Supplementary Information

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

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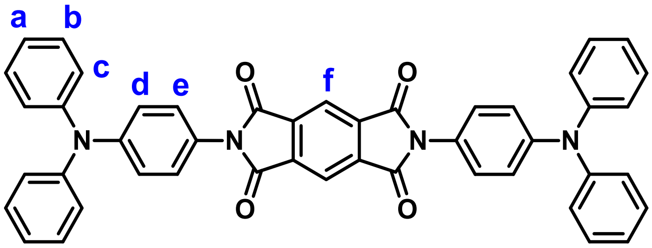
Monomer Synthesis

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

A mixture of 2.86 g (11 mmol) of **TPA-NH$_2$** 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.

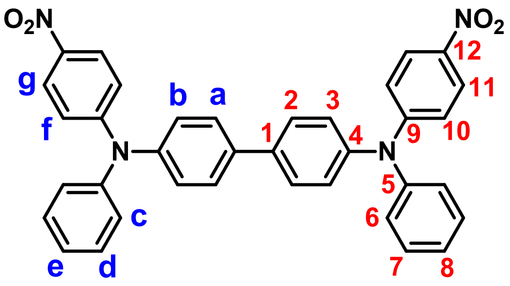
IR (KBr): 1769 and 1715 cm^{-1} (imide ring C=O stretching). ^{1}H NMR (600 MHz, CDCl$_3$, δ, ppm): 7.11 (t, *J* = 7.4 Hz, 4H, H$_a$), 7.19 (d, *J* = 8.7 Hz, 12H, H$_c$ + H$_d$), 7.31 (d, *J* = 8.7 Hz, 4H, H$_e$), 7.32 (t, *J* = 7.5 Hz, 8H, H$_b$), 8.49 (s, 2H, H$_f$). TOF MS ES$^+$: Calcd for $(C_{46}H_{30}N_4O_4)^+$: 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.,[22] 201 °C), measured by DSC at 10°C /min.

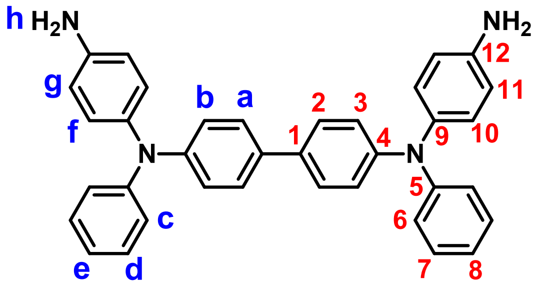
IR (KBr): 1580 and 1320 cm^{-1} (−NO_2 stretching). ^1H NMR (600 MHz, DMSO-d_6, δ, ppm): 6.89 (d, J = 9.3 Hz, 4H, H_f), 7.29−7.33 (m, 10H, H_b + $H_{c\,+}$ H_e), 7.48 (t, J = 8.2 Hz, 4H, H_d), 7.75 (d, J = 8.5 Hz, 4H, H_a), 8.10 (d, J = 9.3 Hz, 4H, H_g) ^{13}C NMR (150 MHz, DMSO-d_6, δ, ppm): 117.42 (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^5), 144.88 (C^4), 153.10 (C^9). 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)

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 ^{o}C under hydrogen atmosphere. After a further 48 h further stirring at 60 ^{o}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 ^{o}C to give 3.19 g of **3** as white powder in 89 % yield; m.p. = 285.4−287.4 ^{o}C (DSC endotherm peak temperature) (lit.,[22] 289 ^{o}C), measured by DSC at 10 ^{o}C/min

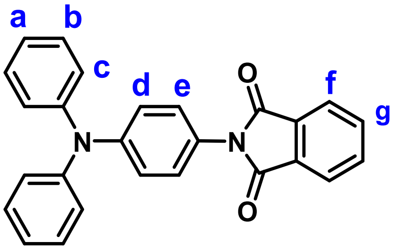
FT-IR (KBr): 3460, 3370 cm^{-1} (−NH$_2$ stretch). ^{1}H NMR (600 MHz, DMSO-d_6, δ, ppm): 5.08 (s, 4H, H$_h$), 6.59 (d, J = 8.6 Hz, 4H, H$_g$), 6.83 (d, J = 8.6 Hz, 4H, H$_f$), 6.89-6.96 (m, 10H, H$_b$ + H$_c$ + H$_e$), 7.21 (t, J = 8.2 Hz, 4H, H$_d$), 7.45 (d, J = 8.5 Hz, 4H, H$_a$). ^{13}C NMR (150 MHz, DMSO-d_6, δ, ppm): 114.90 (C^{11}), 121.20 (C^8), 121.26 (C^3), 121.64 (C^6), 126.53 (C^2), 128.04 (C^{10}), 129.02 (C^7), 132.30 (C^1), 134.96 (C^9), 146.24 (C^5), 146.62 (C^4), 147.65 (C^{12}). EI MS: Calcd for $(C_{36}H_{30}N_4)^{+\cdot}$: m/z 518.2; Found: m/z 518.2.



