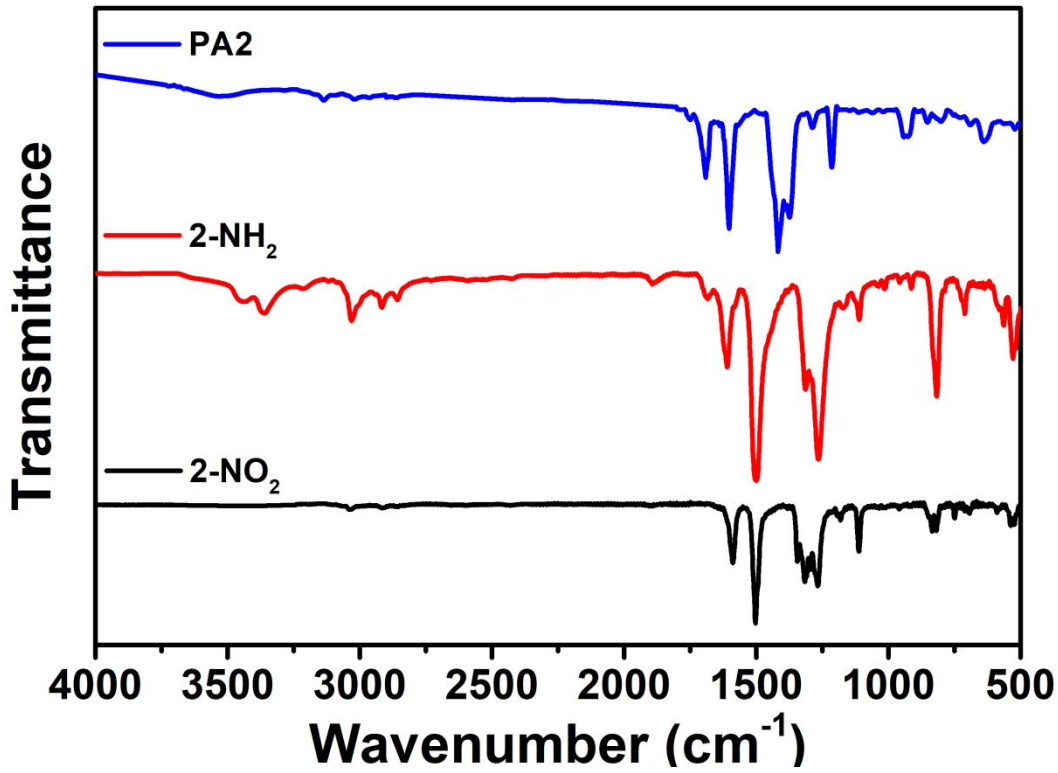

Figure S2. FT-IR spectra of **2-NO_2**, **2-NH_2**, and **PA2**.

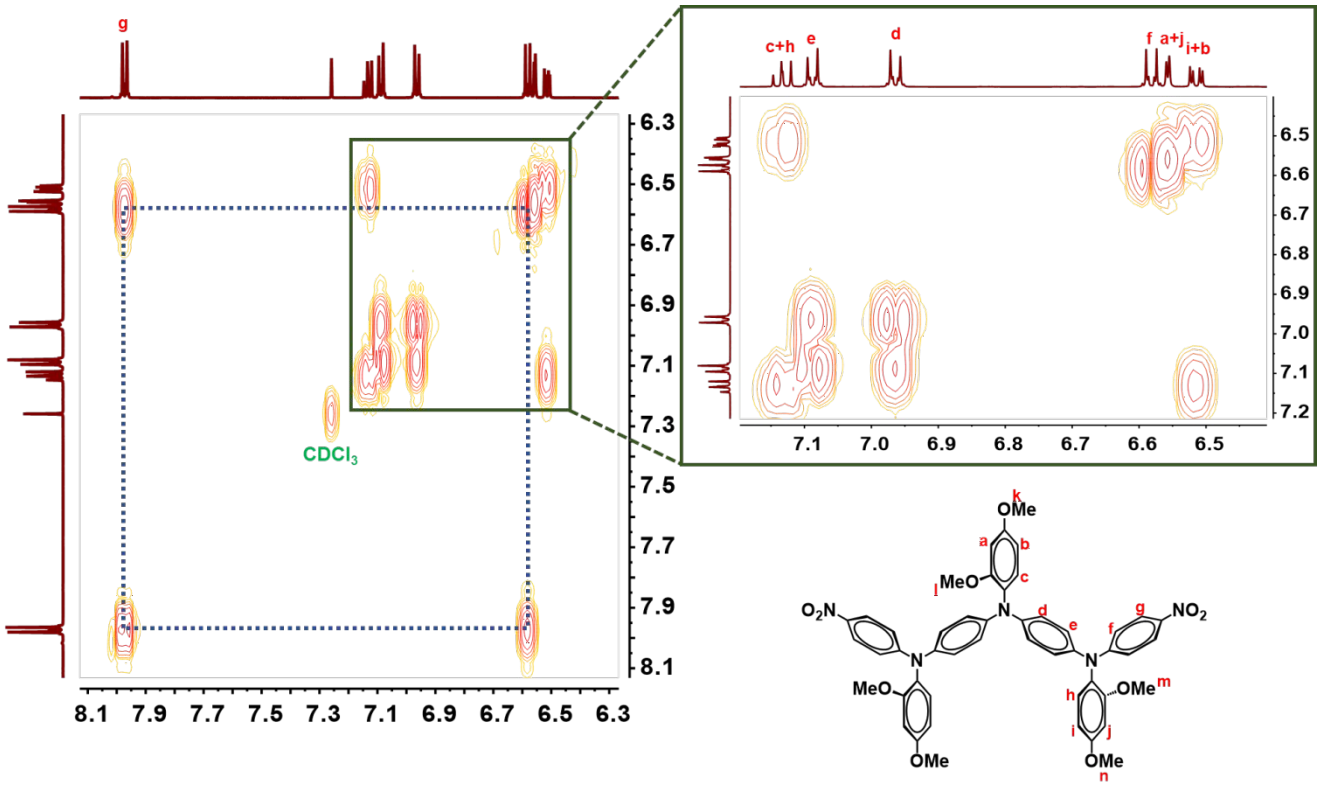

Figure S3. ^{1}H-^{1}H COSY spectrum NMR of **1-NO$_2$**. ($CDCl_3$)

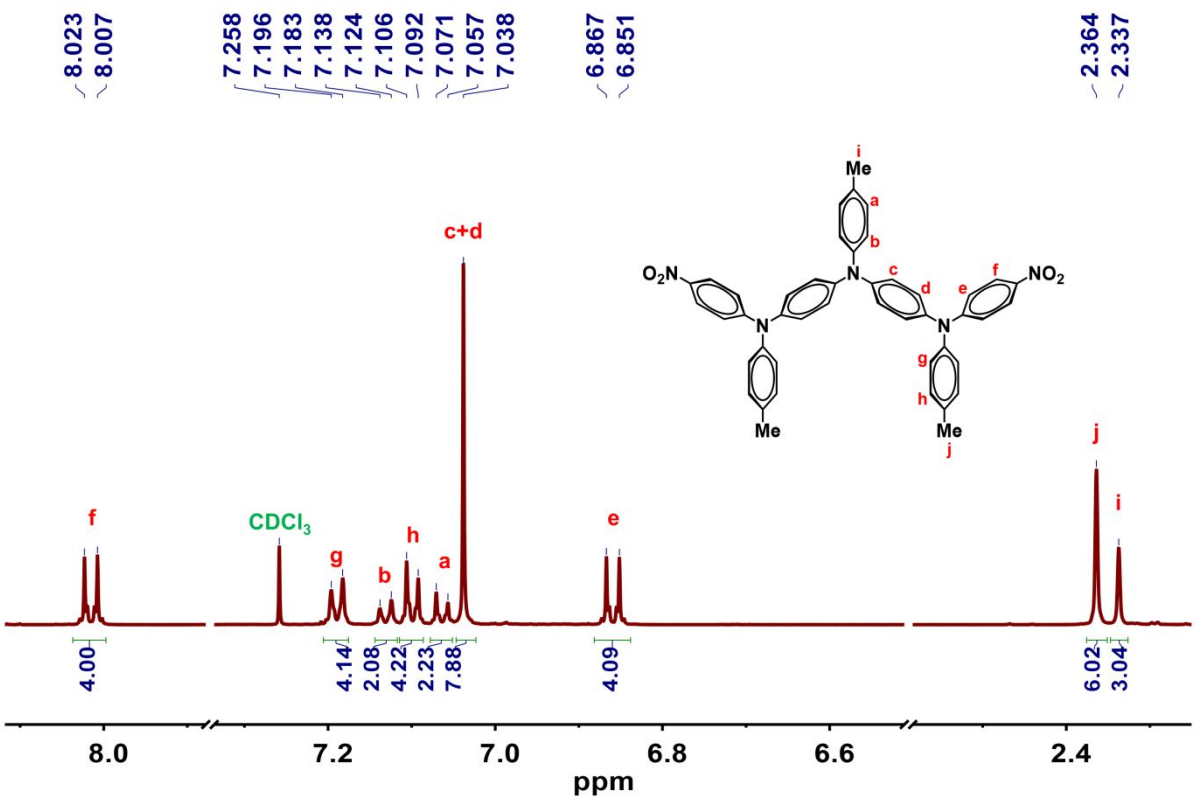

Figure S4. ^{1}H-NMR spectrum of 2-NO_2. ($CDCl_3$)

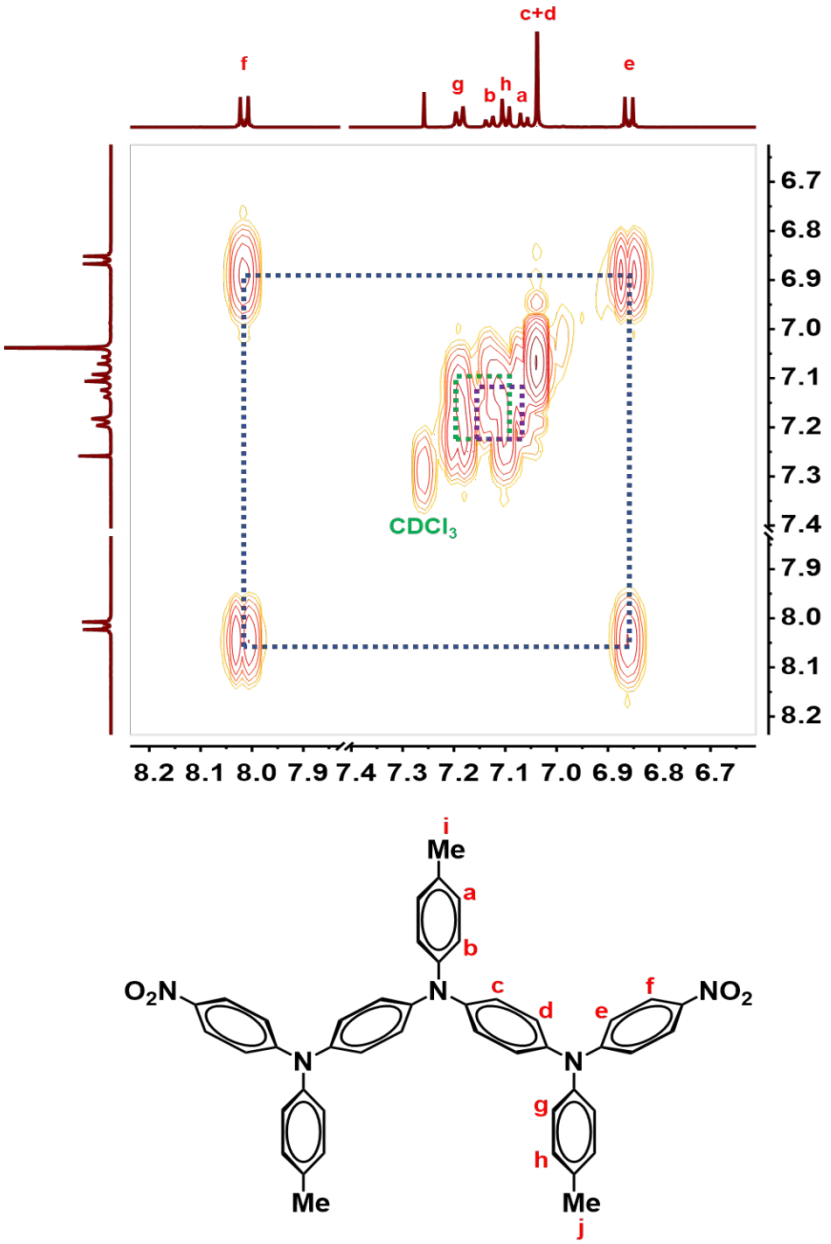

Figure S5. ^{1}H-^{1}H COSY spectrum of **2-NO$_2$**. ($CDCl_3$)