N-(4-Diphenylaminophenyl)phthalimide (M$_1$)

A mixture of 2.86 g (11 mmol) TPA-NH$_2$ 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 ^{o}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 **M$_1$** as yellow crystals with a melting point of 205.3−206.2 ^{o}C (DSC endotherm peak temperature), measured by DSC at 10 °C /min.

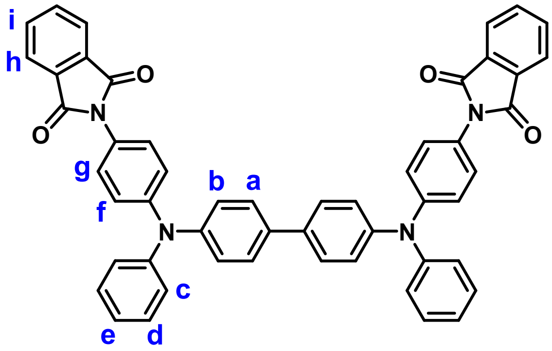
IR (KBr): 1742 and 1711 cm^{-1} (imide ring C=O stretching). ^{1}H NMR (600 MHz, DMSO-*d$_6$*, δ, ppm): 7.05–7.11 (m, 8H, H$_a$ + H$_c$ + H$_d$), 7.32–7.36 (m, 6H, H$_b$ + H$_e$), 7.88–7.91 (m, 2H, H$_g$), 7.94–7.97 (m, 2H, H$_f$).



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$_3$, δ, ppm): 7.09 (t, *J* = 7.4 Hz, 2H, H$_e$), 7.19-7.21 (m, 12H, H$_b$+ Hc + H$_f$), 7.28–7.32 (m, 8H, H$_a$ + H$_d$), 7.50 (d, *J* = 8.6 Hz, 4H, H$_g$), 7.80 (dd, 4H, H$_i$), 7.96 (dd, 4H, H$_h$).