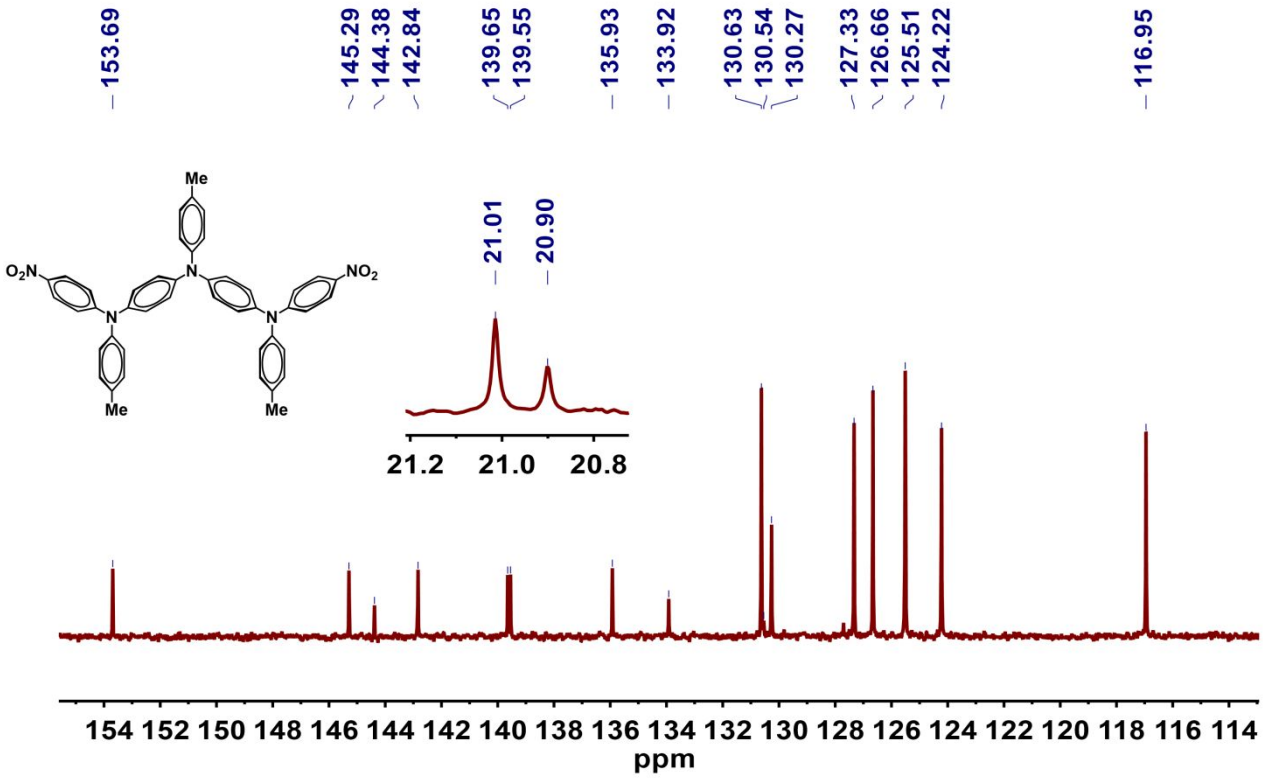

Figure S6. ^{13}C-NMR spectrum of **2-NO_2**. ($CDCl_3$)

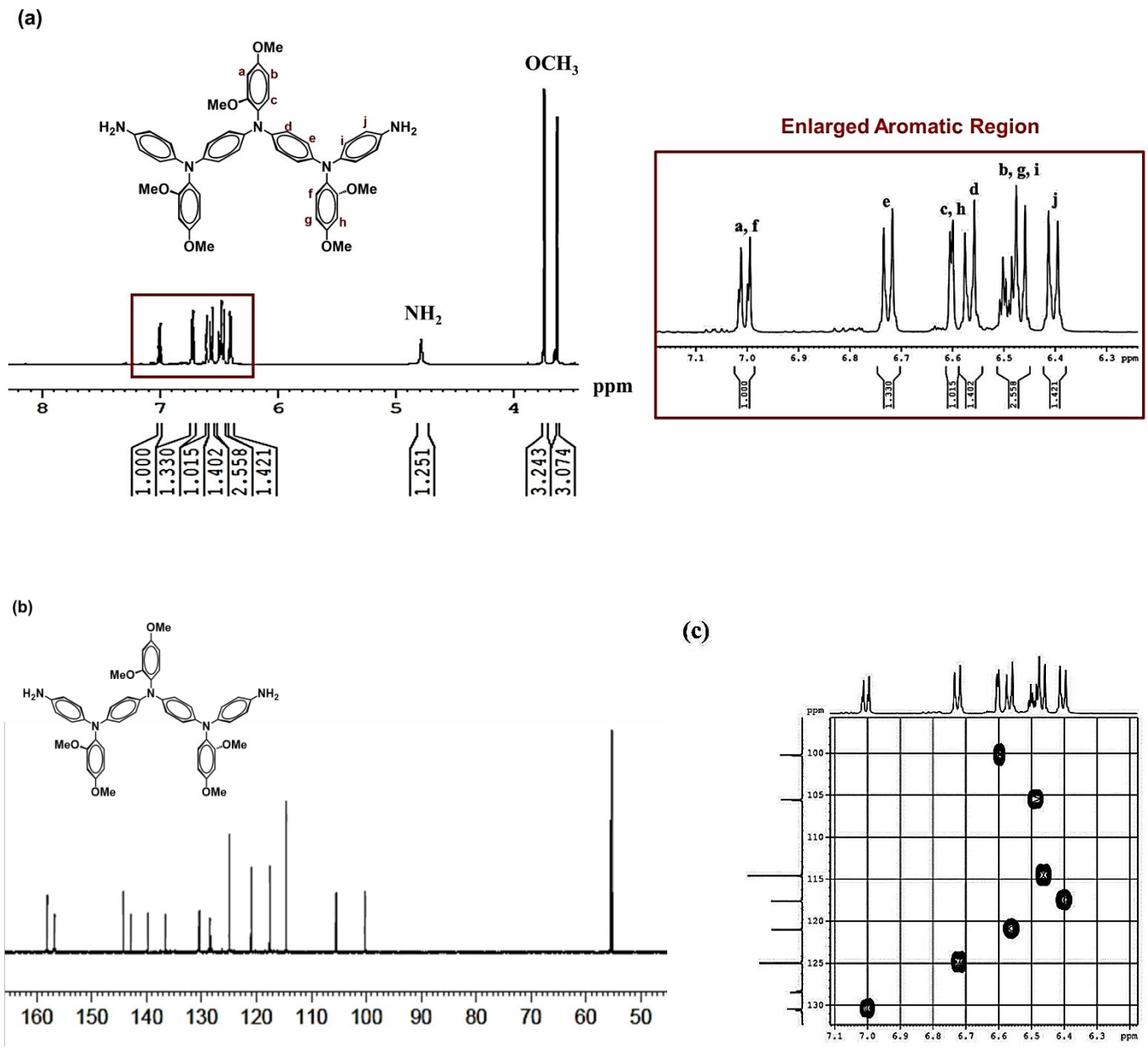

Figure S7. (a) ^{1}H, (b) ^{13}C, and (c) ^{13}C-^{1}H HMQC NMR spectra of **1-NH$_2$**. (DMSO-d_6)

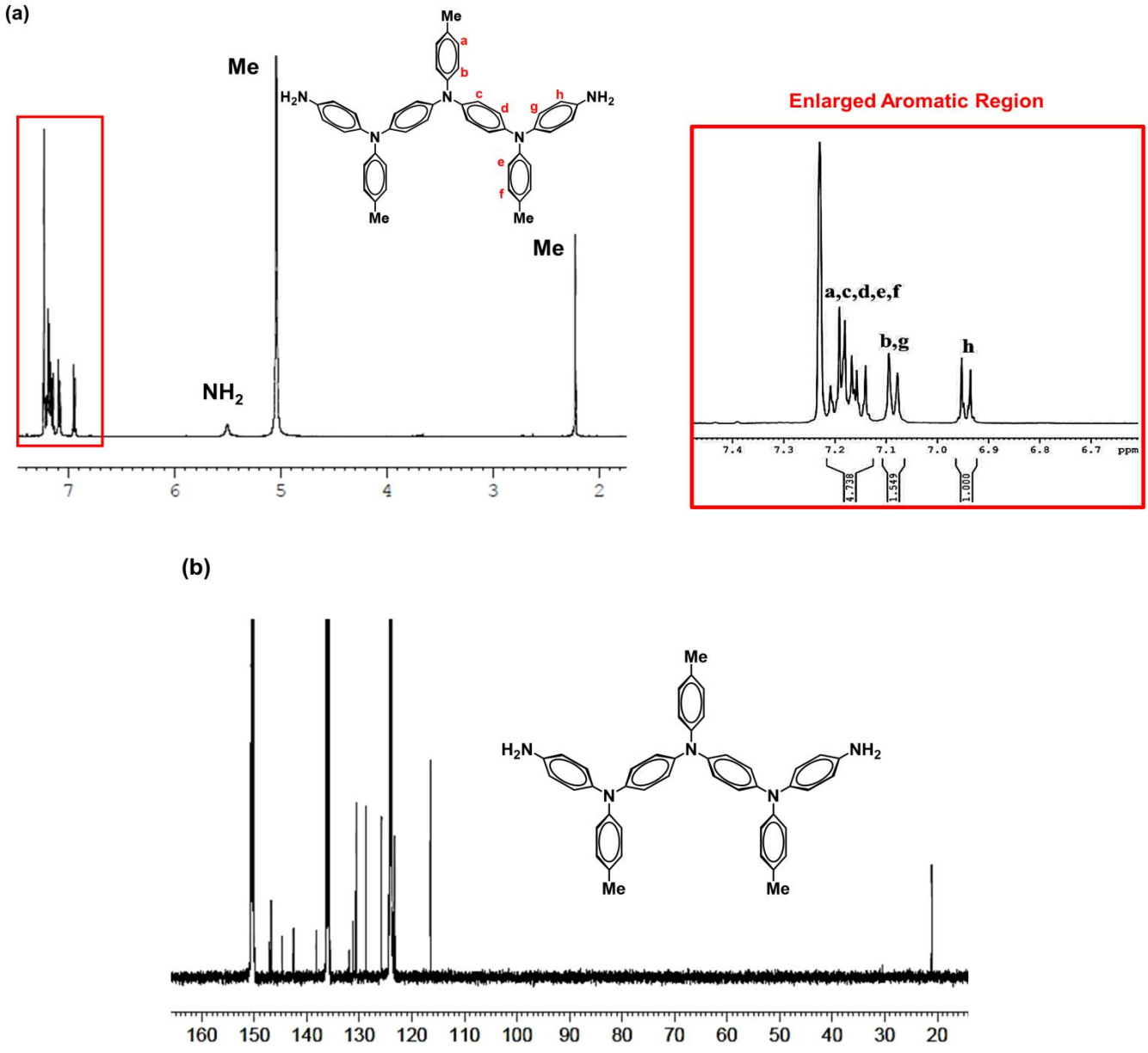

Figure S8. (a) ^{1}H and (b) ^{13}C NMR spectra of **2-NH_2**. ($CDCl_3$)

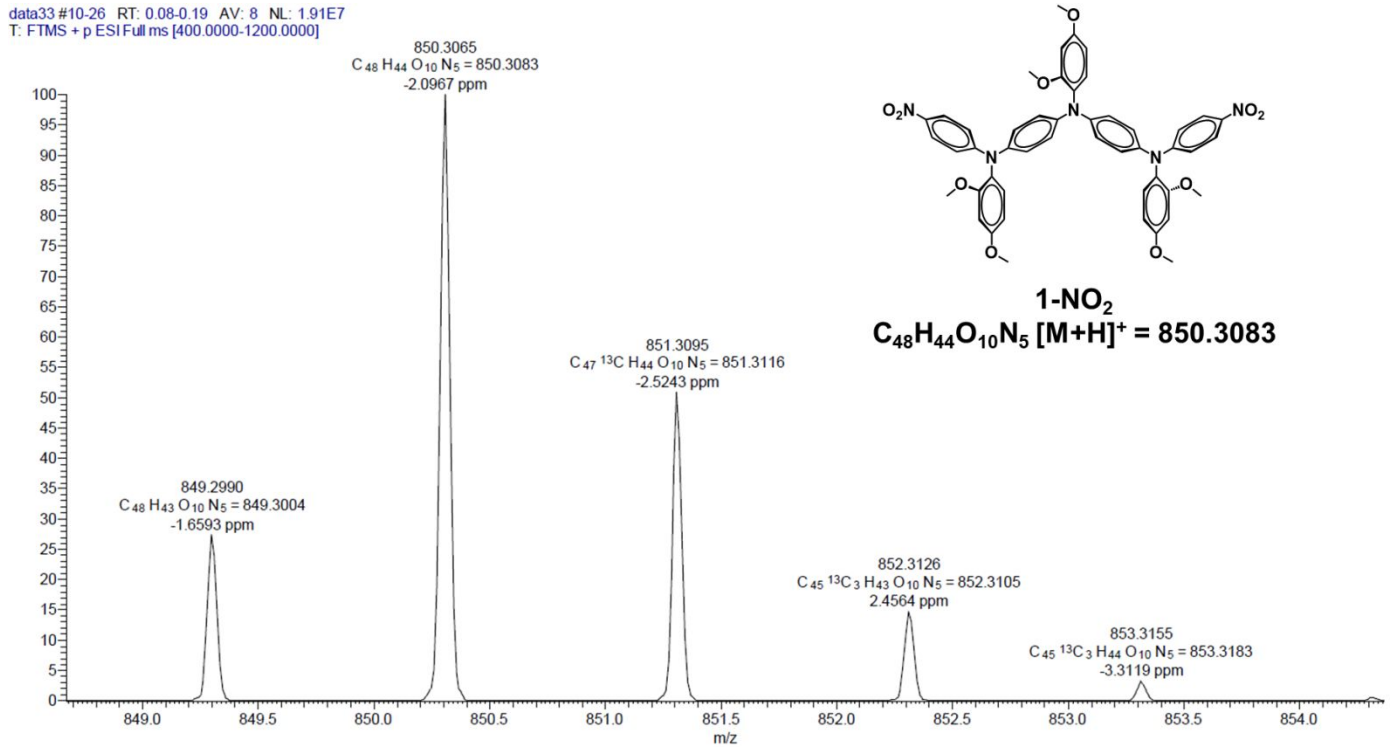

Figure S9. ESI mass spectrum of **1-NO_2**.

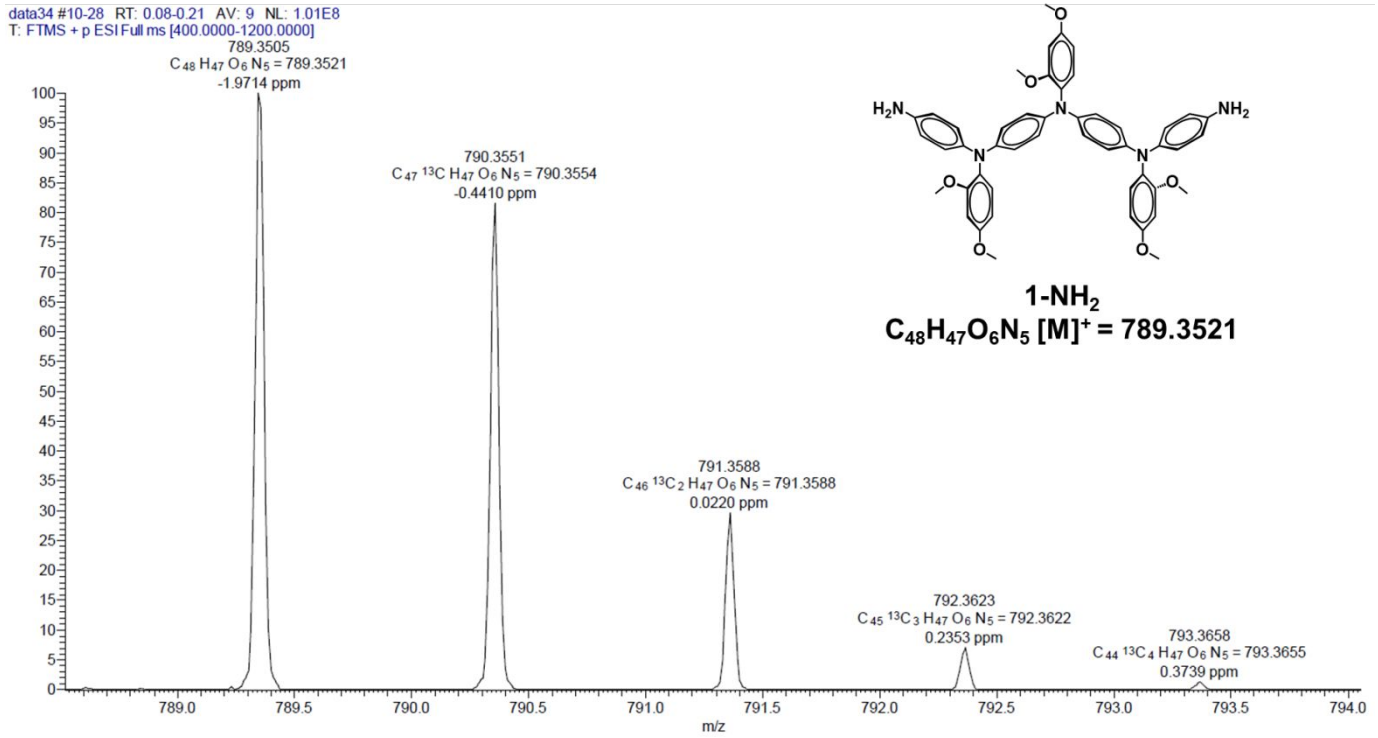

Figure S10. ESI mass spectrum of **1-NH_2**.

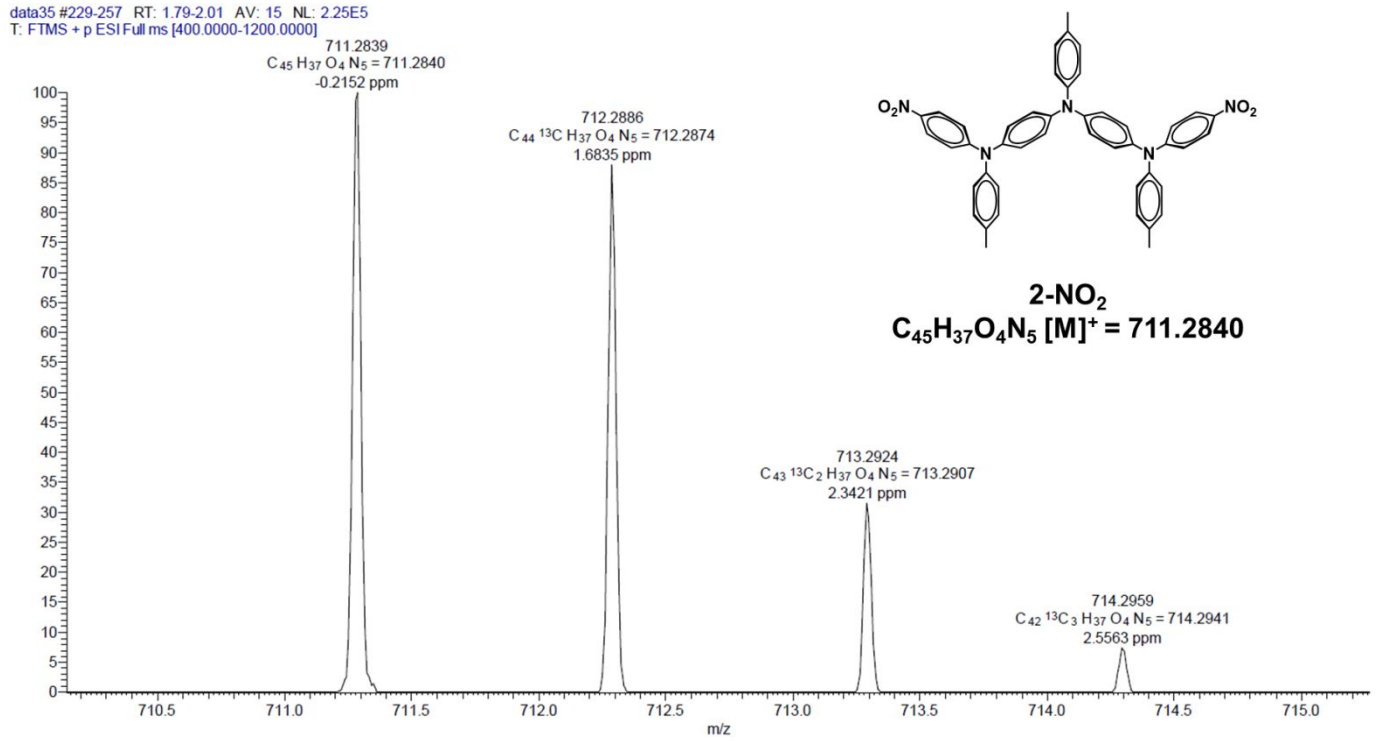

Figure S11. ESI mass spectrum of **2-NO_2**.

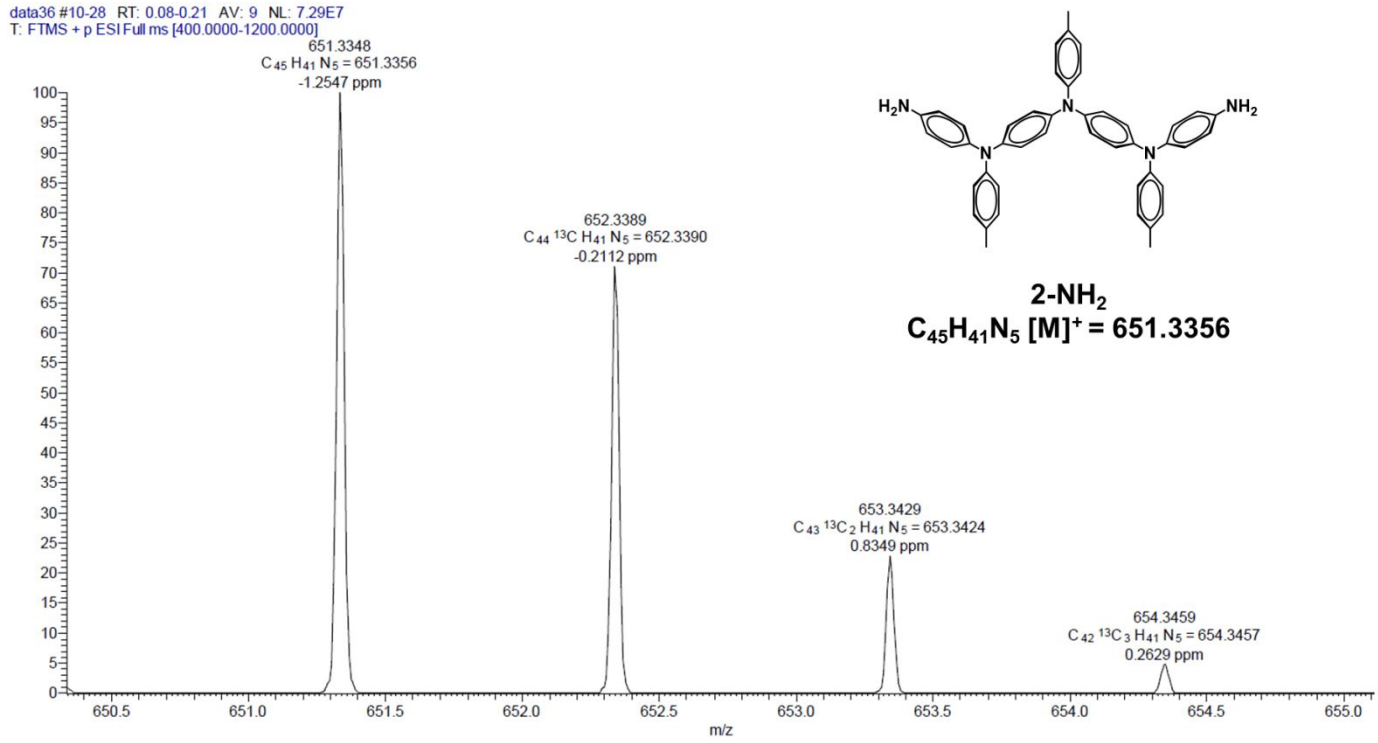

Figure S12. ESI mass spectrum of **2-NH_2**.

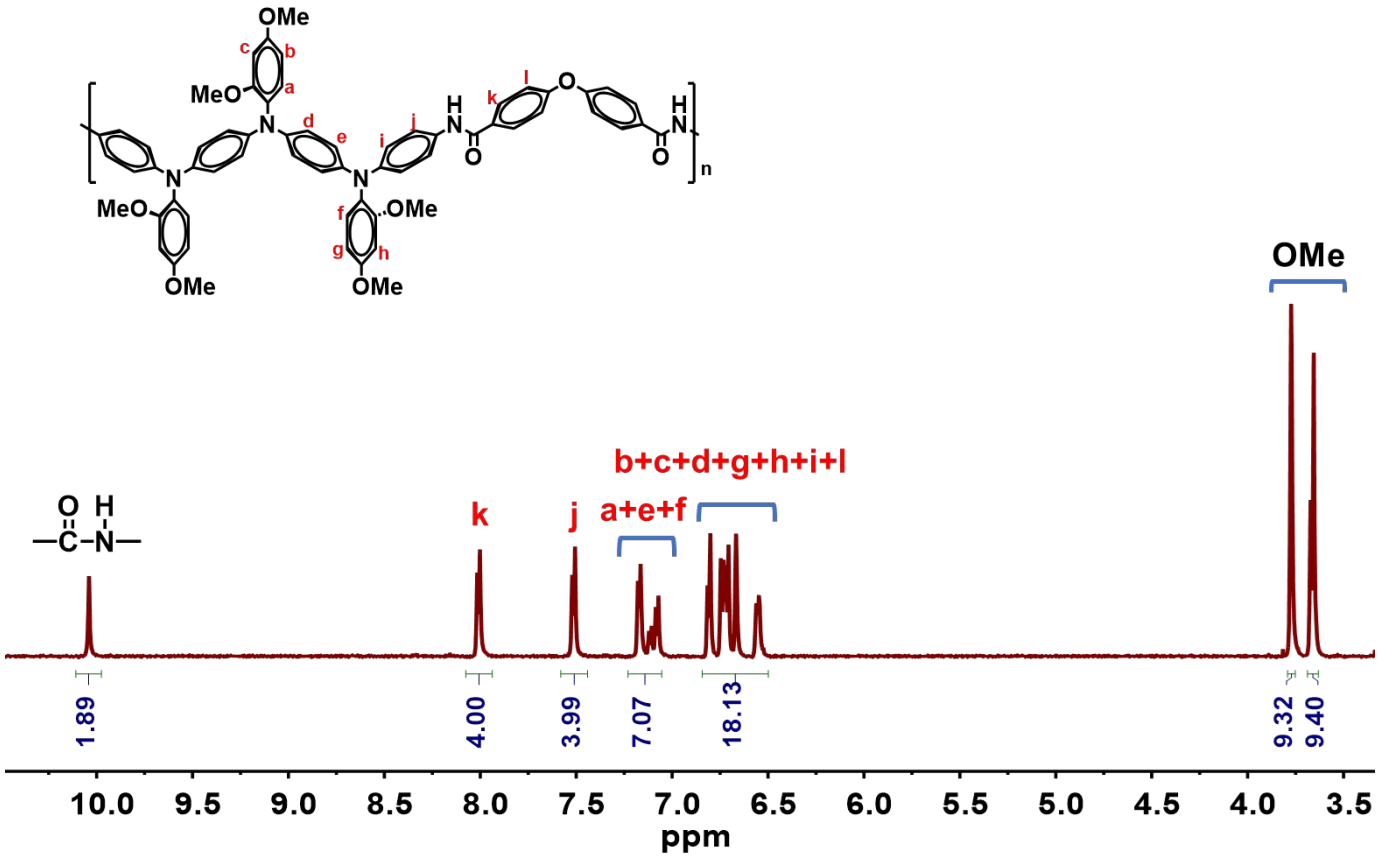

Figure S13. ^{1}H NMR spectrum of **PA1**. (DMSO-d_6)