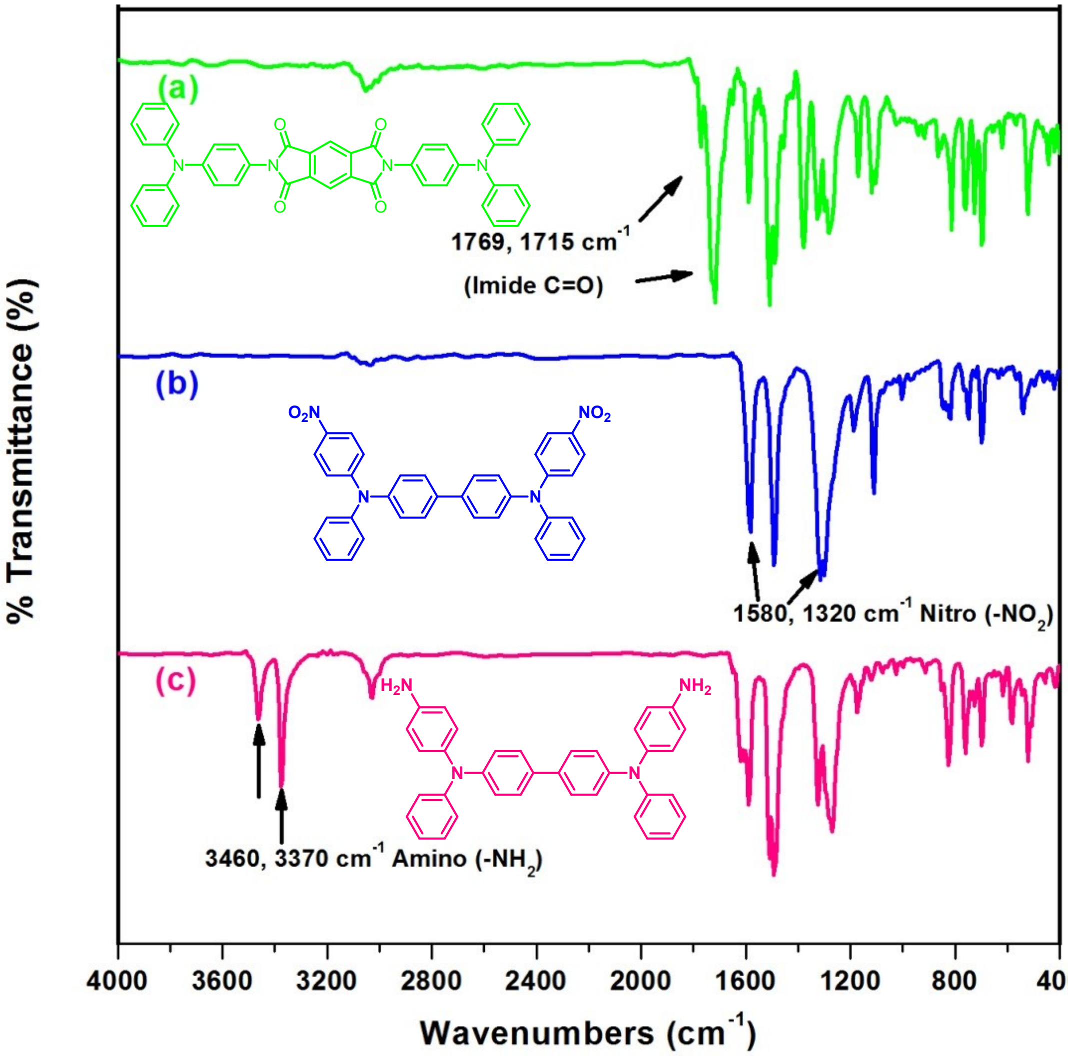
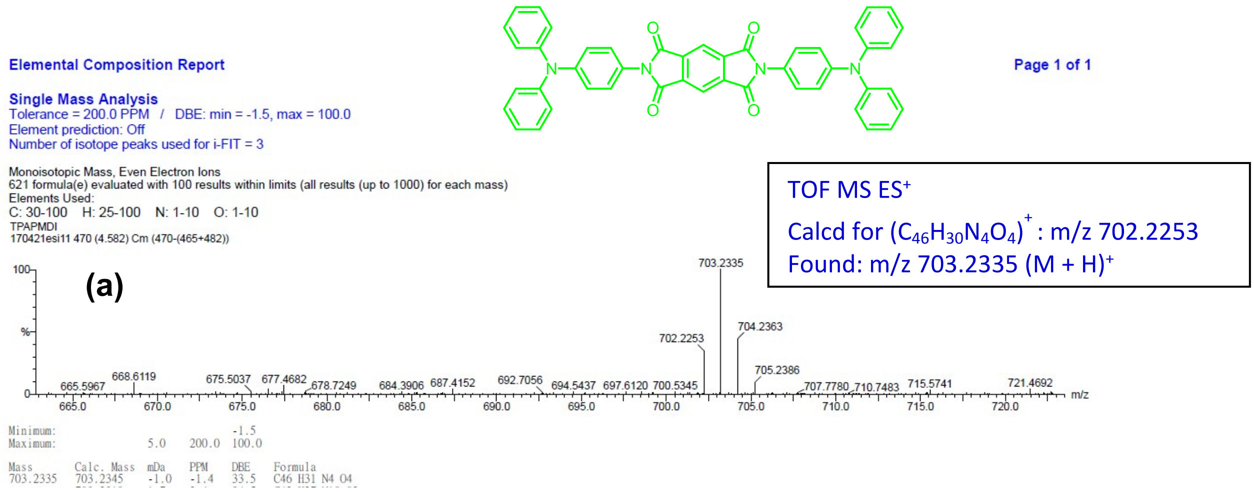


Figure S1 IR spectra of (a) TPA-PMDI, (b) dinitro compound **2** and (c) diamine monomer **3**.



Elemental Composition Report

Page 1 of 1

Single Mass Analysis
Tolerance = 200.0 PPM / DBE: min = -1.5, max = 100.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions
621 formula(e) evaluated with 100 results within limits (all results (up to 1000) for each mass)
Elements Used:
C: 30-100 H: 25-100 N: 1-10 O: 1-10
TPAPMDI
170421esi11 470 (4.582) Cm (470-(465+482))