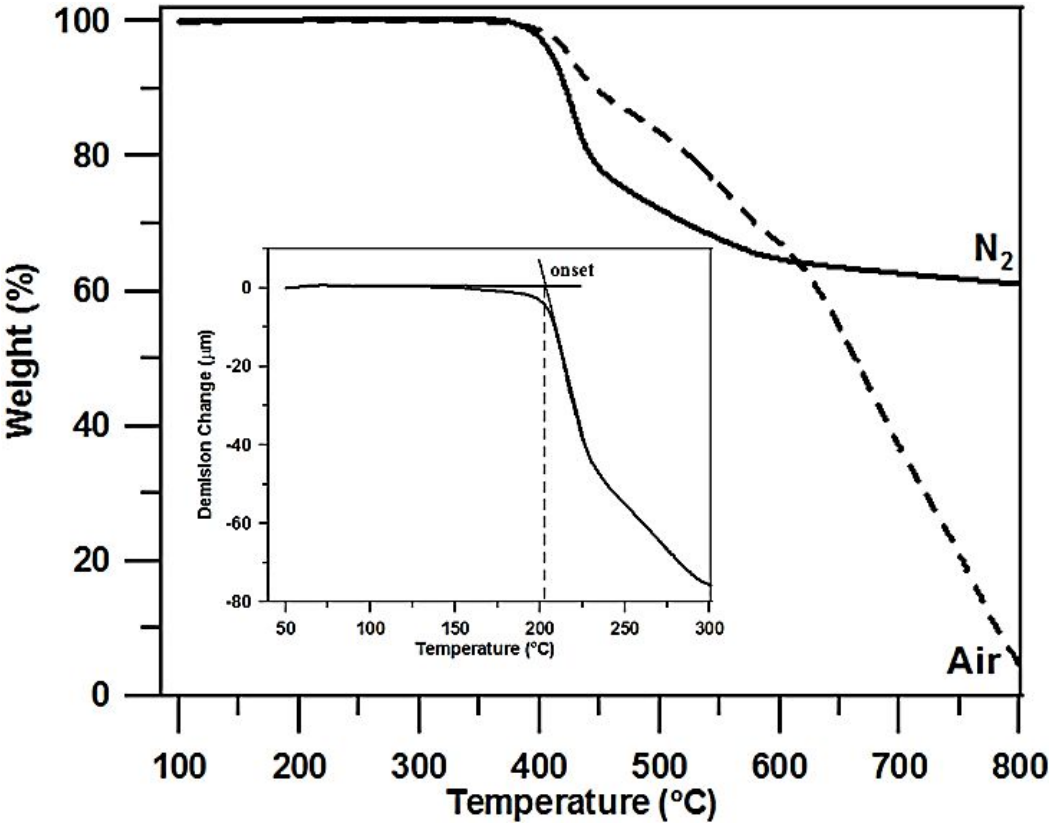

Figure S14. TMA and TGA curves of **PA1** at a heating rate of 10 ℃/min and 20 ℃/min.

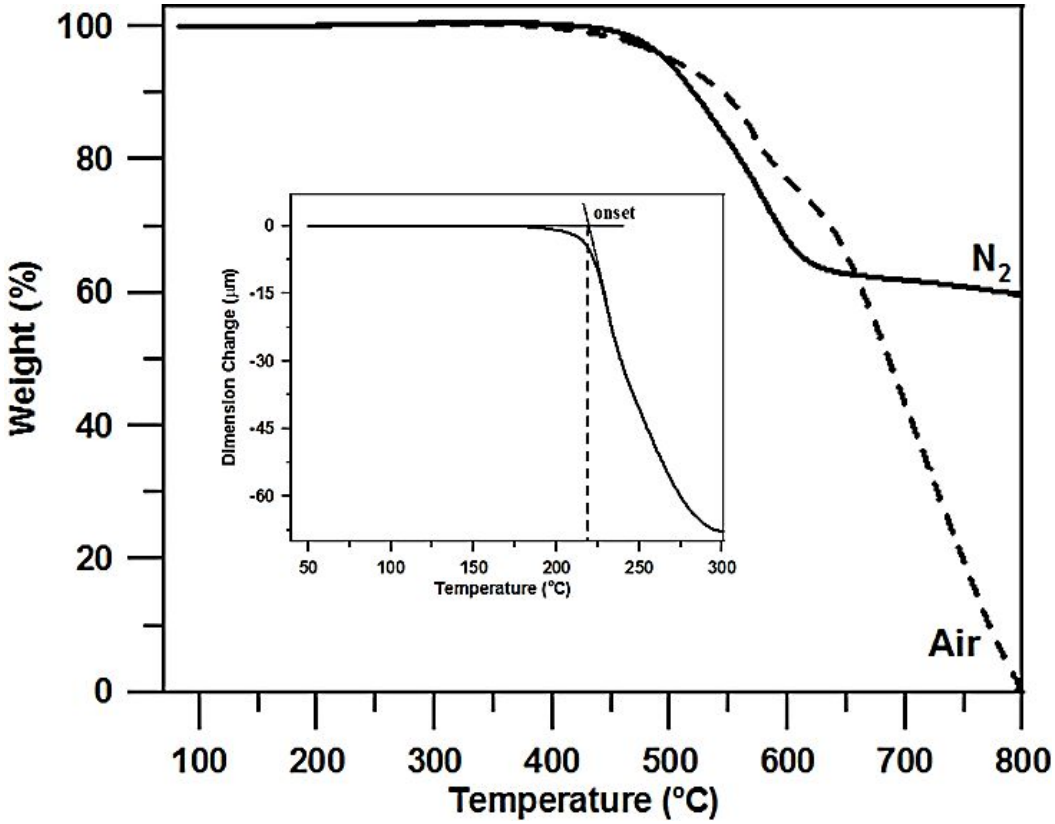

Figure S15. TMA and TGA curves of **PA2** at a heating rate of 10 ℃/min and 20 ℃/min.

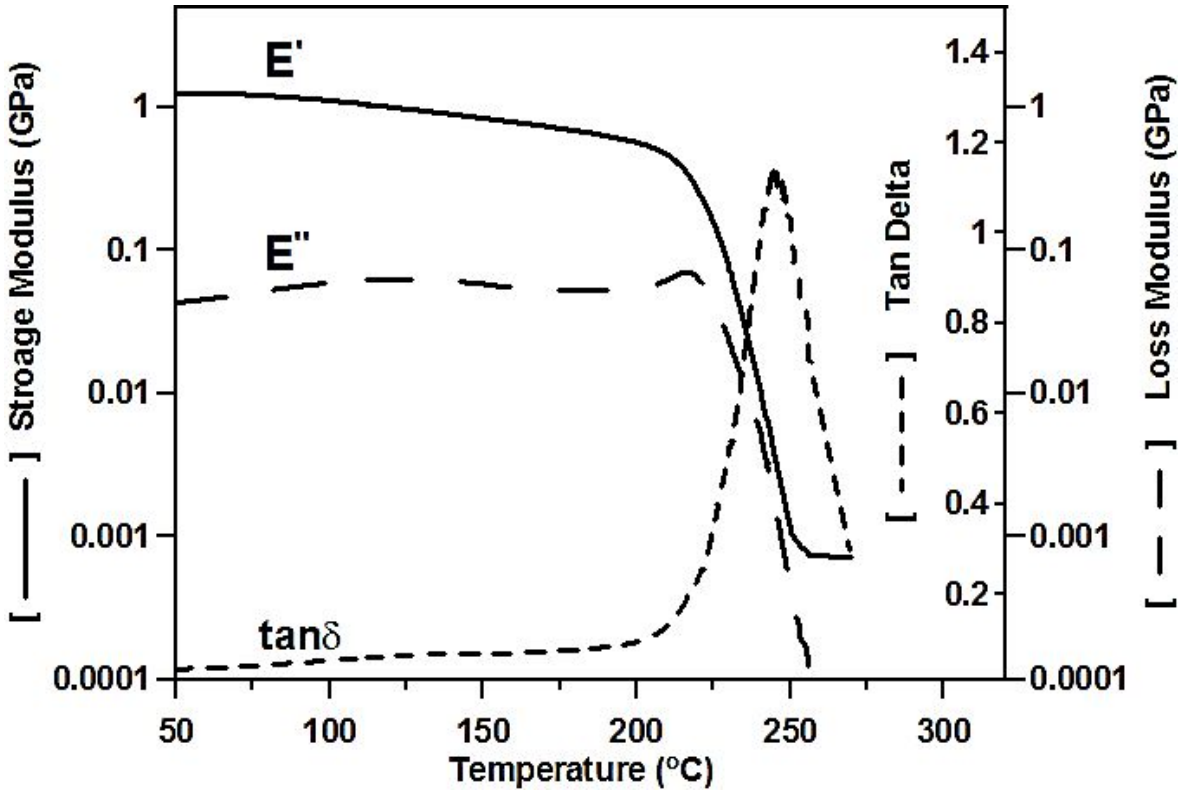

Figure S16. DMA curve of **PA1** at heating rate 5℃/min.

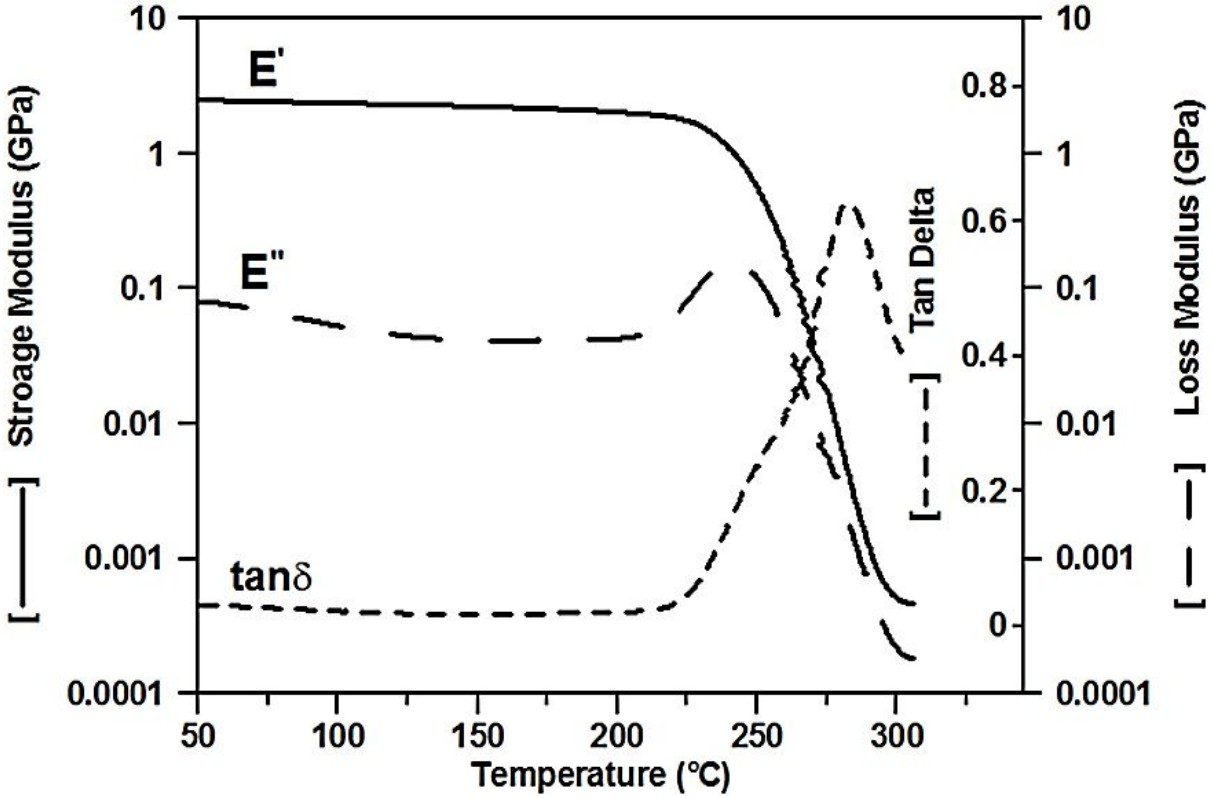

Figure S17. DMA curve of **PA2** at heating rate 5℃/min.

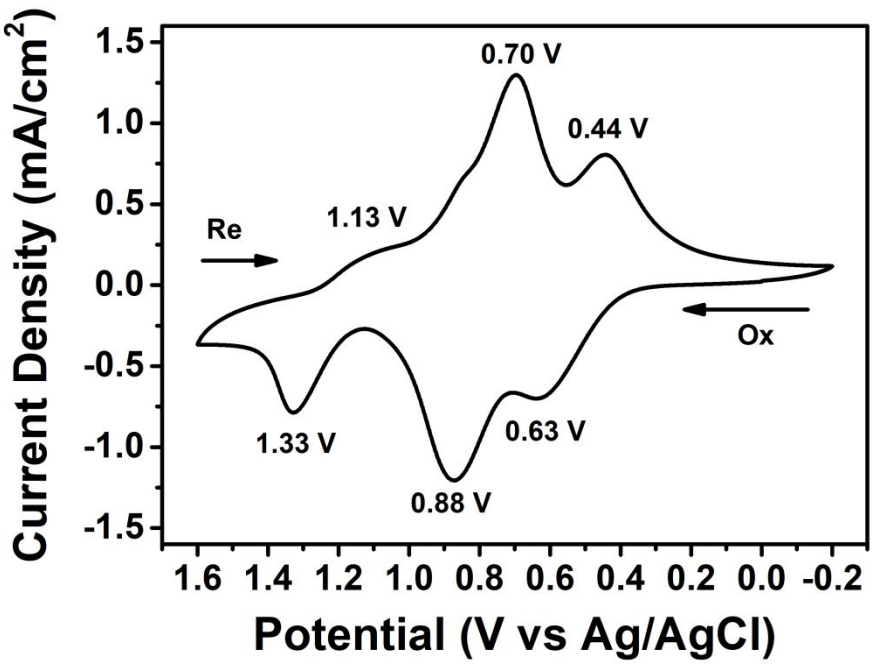

Figure S18. Cyclic voltammetric diagram of **PA2** film (thickness:180 ± 20 nm) at a scan rate of 50 mV/s from -0.20 V to 1.55 V in 0.1 M TBAP/MeCN.

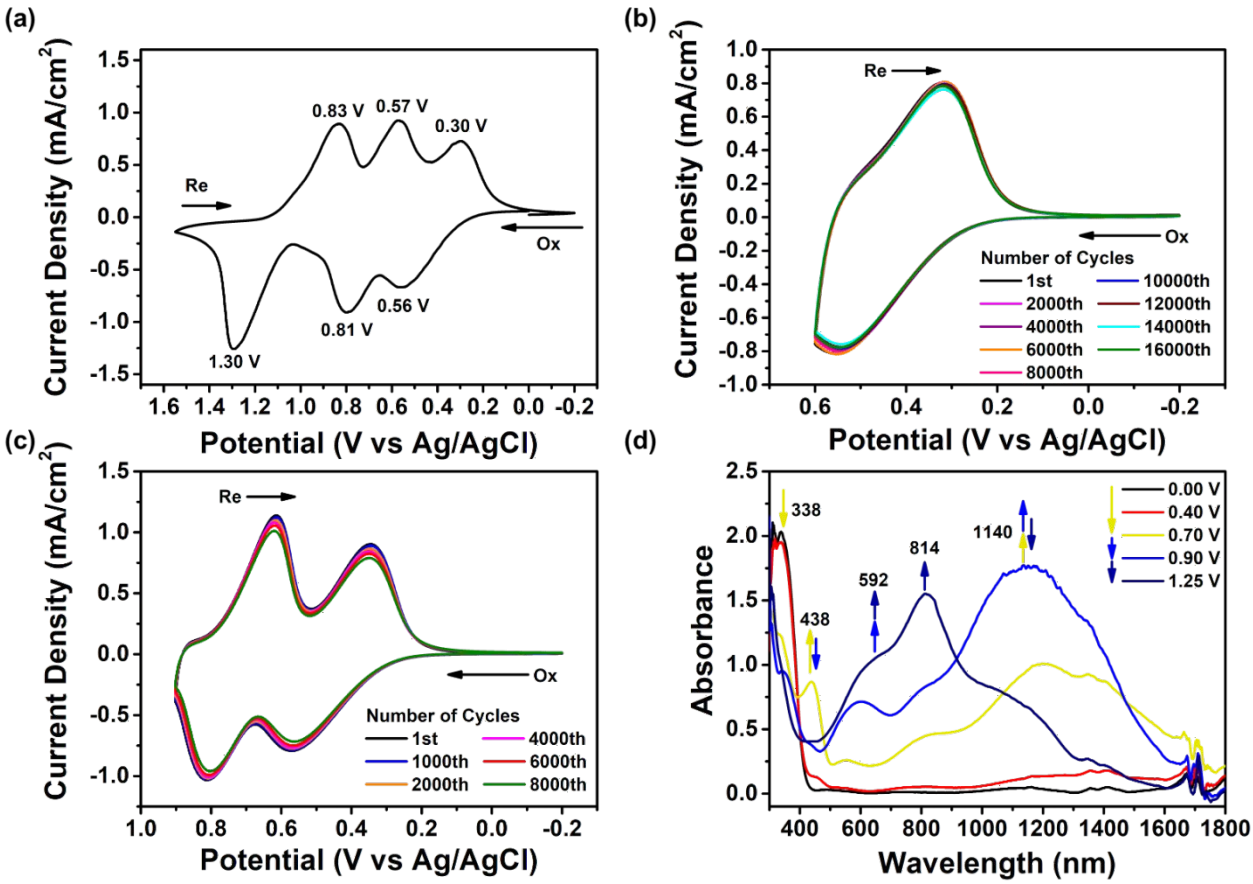

Figure S19. Cyclic voltammetric diagram of **PA1′** film (thickness:175 ± 10 nm) at a scan rate of 50 mV/s (a) from -0.20 V to 1.55 V and its cyclic stabilities at (b) first oxidation stage (-0.20 V to 0.60 V) for 16,000 cycles and second oxidation stage (-0.20 V to 0.90 V) for 8,000 cycles in 0.1 M TBAP/MeCN. (d) Spectroelectrochemistry of **PA1′** (thickness: 330 ± 20 nm) at various applied potentials in 0.1 M TBAP/MeCN.

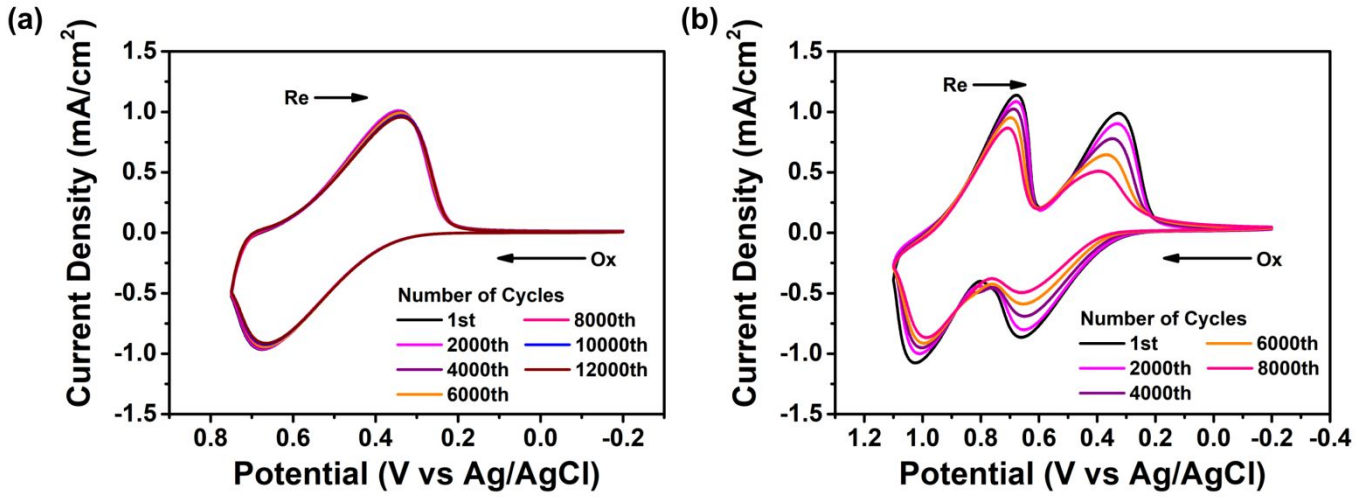

Figure S20. Cyclic stabilities of **PA3** film (thickness:180 ± 10 nm) at (b) first oxidation stage (-0.20 V to 0.75 V) for 12,000 cycles and (b) second oxidation stage (-0.20 V to 1.10 V) for 8,000 cycles in 0.1 M TBAP/MeCN.

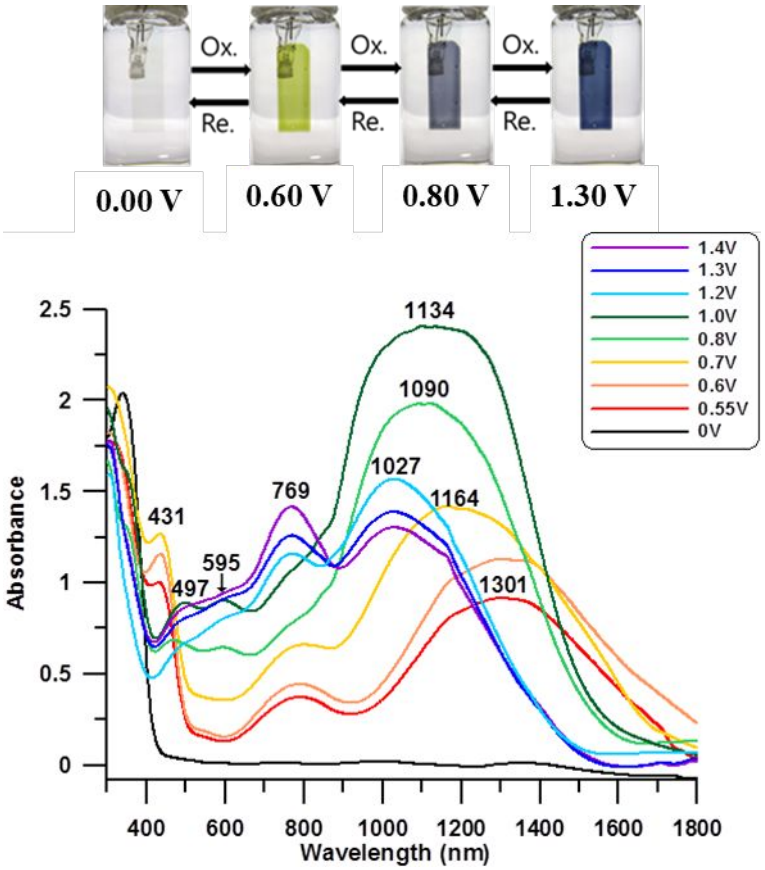

Figure S21. Spectroelectrochemistry of **PA2** at various applied potentials in 0.1 M TBAP/MeCN.

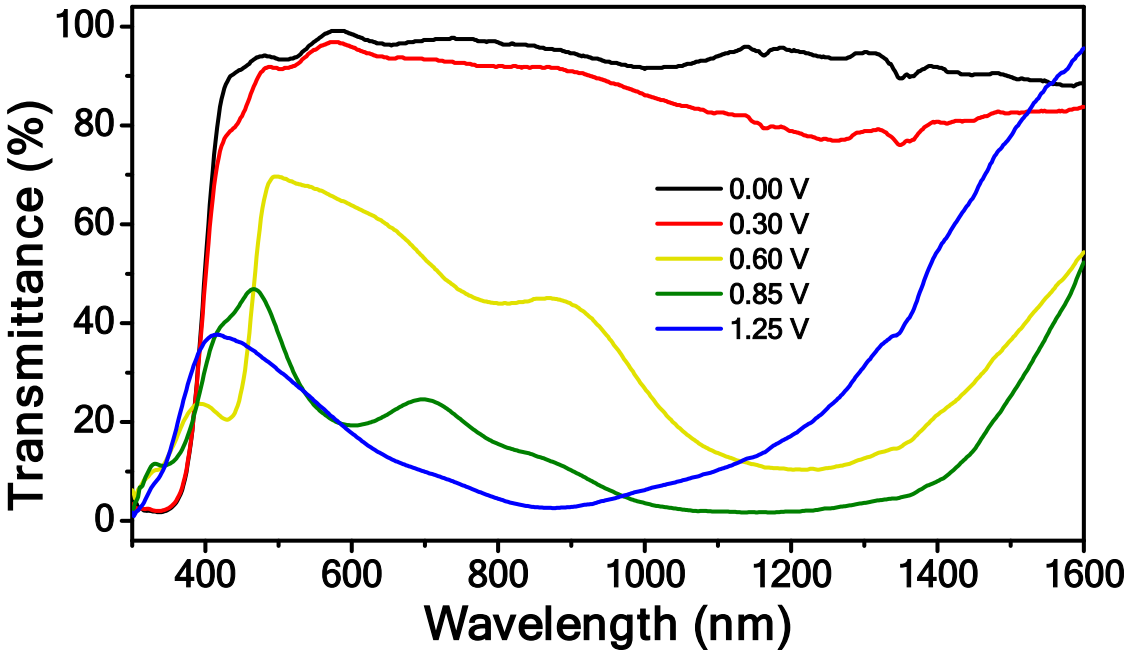

Figure S22. Optical change in transmittance of **PA1** at various applied potentials in 0.1 M TBAP/MeCN. (Thickness: 330 ± 20 nm)

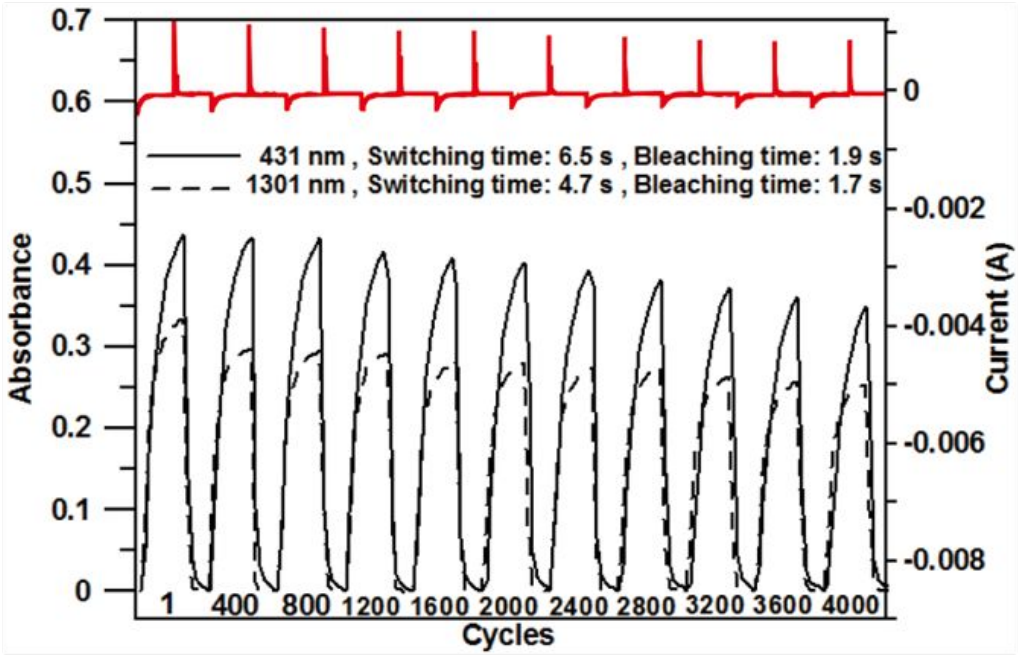

Figure S23. Potential step absorptometry and current consumption of **PA2** (in MeCN with 0.1M TBAP as the supporting electrolyte) by applying a potential step 0.00 V ↔ 0.55V, and cycle time 20 s.