TOF MS ES^+
Calcd for $(C_{46}H_{30}N_4O_4)^+$: m/z 702.2253
Found: m/z 703.2335 $(M + H)^+$

```
Minimum:                        -1.5
Maximum:          5.0   200.0  100.0

Mass      Calc. Mass  mDa    PPM    DBE    Formula
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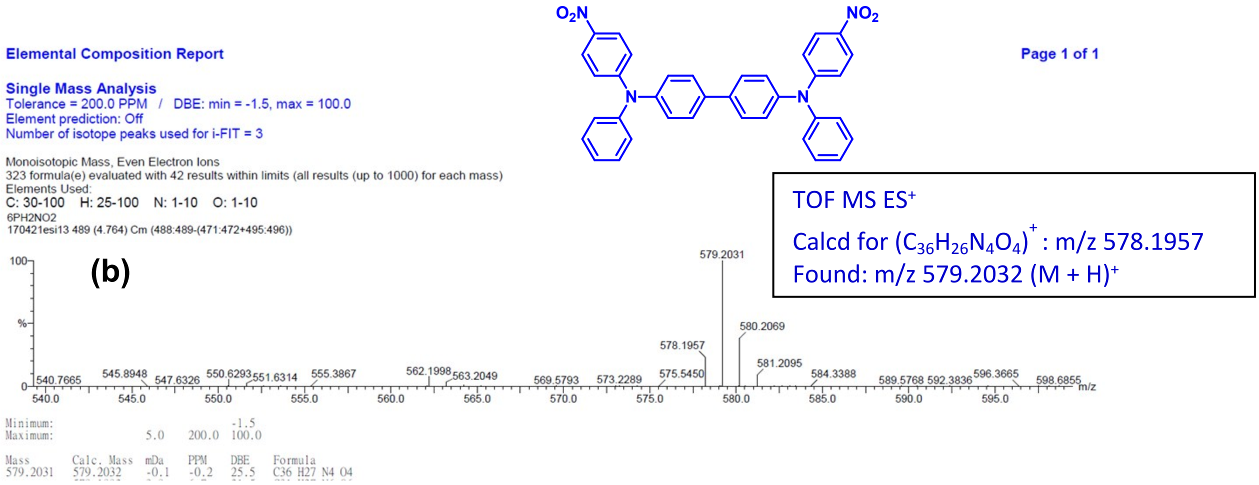

Elemental Composition Report

Page 1 of 1

Single Mass Analysis
Tolerance = 200.0 PPM / DBE: min = -1.5, max = 100.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions
323 formula(e) evaluated with 42 results within limits (all results (up to 1000) for each mass)
Elements Used:
C: 30-100 H: 25-100 N: 1-10 O: 1-10
6PH2NO2
170421esi13 489 (4.764) Cm (488:489-(471:472+495:496))

TOF MS ES^+
Calcd for $(C_{36}H_{26}N_4O_4)^+$: m/z 578.1957
Found: m/z 579.2032 $(M + H)^+$

```
Minimum:                        -1.5
Maximum:          5.0   200.0  100.0

Mass      Calc. Mass  mDa    PPM    DBE    Formula
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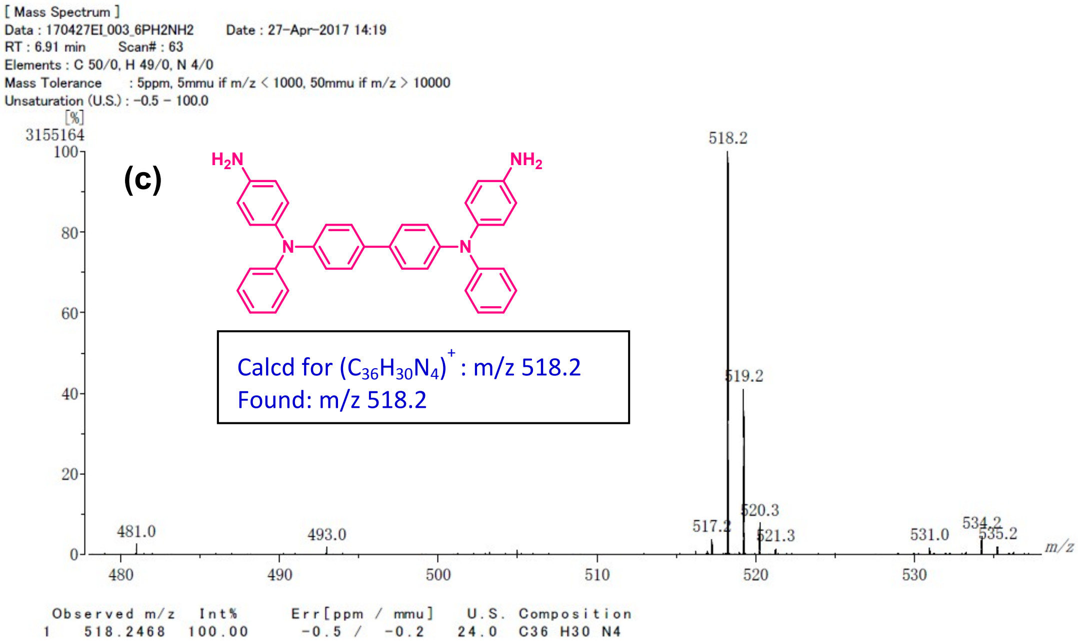

[Mass Spectrum]
Data : 170427EI_003_6PH2NH2 Date : 27-Apr-2017 14:19
RT : 6.91 min Scan# : 63
Elements : C 50/0, H 49/0, N 4/0
Mass Tolerance : 5ppm, 5mmu if m/z < 1000, 50mmu if m/z > 10000
Unsaturation (U.S.) : -0.5 – 100.0

Calcd for $(C_{36}H_{30}N_4)^+$: m/z 518.2
Found: m/z 518.2

```
   Observed m/z   Int%      Err[ppm / mmu]    U.S.  Composition
1   518.2468    100.00     -0.5 /  -0.2      24.0  C36 H30 N4
```

Figure S2 Mass spectra of (a) TPA-PMDI, (b) dinitro compound **2** and (c) diamine monomer **3**.

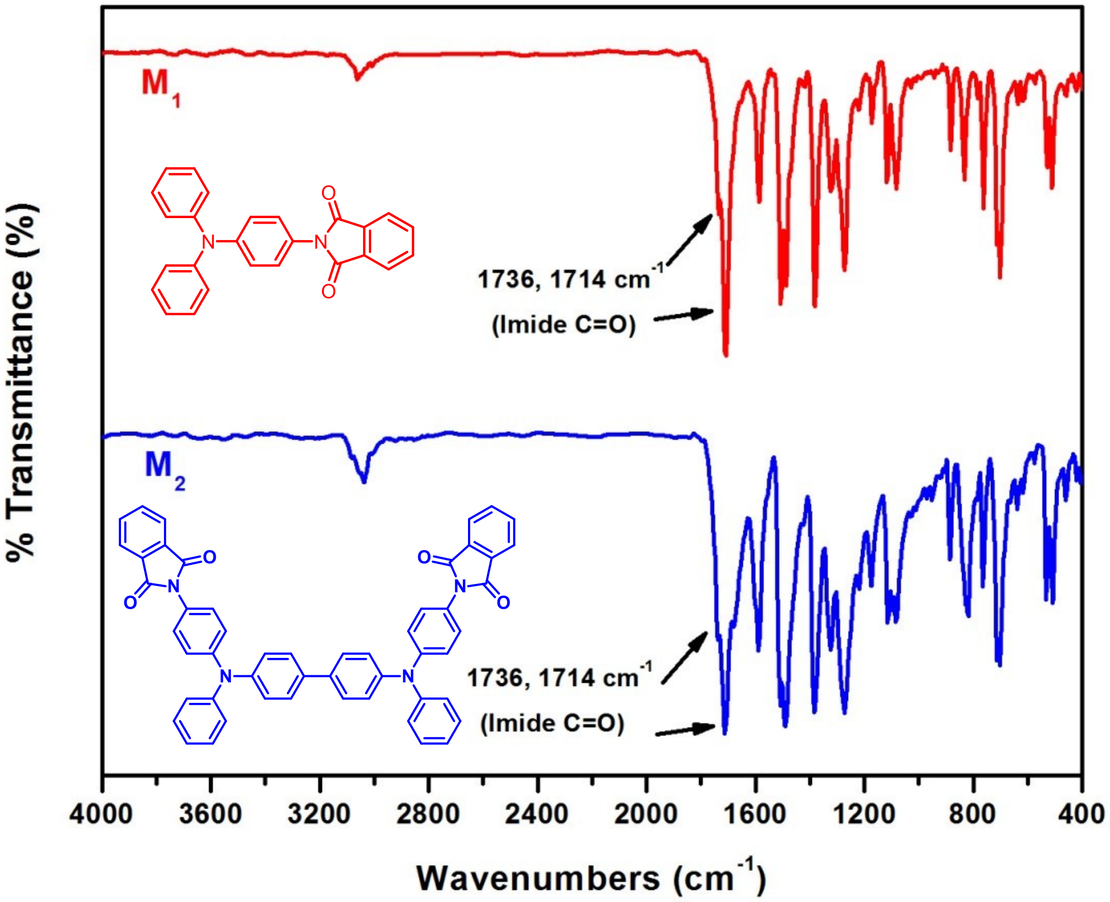

Figure S3. IR spectra of model compounds $\mathbf{M_1}$ and $\mathbf{M_2}$.