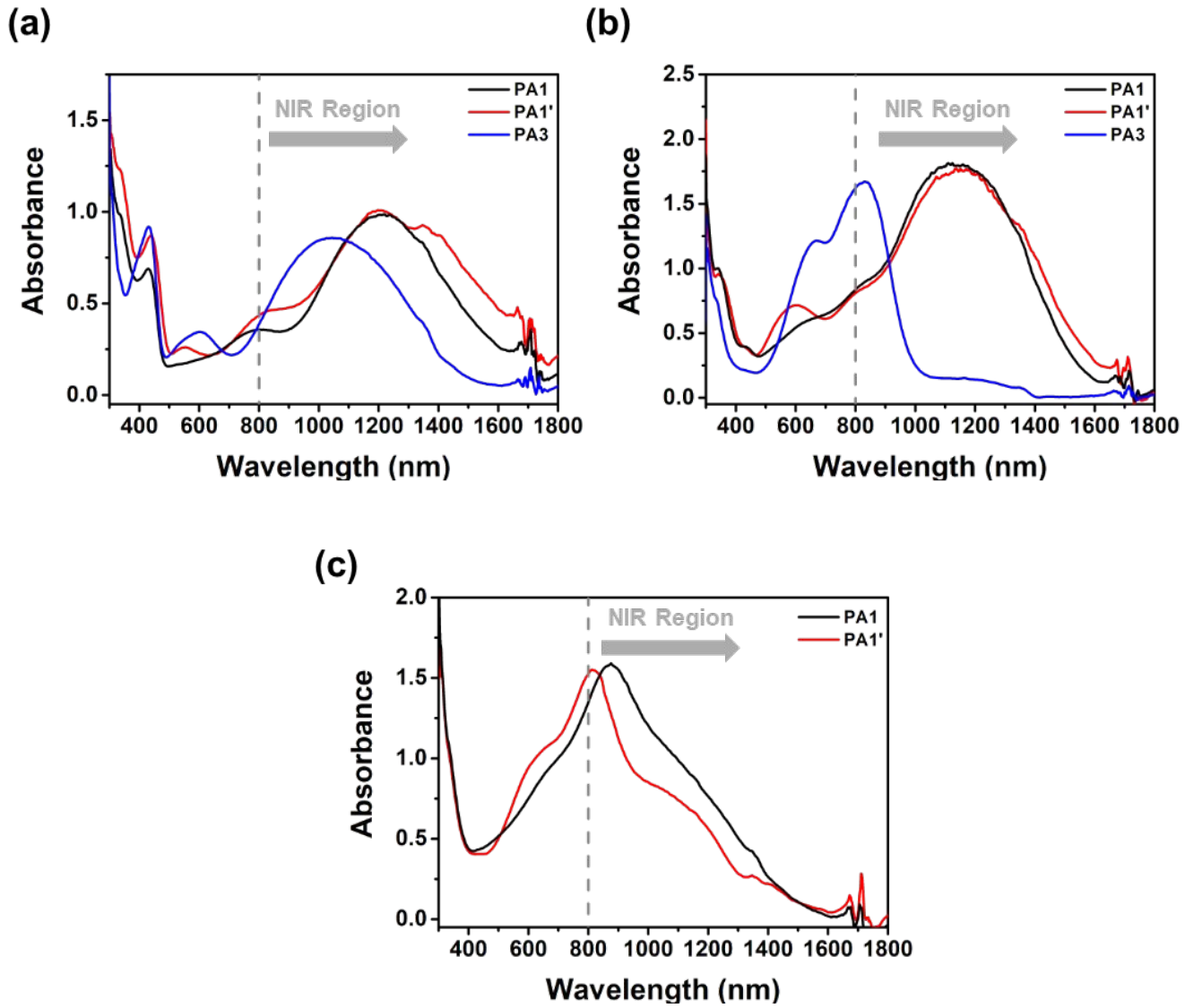

Figure S24. UV-vis-NIR absorption spectra of **PA1** (thickness: 330 ± 20 nm), **PA1′** (thickness: 330 ± 20 nm), and **PA3** (thickness: 310 ± 20 nm) films at (a) first, (b) second, and (c) third (only **PA1** and **PA1′**) oxidation stage.

Table S1. Inherent Viscosity and Solubility[a] of PA

PAs	η_{inh} (dL/g)[b]	M_w (kDa)[c]	M_n (kDa)[c]	PDI[d]	NMP	DMAc	*o*-Chlorophenol	*m*-cresol	Cyclohexanone
PA1	0.49	65.0	37.3	1.74	++	++	++	++	+
PA2	0.42	62.5	34.9	1.79	+	+–	++	+–	+–

[a] Qualitative solubility was determined using 0.01 g of polymer in 1 mL of solvent. **++:** soluble at room temperature; **+:** soluble on heating at 60 °C; **+–:** partically soluble on heating at 60 °C. [b] Measured in NMP on 0.5g/dL at 30 ℃. [c] Used polystyrene as standards, employing NMP as the eluent with 20 mM LiCl at a consistent flow rate of 0.35 mL/min, maintained at 40 ℃. [d] Polydispersity index = M_w/M_n.

Table S2. Thermal Properties of PAs

PA	Tg (°C)[a]	Ts (°C)[b]	Td (°C)[c]		Char yield (%)[d]
			In Air	In N_2	
PA1	236	199	450	430	57
PA2	269	217	551	521	60

[a] Temperature at which the inflection points of storage modulus occurred as recorded by DMA at a heating rate of 5 ℃/ min. [b] Softening temperature defined as the onset temperature of the probe displacement on the penetration TMA trace. [c] Temperature at which 10% weight loss recorded by thermogravimetry at a heating rate of 20 ℃/min. [d] Residual weight% at 800 ℃ in nitrogen.

Table S3. Optical and Electrochemical Properties of PAs.

PAs	Solution/film (nm)			Oxidation potential (V)				HOMO[d] (eV)	LUMO[e] (eV)
					$E_{1/2}$[c]				
	λ_{max}[a]	λ_{onset}[a]	E_g[b](eV)	E_{onset}	1st	2nd	3rd		
PA1	272(322)	410(415)	2.98	0.19	0.39	0.70	1.10	-4.75	-1.77
PA2	310(326)	405(440)	2.82	0.34	0.54	0.79	1.23	-4.90	-2.08

[a] UV/vis absorption measurement in NMP (1×10^{-5} M) at room temperature, values in parentheses are polymer of the film state. [b] The data were calculated from polymer films by the equation: $E_g = 1240/\lambda_{onset}$ (energy gap between HOMO and LUMO). [c] From cyclic voltammograms versus Ag/AgCl in MeCN. $E_{1/2}$: Average potential of the redox couple peaks. [d] The HOMO energy levels were calculated from cyclic voltammetry and were referenced to ferrocene (-4.8 eV; $E_{1/2}$ = 0.44 V). [e] LUMO = HOMO – gap.

Table S4. Optical and electrochemical coloration efficiency of **PA1**

Cycles[a]	ΔOD[b]	ΔT(%)[c]	Q(mC/cm^2)[d]	η(cm^2/C)[e]	decay(%)[f]
1	0.390(0.337)[g]	59.2(54.0)	1.64(1.72)	237(195)	0.00(0.00)
1500	0.382(0.330)	58.5(53.3)	1.62(1.71)	236(195)	0.42(0.00)
3000	0.379(0.323)	58.2(52.4)	1.61(1.70)	235(193)	0.84(1.03)
4500	0.372(0.321)	57.5(52.2)	1.59(1.69)	234(191)	1.26(2.05)
6000	0.369(0.317)	57.2(51.9)	1.58(1.67)	233(190)	1.69(2.56)
7500	0.366(0.316)	56.9(51.7)	1.58(1.66)	233(190)	1.69(2.56)
9000	0.365(0.310)	56.8(51.1)	1.57(1.64)	232(190)	2.11(2.56)
10500	0.363(0.308)	56.6(50.8)	1.57(1.63)	232(190)	2.11(2.56)
12000	0.362(0.304)	56.5(50.3)	1.56(1.62)	232(189)	2.11(3.08)
13500	0.361(0.303)	56.4(50.2)	1.56(1.61)	231(189)	2.53(3.08)
15000	0.358(0.301)	56.2(50.0)	1.55(1.59)	231(187)	2.53(4.10)

[a] Times of the cyclic scan by applying potential step: 0.00 V ↔ 0.40 V (V vs Ag/AgCl). [b] Optical density change at 1252 nm. [c] Optical transmittance change at 1252 nm. [d] Ejected charge, determined from in situ experiments. [e] Coloration efficiency is derived from the equation: $\eta=\Delta OD/Q$. [f] Decay of coloration efficiency after cyclic scans. [g] Data in parentheses are optical density changes at 422 nm

Table S5. Optical and electrochemical coloration efficiency of **PA1**

Cycles[a]	△OD[b]	△T(%)[c]	Q(mC/cm^2)[d]	η(cm^2/C)[e]	decay(%)[f]
1	1.061	91.3	3.15	336	0.00
450	1.008	90.2	3.15	321	4.46
900	1.008	90.2	3.14	320	4.76
1350	1.006	90.1	3.14	320	4.76
1800	0.985	89.6	3.13	315	6.25
2250	0.983	89.6	3.13	314	6.55
2700	0.979	89.5	3.12	314	6.55
3150	0.971	89.3	3.11	312	7.14
3600	0.968	89.2	3.11	311	7.44
4050	0.961	89.1	3.10	310	7.74
4500	0.944	88.6	3.10	305	9.23

[a] Times of the cyclic scan by applying potential step: 0.00 V→0.68 V (V vs Ag/AgCl). [b] Optical density change at 1150 nm. [c] Optical transmittance change at 1150 nm. [d] Ejected charge, determined from in situ experiments. [e] Coloration efficiency is derived from the equation: $\eta=\Delta OD/Q$. [f] Decay of coloration efficiency after cyclic scans.

Table S6. Optical, electrochemical data, and coloration efficiency measurements of **PA2** at 0.55 V.

Cycles[a]	ΔOD[b]	ΔT(%)[c]	Q(mC/cm^2)[d]	η(cm^2/C)[e]	decay(%)[f]
1	0.333(0.437)g	53.5 (63.4)	1.40 (2.22)	238 (200)	0.00 (0.00)
400	0.297(0.434)	49.5 (63.2)	1.38 (2.20)	219 (198)	7.98 (1.00)
800	0.294(0.434)	49.2 (63.2)	1.36 (2.17)	218 (197)	8.40 (1.50)
1200	0.293(0.418)	49.1 (61.8)	1.34 (2.15)	216 (195)	9.24 (2.50)
1600	0.283(0.410)	47.9 (61.1)	1.33 (2.12)	215 (193)	9.66 (3.50)
2000	0.281(0.404)	47.6 (60.6)	1.31 (2.10)	215 (193)	9.85 (3.50)
2400	0.275(0.393)	46.9 (59.5)	1.29 (2.07)	214 (190)	10.1 (5.00)
2800	0.274(0.382)	46.8(58.5)	1.27 (2.05)	213 (189)	10.5 (5.50)
3200	0.264(0.373)	45.5 (57.6)	1.25 (2.02)	208 (182)	12.6 (9.00)
3600	0.255(0.361)	44.4 (56.4)	1.24 (2.00)	207 (181)	13.0 (9.50)
4000	0.252(0.349)	44.0 (55.2)	1.22 (1.97)	206 (177)	13.5 (11.5)

[a] Times of the cyclic scan by applying potential step: 0.00 V↔0.55 V (V vs Ag/AgCl). [b] Optical density change at 1301 nm. [c] Optical transmittance change at 1301 nm. [d] Ejected charge, determined from in situ experiments. [e] Coloration efficiency is derived from the equation: η=ΔOD/Q. [f] Decay of coloration efficiency after cyclic scans. [g] Data in parentheses are optical density changes at 431 nm.

Table S5. NIR absorption of polymers at the first stage of oxidation.

Polymer	Potential[a](V)	λ_{max}[b](nm)	Absorption Range(nm)
PA1	0.40	1252	800-1800
PA2	0.55	1301	800-1800
PA3	0.75	1062	800-1550

[a] Applied potential for the first stage oxidation. [b] NIR absorption.

Table S6. Crystal data and structure refinement for 1-NO_2.