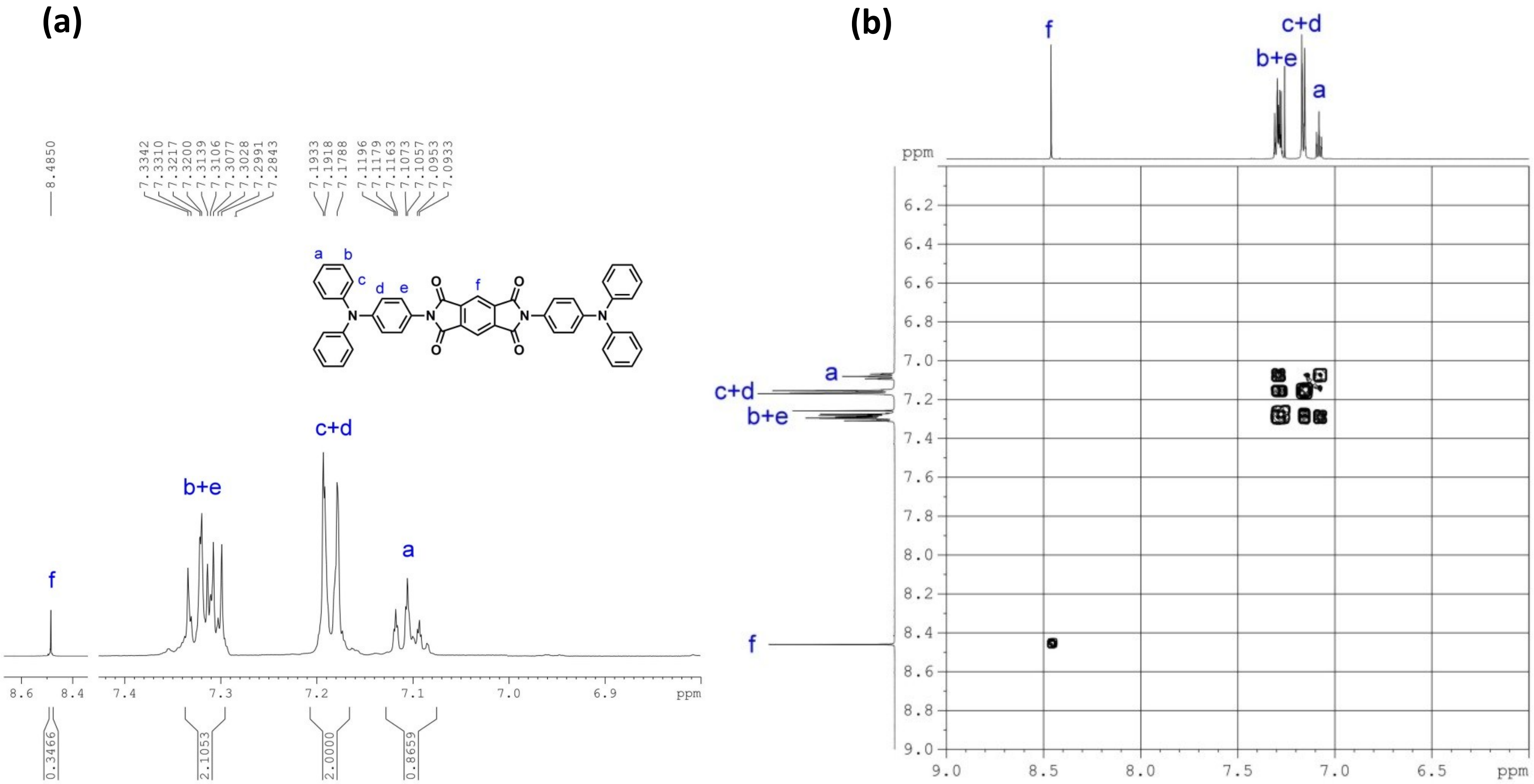

Figure S4. (a) ^{1}H NMR and (b) H-H COSY spectra of diimide compound TPA-PMDI in $CDCl_3$.

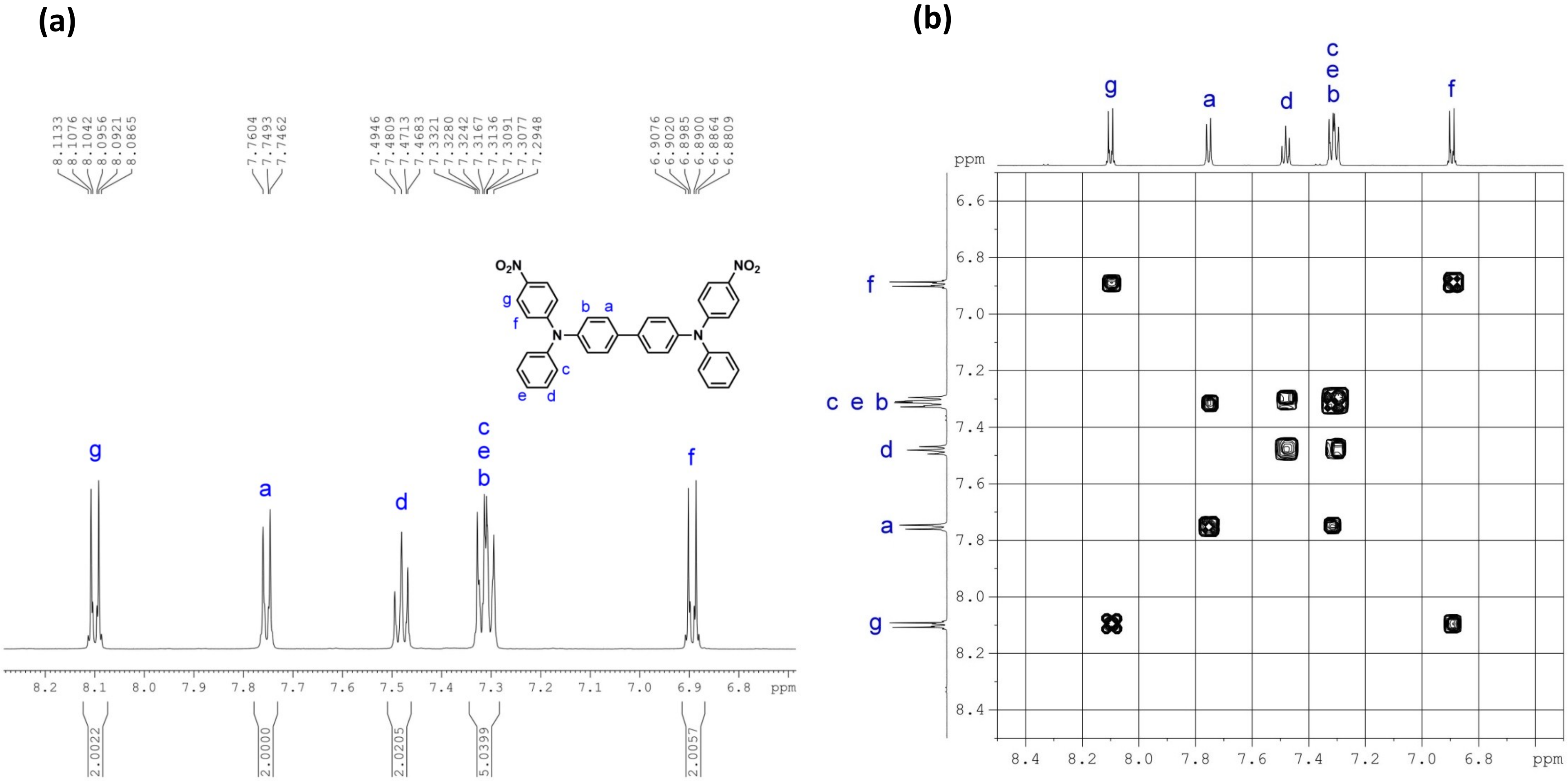

Figure S5. (a) ^{1}H NMR and (b) H-H COSY spectra of dinitro compound **2** in DMSO-d_6.