Identification code	ch14150	
Empirical formula	C48 H43 N5 O10	
Formula weight	849.87	
Temperature	200(2) K	
Wavelength	0.71069 Å	
Crystal system	Triclinic	
Space group	P -1	
Unit cell dimensions	a = 11.749(5) Å	α= 74.340(5)°.
	b = 12.554(5) Å	β= 74.891(5)°.
	c = 17.253(5) Å	γ = 87.680(5)°.
Volume	2364.4(15) $Å^3$	
Z	2	
Density (calculated)	1.194 Mg/m^3	
Absorption coefficient	0.085 mm^{-1}	
F(000)	892	
Crystal size	0.58 x 0.18 x 0.04 mm^3	
Theta range for data collection	1.27 to 25.05°.	
Index ranges	-13<=h<=13, -13<=k<=14, -19<=l<=20	
Reflections collected	19644	
Independent reflections	8132 [R(int) = 0.0670]	
Completeness to theta = 25.05°	97.3 %	
Absorption correction	None	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	8132 / 0 / 568	
Goodness-of-fit on F^2	0.894	
Final R indices [I>2sigma(I)]	R1 = 0.0807, wR2 = 0.1968	
R indices (all data)	R1 = 0.1988, wR2 = 0.2336	
Largest diff. peak and hole	0.475 and -0.366 $e.Å^{-3}$	

Table S7. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for 1-NO_2. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
C(1)	12669(4)	-5369(4)	7669(3)	48(1)
C(2)	12495(5)	-4337(4)	7818(3)	49(1)
C(3)	11369(4)	-4040(4)	8183(3)	42(1)
C(4)	10400(4)	-4791(4)	8379(3)	38(1)
C(5)	10590(4)	-5806(4)	8178(3)	40(1)
C(6)	11710(5)	-6091(4)	7841(3)	52(1)
C(7)	8240(4)	-5157(4)	8875(3)	45(1)
C(8)	7796(4)	-5122(4)	8183(3)	46(1)
C(9)	7990(5)	-4421(5)	6725(3)	71(2)
C(10)	6728(4)	-5657(4)	8313(4)	52(2)
C(11)	6136(5)	-6222(5)	9092(5)	70(2)
C(12)	4148(12)	-6828(12)	9844(8)	82(4)
C(12')	4501(12)	-7456(12)	9997(8)	82(4)
C(13)	6553(5)	-6311(5)	9773(4)	71(2)
C(14)	7615(5)	-5768(4)	9651(3)	58(2)
C(15)	9082(4)	-3473(4)	8980(3)	37(1)
C(16)	9323(4)	-3332(4)	9690(3)	41(1)
C(17)	9129(4)	-2328(4)	9877(3)	43(1)
C(18)	8686(4)	-1436(4)	9361(3)	36(1)
C(19)	8448(4)	-1613(4)	8649(3)	40(1)
C(20)	8661(4)	-2620(4)	8462(3)	39(1)
C(21)	8601(4)	540(4)	8796(3)	35(1)
C(22)	9675(4)	977(4)	8303(3)	40(1)
C(23)	9779(4)	1819(4)	7576(3)	44(1)
C(24)	8758(5)	2223(4)	7365(3)	45(1)
C(25)	9857(5)	3509(5)	6119(3)	72(2)
C(26)	7654(4)	1793(4)	7861(3)	45(1)
C(27)	7573(4)	940(4)	8579(3)	36(1)
C(28)	5474(4)	691(5)	8799(3)	58(2)
C(29)	8065(4)	-223(4)	10328(3)	34(1)
C(30)	7524(4)	-1045(4)	11015(3)	37(1)
C(31)	7054(4)	-823(4)	11793(3)	43(1)
C(32)	7140(4)	228(4)	11863(3)	37(1)
C(33)	7689(4)	1053(4)	11169(3)	44(1)
C(34)	8163(4)	834(4)	10410(3)	40(1)
C(35)	5316(5)	408(5)	12868(3)	48(1)

C(36)	4686(4)	1336(5)	12555(3)	49(1)
C(37)	4729(5)	3268(5)	11914(4)	82(2)
C(38)	3472(4)	1273(5)	12775(3)	52(1)
C(39)	2874(5)	304(5)	13278(3)	54(2)
C(40)	974(5)	-532(5)	14065(3)	74(2)
C(41)	3464(5)	-604(5)	13591(3)	56(2)
C(42)	4698(5)	-539(5)	13380(3)	57(2)
C(43)	7177(4)	983(4)	13040(3)	40(1)
C(44)	6551(5)	1508(4)	13638(3)	54(2)
C(45)	7159(5)	2045(5)	14038(3)	59(2)
C(46)	8355(5)	2029(5)	13844(3)	54(2)
C(47)	9005(5)	1505(5)	13260(3)	54(2)
C(48)	8399(4)	1009(4)	12858(3)	46(1)
N(1)	13854(4)	-5674(5)	7314(3)	65(1)
N(2)	9290(3)	-4530(3)	8783(2)	42(1)
N(3)	8516(3)	-387(3)	9516(2)	37(1)
N(4)	6575(3)	470(3)	12644(2)	43(1)
N(5)	8992(6)	2600(5)	14270(3)	80(2)
O(1)	14002(4)	-6617(4)	7237(3)	107(2)
O(2)	14654(3)	-4989(4)	7098(3)	82(1)
O(3)	8444(3)	-4504(3)	7435(2)	60(1)
O(4)	5075(4)	-6689(4)	9121(3)	102(2)
O(5)	8728(3)	3037(3)	6655(2)	60(1)
O(6)	6535(3)	446(3)	9089(2)	47(1)
O(7)	5336(3)	2242(3)	12076(2)	66(1)
O(8)	1662(3)	338(3)	13428(2)	72(1)
O(9)	8413(5)	3149(5)	14711(4)	128(2)
O(10)	10051(5)	2454(4)	14160(3)	103(2)

Table S8. Bond lengths [Å] and angles [°] for 1-NO_2.

C(1)-C(2)	1.384(7)
C(1)-C(6)	1.394(6)
C(1)-N(1)	1.449(6)
C(2)-C(3)	1.392(6)
C(2)-H(2)	0.9500
C(3)-C(4)	1.418(6)
C(3)-H(3)	0.9500
C(4)-N(2)	1.382(5)
C(4)-C(5)	1.403(6)
C(5)-C(6)	1.368(6)
C(5)-H(5)	0.9500
C(6)-H(6)	0.9500
C(7)-C(14)	1.378(7)
C(7)-C(8)	1.413(7)
C(7)-N(2)	1.440(6)
C(8)-O(3)	1.358(6)
C(8)-C(10)	1.383(6)
C(9)-O(3)	1.436(6)
C(9)-H(9A)	0.9800
C(9)-H(9B)	0.9800
C(9)-H(9C)	0.9800
C(10)-C(11)	1.354(7)
C(10)-H(10)	0.9500
C(11)-C(13)	1.363(8)
C(11)-O(4)	1.382(6)
C(12)-O(4)	1.400(13)
C(12)-H(12A)	0.9800
C(12)-H(12B)	0.9800
C(12)-H(12C)	0.9800
C(12')-O(4)	1.550(13)
C(12')-H(12D)	0.9800
C(12')-H(12E)	0.9800
C(12')-H(12F)	0.9800
C(13)-C(14)	1.385(7)
C(13)-H(13)	0.9500
C(14)-H(14)	0.9500
C(15)-C(20)	1.364(6)
C(15)-C(16)	1.385(6)
C(15)-N(2)	1.453(6)
C(16)-C(17)	1.379(6)

C(16)-H(16)	0.9500
C(17)-C(18)	1.404(6)
C(17)-H(17)	0.9500
C(18)-C(19)	1.402(6)
C(18)-N(3)	1.410(6)
C(19)-C(20)	1.384(6)
C(19)-H(19)	0.9500
C(20)-H(20)	0.9500
C(21)-C(22)	1.364(6)
C(21)-C(27)	1.391(6)
C(21)-N(3)	1.440(5)
C(22)-C(23)	1.386(6)
C(22)-H(22)	0.9500
C(23)-C(24)	1.381(6)
C(23)-H(23)	0.9500
C(24)-O(5)	1.375(6)
C(24)-C(26)	1.391(6)
C(25)-O(5)	1.446(5)
C(25)-H(25A)	0.9800
C(25)-H(25B)	0.9800
C(25)-H(25C)	0.9800
C(26)-C(27)	1.387(6)
C(26)-H(26)	0.9500
C(27)-O(6)	1.361(5)
C(28)-O(6)	1.453(5)
C(28)-H(28A)	0.9800
C(28)-H(28B)	0.9800
C(28)-H(28C)	0.9800
C(29)-C(30)	1.369(6)
C(29)-C(34)	1.384(6)
C(29)-N(3)	1.430(5)
C(30)-C(31)	1.410(6)
C(30)-H(30)	0.9500
C(31)-C(32)	1.367(6)
C(31)-H(31)	0.9500
C(32)-C(33)	1.381(6)
C(32)-N(4)	1.444(6)
C(33)-C(34)	1.379(6)
C(33)-H(33)	0.9500
C(34)-H(34)	0.9500
C(35)-C(42)	1.374(7)
C(35)-C(36)	1.413(7)

C(35)-N(4)	1.428(6)
C(36)-O(7)	1.340(5)
C(36)-C(38)	1.377(7)
C(37)-O(7)	1.443(6)
C(37)-H(37A)	0.9800
C(37)-H(37B)	0.9800
C(37)-H(37C)	0.9800
C(38)-C(39)	1.381(7)
C(38)-H(38)	0.9500
C(39)-C(41)	1.367(7)
C(39)-O(8)	1.381(6)
C(40)-O(8)	1.420(6)
C(40)-H(40A)	0.9800
C(40)-H(40B)	0.9800
C(40)-H(40C)	0.9800
C(41)-C(42)	1.400(7)
C(41)-H(41)	0.9500
C(42)-H(42)	0.9500
C(43)-N(4)	1.383(6)
C(43)-C(48)	1.387(6)
C(43)-C(44)	1.404(6)
C(44)-C(45)	1.411(7)
C(44)-H(44)	0.9500
C(45)-C(46)	1.358(7)
C(45)-H(45)	0.9500
C(46)-C(47)	1.395(7)
C(46)-N(5)	1.492(7)
C(47)-C(48)	1.379(6)
C(47)-H(47)	0.9500
C(48)-H(48)	0.9500
N(1)-O(2)	1.214(5)
N(1)-O(1)	1.227(5)
N(5)-O(10)	1.223(6)
N(5)-O(9)	1.222(7)

C(2)-C(1)-C(6)	120.2(5)
C(2)-C(1)-N(1)	119.1(5)
C(6)-C(1)-N(1)	120.7(5)
C(1)-C(2)-C(3)	120.0(5)
C(1)-C(2)-H(2)	120.0
C(3)-C(2)-H(2)	120.0
C(2)-C(3)-C(4)	119.5(5)

C(2)-C(3)-H(3)	120.3
C(4)-C(3)-H(3)	120.3
N(2)-C(4)-C(5)	120.8(4)
N(2)-C(4)-C(3)	119.9(4)
C(5)-C(4)-C(3)	119.3(4)
C(6)-C(5)-C(4)	120.1(5)
C(6)-C(5)-H(5)	120.0
C(4)-C(5)-H(5)	120.0
C(5)-C(6)-C(1)	120.8(5)
C(5)-C(6)-H(6)	119.6
C(1)-C(6)-H(6)	119.6
C(14)-C(7)-C(8)	118.3(5)
C(14)-C(7)-N(2)	120.5(5)
C(8)-C(7)-N(2)	121.1(5)
O(3)-C(8)-C(10)	125.1(5)
O(3)-C(8)-C(7)	115.8(5)
C(10)-C(8)-C(7)	119.0(5)
O(3)-C(9)-H(9A)	109.5
O(3)-C(9)-H(9B)	109.5
H(9A)-C(9)-H(9B)	109.5
O(3)-C(9)-H(9C)	109.5
H(9A)-C(9)-H(9C)	109.5
H(9B)-C(9)-H(9C)	109.5
C(11)-C(10)-C(8)	120.1(6)
C(11)-C(10)-H(10)	119.9
C(8)-C(10)-H(10)	119.9
C(10)-C(11)-C(13)	122.8(6)
C(10)-C(11)-O(4)	113.1(6)
C(13)-C(11)-O(4)	124.1(6)
O(4)-C(12)-H(12A)	109.5
O(4)-C(12)-H(12B)	109.5
H(12A)-C(12)-H(12B)	109.5
O(4)-C(12)-H(12C)	109.5
H(12A)-C(12)-H(12C)	109.5
H(12B)-C(12)-H(12C)	109.5
O(4)-C(12')-H(12D)	109.5
O(4)-C(12')-H(12E)	109.5
H(12D)-C(12')-H(12E)	109.5
O(4)-C(12')-H(12F)	109.5
H(12D)-C(12')-H(12F)	109.5
H(12E)-C(12')-H(12F)	109.5
C(11)-C(13)-C(14)	117.6(5)

C(11)-C(13)-H(13)	121.2
C(14)-C(13)-H(13)	121.2
C(7)-C(14)-C(13)	122.1(6)
C(7)-C(14)-H(14)	118.9
C(13)-C(14)-H(14)	118.9
C(20)-C(15)-C(16)	120.2(5)
C(20)-C(15)-N(2)	120.0(4)
C(16)-C(15)-N(2)	119.8(4)
C(17)-C(16)-C(15)	119.8(5)
C(17)-C(16)-H(16)	120.1
C(15)-C(16)-H(16)	120.1
C(16)-C(17)-C(18)	121.4(5)
C(16)-C(17)-H(17)	119.3
C(18)-C(17)-H(17)	119.3
C(19)-C(18)-C(17)	117.1(5)
C(19)-C(18)-N(3)	120.0(4)
C(17)-C(18)-N(3)	122.9(4)
C(20)-C(19)-C(18)	121.1(5)
C(20)-C(19)-H(19)	119.5
C(18)-C(19)-H(19)	119.5
C(15)-C(20)-C(19)	120.5(5)
C(15)-C(20)-H(20)	119.8
C(19)-C(20)-H(20)	119.8
C(22)-C(21)-C(27)	120.3(4)
C(22)-C(21)-N(3)	120.6(4)
C(27)-C(21)-N(3)	118.9(4)
C(21)-C(22)-C(23)	121.6(5)
C(21)-C(22)-H(22)	119.2
C(23)-C(22)-H(22)	119.2
C(24)-C(23)-C(22)	118.1(4)
C(24)-C(23)-H(23)	120.9
C(22)-C(23)-H(23)	120.9
O(5)-C(24)-C(23)	124.5(4)
O(5)-C(24)-C(26)	114.2(5)
C(23)-C(24)-C(26)	121.3(5)
O(5)-C(25)-H(25A)	109.5
O(5)-C(25)-H(25B)	109.5
H(25A)-C(25)-H(25B)	109.5
O(5)-C(25)-H(25C)	109.5
H(25A)-C(25)-H(25C)	109.5
H(25B)-C(25)-H(25C)	109.5
C(27)-C(26)-C(24)	119.6(5)

C(27)-C(26)-H(26)	120.2
C(24)-C(26)-H(26)	120.2
O(6)-C(27)-C(26)	123.8(4)
O(6)-C(27)-C(21)	117.1(4)
C(26)-C(27)-C(21)	119.2(4)
O(6)-C(28)-H(28A)	109.5
O(6)-C(28)-H(28B)	109.5
H(28A)-C(28)-H(28B)	109.5
O(6)-C(28)-H(28C)	109.5
H(28A)-C(28)-H(28C)	109.5
H(28B)-C(28)-H(28C)	109.5
C(30)-C(29)-C(34)	118.9(4)
C(30)-C(29)-N(3)	123.5(4)
C(34)-C(29)-N(3)	117.5(4)
C(29)-C(30)-C(31)	120.9(5)
C(29)-C(30)-H(30)	119.5
C(31)-C(30)-H(30)	119.5
C(32)-C(31)-C(30)	119.6(5)
C(32)-C(31)-H(31)	120.2
C(30)-C(31)-H(31)	120.2
C(31)-C(32)-C(33)	119.2(5)
C(31)-C(32)-N(4)	119.3(4)
C(33)-C(32)-N(4)	121.2(5)
C(34)-C(33)-C(32)	121.2(5)
C(34)-C(33)-H(33)	119.4
C(32)-C(33)-H(33)	119.4
C(33)-C(34)-C(29)	120.1(4)
C(33)-C(34)-H(34)	120.0
C(29)-C(34)-H(34)	120.0
C(42)-C(35)-C(36)	119.0(5)
C(42)-C(35)-N(4)	121.5(5)
C(36)-C(35)-N(4)	119.5(5)
O(7)-C(36)-C(38)	124.5(5)
O(7)-C(36)-C(35)	116.2(5)
C(38)-C(36)-C(35)	119.3(5)
O(7)-C(37)-H(37A)	109.5
O(7)-C(37)-H(37B)	109.5
H(37A)-C(37)-H(37B)	109.5
O(7)-C(37)-H(37C)	109.5
H(37A)-C(37)-H(37C)	109.5
H(37B)-C(37)-H(37C)	109.5
C(36)-C(38)-C(39)	120.4(5)

C(36)-C(38)-H(38)	119.8
C(39)-C(38)-H(38)	119.8
C(41)-C(39)-C(38)	121.3(5)
C(41)-C(39)-O(8)	124.1(5)
C(38)-C(39)-O(8)	114.7(5)
O(8)-C(40)-H(40A)	109.5
O(8)-C(40)-H(40B)	109.5
H(40A)-C(40)-H(40B)	109.5
O(8)-C(40)-H(40C)	109.5
H(40A)-C(40)-H(40C)	109.5
H(40B)-C(40)-H(40C)	109.5
C(39)-C(41)-C(42)	118.5(5)
C(39)-C(41)-H(41)	120.8
C(42)-C(41)-H(41)	120.8
C(35)-C(42)-C(41)	121.5(6)
C(35)-C(42)-H(42)	119.3
C(41)-C(42)-H(42)	119.3
N(4)-C(43)-C(48)	121.8(5)
N(4)-C(43)-C(44)	119.9(4)
C(48)-C(43)-C(44)	118.3(5)
C(43)-C(44)-C(45)	120.3(5)
C(43)-C(44)-H(44)	119.8
C(45)-C(44)-H(44)	119.8
C(46)-C(45)-C(44)	118.7(5)
C(46)-C(45)-H(45)	120.6
C(44)-C(45)-H(45)	120.6
C(45)-C(46)-C(47)	122.4(5)
C(45)-C(46)-N(5)	118.4(6)
C(47)-C(46)-N(5)	119.1(6)
C(48)-C(47)-C(46)	118.1(5)
C(48)-C(47)-H(47)	121.0
C(46)-C(47)-H(47)	121.0
C(47)-C(48)-C(43)	122.0(5)
C(47)-C(48)-H(48)	119.0
C(43)-C(48)-H(48)	119.0
O(2)-N(1)-O(1)	122.8(5)
O(2)-N(1)-C(1)	119.0(5)
O(1)-N(1)-C(1)	118.2(5)
C(4)-N(2)-C(7)	122.7(4)
C(4)-N(2)-C(15)	121.1(4)
C(7)-N(2)-C(15)	115.0(4)
C(18)-N(3)-C(29)	123.9(4)

C(18)-N(3)-C(21)	116.0(4)
C(29)-N(3)-C(21)	119.0(4)
C(43)-N(4)-C(35)	120.9(4)
C(43)-N(4)-C(32)	122.0(4)
C(35)-N(4)-C(32)	115.3(4)
O(10)-N(5)-O(9)	125.5(6)
O(10)-N(5)-C(46)	116.7(7)
O(9)-N(5)-C(46)	117.7(7)
C(8)-O(3)-C(9)	117.0(4)
C(11)-O(4)-C(12)	118.9(7)
C(11)-O(4)-C(12')	111.7(7)
C(12)-O(4)-C(12')	34.4(7)
C(24)-O(5)-C(25)	116.3(4)
C(27)-O(6)-C(28)	118.2(3)
C(36)-O(7)-C(37)	117.2(4)
C(39)-O(8)-C(40)	118.1(5)

Symmetry transformations used to generate equivalent atoms:

Table S9. Anisotropic displacement parameters ($Å^2$x 10^3)for 1-NO_2. The anisotropic displacement factor exponent takes the form: -2p2[h2a*2U11 + ... + 2 h k a* b* U12]

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
C(1)	47(3)	43(4)	53(3)	-15(3)	-8(3)	0(3)
C(2)	48(3)	42(4)	57(3)	-10(3)	-13(3)	-8(3)
C(3)	46(3)	37(3)	43(3)	-13(3)	-11(3)	-1(3)
C(4)	42(3)	37(3)	32(3)	-4(2)	-11(2)	-3(2)
C(5)	42(3)	28(3)	50(3)	-14(2)	-11(3)	1(2)
C(6)	60(4)	36(3)	64(4)	-20(3)	-16(3)	3(3)
C(7)	40(3)	39(3)	57(4)	-17(3)	-9(3)	2(3)
C(8)	50(3)	38(3)	49(3)	-12(3)	-12(3)	-2(3)
C(9)	88(5)	72(4)	66(4)	-21(3)	-39(4)	-2(4)
C(10)	47(3)	44(4)	69(4)	-21(3)	-15(3)	-4(3)
C(11)	47(4)	77(5)	91(5)	-38(4)	-6(4)	-22(3)
C(13)	67(4)	75(5)	58(4)	-16(4)	7(3)	-32(3)
C(14)	61(4)	58(4)	49(4)	-11(3)	-7(3)	-17(3)
C(15)	37(3)	34(3)	41(3)	-10(3)	-8(2)	-3(2)
C(16)	44(3)	34(3)	49(3)	-8(3)	-22(3)	4(2)
C(17)	48(3)	38(3)	44(3)	-11(3)	-15(3)	5(3)
C(18)	32(3)	36(3)	37(3)	-8(2)	-4(2)	-5(2)
C(19)	43(3)	36(3)	40(3)	-10(2)	-11(2)	4(2)
C(20)	41(3)	39(3)	37(3)	-13(3)	-7(2)	-2(2)
C(21)	36(3)	33(3)	41(3)	-11(2)	-14(2)	-2(2)
C(22)	32(3)	42(3)	49(3)	-17(3)	-12(2)	-1(2)
C(23)	38(3)	49(3)	42(3)	-19(3)	2(2)	-16(3)
C(24)	55(4)	40(3)	40(3)	-12(3)	-8(3)	-6(3)
C(25)	79(4)	62(4)	55(4)	5(3)	-1(3)	-20(3)
C(26)	39(3)	43(3)	57(3)	-15(3)	-16(3)	1(3)
C(27)	35(3)	30(3)	38(3)	-5(2)	-5(2)	-5(2)
C(28)	31(3)	81(4)	61(4)	-9(3)	-17(3)	-5(3)
C(29)	24(3)	33(3)	41(3)	-10(3)	-5(2)	-1(2)
C(30)	35(3)	34(3)	42(3)	-11(3)	-11(2)	-3(2)
C(31)	33(3)	45(4)	51(3)	-16(3)	-9(2)	-6(2)
C(32)	28(3)	44(3)	39(3)	-12(3)	-11(2)	2(2)
C(33)	48(3)	41(3)	51(3)	-19(3)	-21(3)	2(3)
C(34)	43(3)	39(3)	34(3)	-7(2)	-4(2)	-11(2)
C(35)	52(4)	56(4)	43(3)	-21(3)	-14(3)	2(3)
C(36)	45(3)	52(4)	45(3)	-11(3)	-5(3)	-17(3)
C(37)	78(5)	65(5)	103(5)	-17(4)	-29(4)	14(4)

C(38)	48(4)	66(4)	50(3)	-22(3)	-20(3)	5(3)
C(39)	33(3)	84(5)	43(3)	-21(3)	-5(3)	-9(3)
C(40)	51(4)	95(5)	64(4)	-13(4)	-1(3)	-15(3)
C(41)	45(4)	69(4)	46(3)	-9(3)	-6(3)	-6(3)
C(42)	52(4)	70(4)	46(3)	-20(3)	-2(3)	-13(3)
C(43)	37(3)	48(3)	34(3)	-10(3)	-11(2)	-3(3)
C(44)	48(3)	67(4)	53(3)	-29(3)	-12(3)	7(3)
C(45)	72(4)	64(4)	52(4)	-30(3)	-18(3)	6(3)
C(46)	59(4)	57(4)	52(4)	-15(3)	-22(3)	-16(3)
C(47)	45(3)	72(4)	39(3)	-5(3)	-8(3)	-12(3)
C(48)	44(3)	59(4)	34(3)	-12(3)	-7(2)	-13(3)
N(1)	43(3)	63(4)	85(4)	-27(3)	1(3)	-4(3)
N(2)	37(3)	38(3)	49(3)	-13(2)	-7(2)	-5(2)
N(3)	38(2)	31(2)	45(3)	-12(2)	-13(2)	2(2)
N(4)	26(2)	63(3)	40(2)	-18(2)	-3(2)	-1(2)
N(5)	99(5)	91(5)	62(4)	-21(3)	-36(4)	-23(4)
O(1)	78(3)	65(3)	170(5)	-54(3)	3(3)	9(3)
O(2)	50(3)	82(3)	108(3)	-31(3)	-2(2)	-6(2)
O(3)	68(3)	63(3)	52(2)	-9(2)	-24(2)	-17(2)
O(4)	71(3)	138(4)	97(3)	-53(3)	10(3)	-53(3)
O(5)	71(3)	51(2)	47(2)	4(2)	-14(2)	-8(2)
O(6)	33(2)	53(2)	54(2)	-9(2)	-11(2)	-4(2)
O(7)	63(3)	58(3)	76(3)	-18(2)	-18(2)	9(2)
O(8)	43(2)	97(3)	64(3)	-9(2)	-6(2)	-4(2)
O(9)	146(5)	154(6)	128(5)	-94(4)	-54(4)	4(4)
O(10)	85(4)	135(5)	96(4)	-29(3)	-32(3)	-41(3)

Table S10. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (Å^{2}x 10^3) for 1-NO_2.

	x	y	z	U(eq)
H(2)	13145	-3831	7671	59
H(3)	11250	-3340	8299	50
H(5)	9941	-6295	8275	48
H(6)	11835	-6790	7723	62
H(9A)	8527	-3951	6226	107
H(9B)	7211	-4094	6815	107
H(9C)	7922	-5160	6651	107
H(10)	6410	-5627	7855	63
H(12A)	3455	-7153	9767	123
H(12B)	3953	-6108	9954	123
H(12C)	4388	-7321	10317	123
H(12D)	3751	-7769	9995	124
H(12E)	4357	-7028	10410	124
H(12F)	5032	-8057	10141	124
H(13)	6132	-6730	10312	85
H(14)	7922	-5819	10117	69
H(16)	9620	-3925	10049	49
H(17)	9298	-2237	10365	52
H(19)	8136	-1033	8290	48
H(20)	8512	-2718	7970	46
H(22)	10367	698	8462	48
H(23)	10532	2110	7233	52
H(25A)	9734	4070	5631	108
H(25B)	10342	2924	5937	108
H(25C)	10258	3853	6426	108
H(26)	6960	2083	7708	55
H(28A)	4799	278	9224	88
H(28B)	5570	474	8281	88
H(28C)	5336	1486	8696	88
H(30)	7464	-1776	10967	44
H(31)	6679	-1400	12266	51
H(33)	7742	1786	11215	52
H(34)	8556	1409	9943	48
H(37A)	5297	3866	11562	124
H(37B)	4350	3437	12442	124
H(37C)	4129	3198	11627	124
H(38)	3042	1900	12579	63

H(40A)	136	-411	14096	111
H(40B)	1121	-544	14601	111
H(40C)	1189	-1240	13939	111
H(41)	3046	-1264	13943	67
H(42)	5118	-1163	13596	68
H(44)	5713	1501	13773	65
H(45)	6739	2412	14437	71
H(47)	9840	1490	13143	65
H(48)	8832	674	12443	55