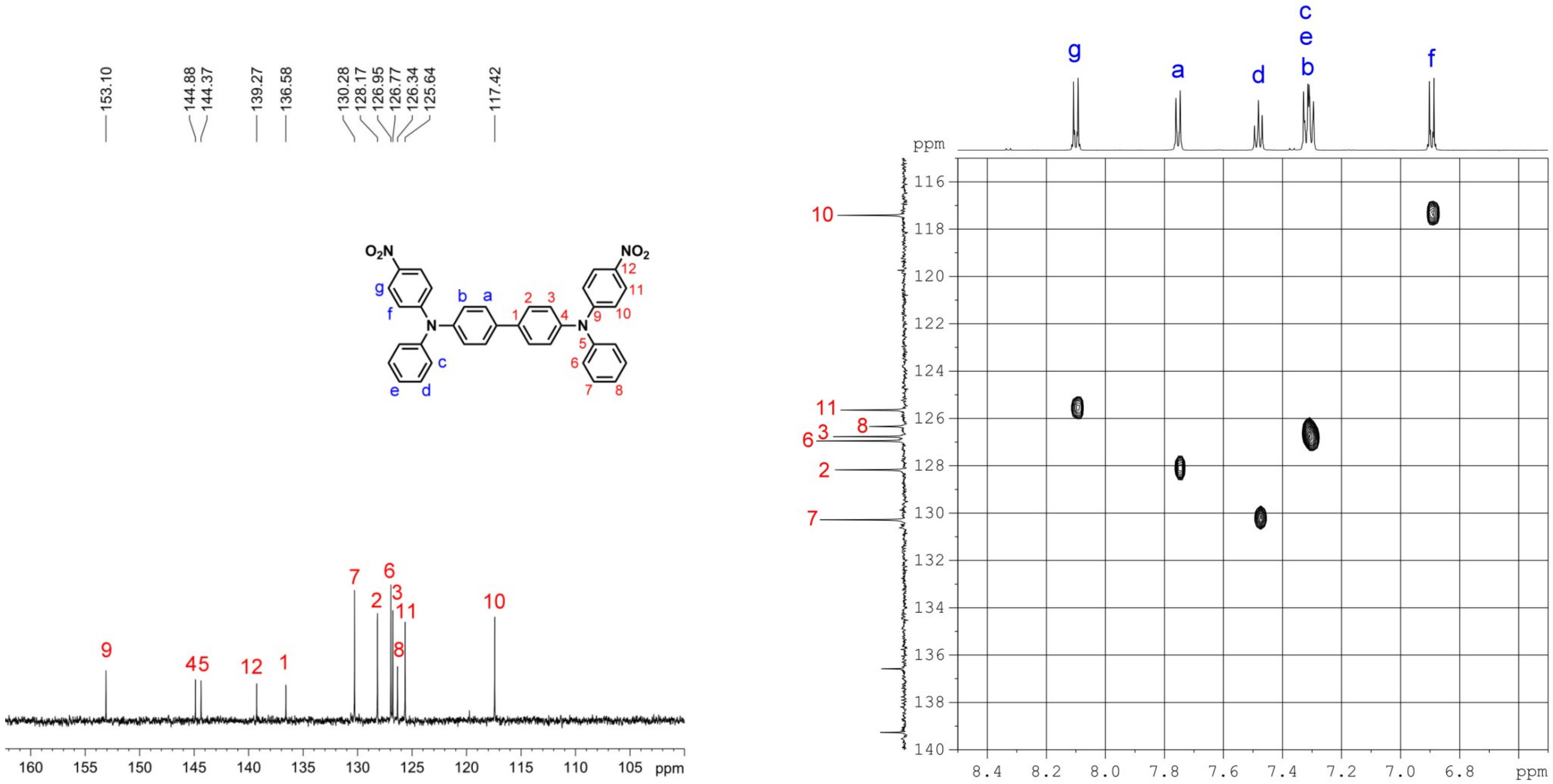

Figure S6. (a) ^{13}C NMR and (b) C-H HMQC spectra of dinitro compound **2** in DMSO-d_6.

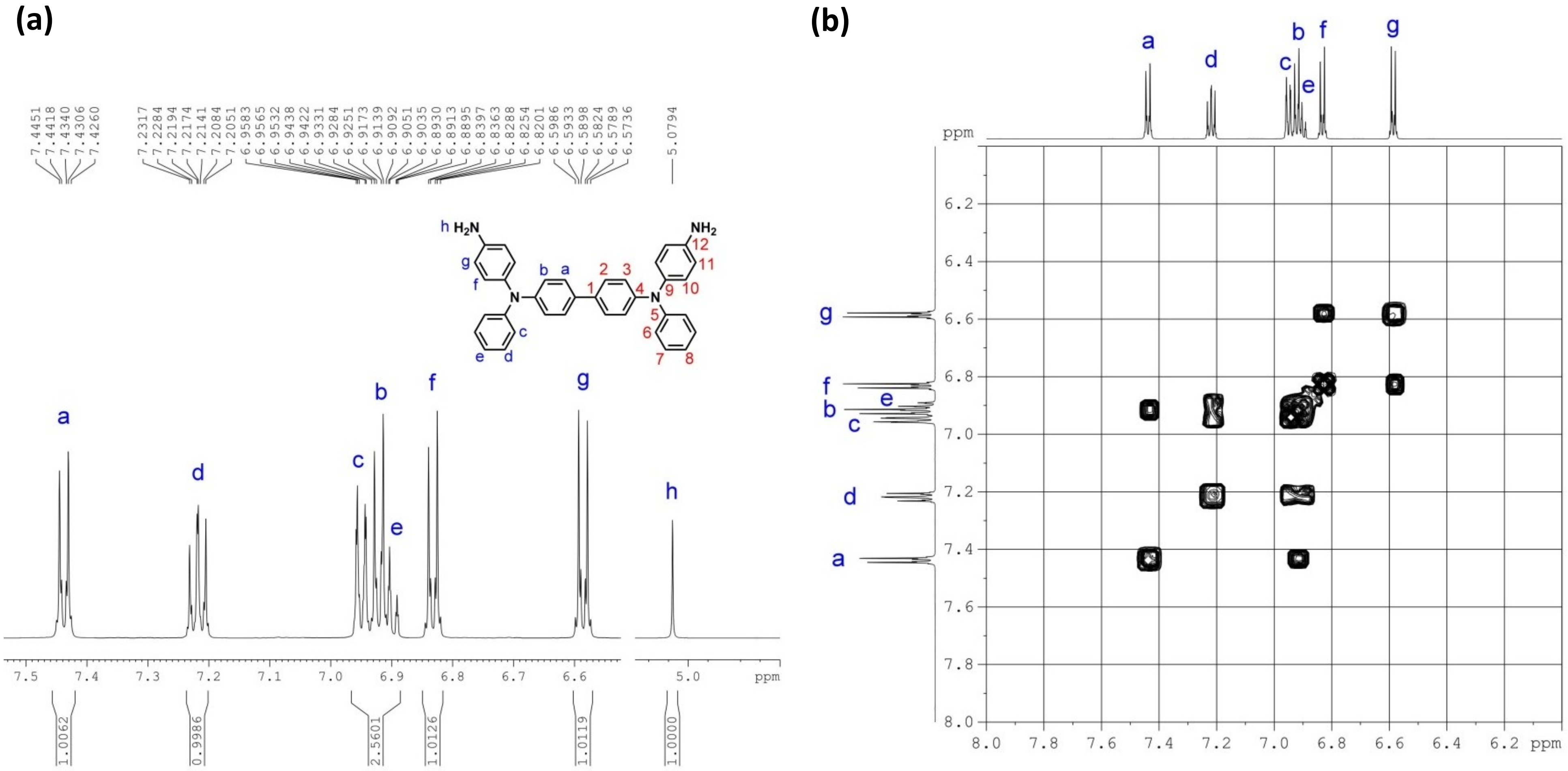

Figure S7. (a) ^{1}H NMR and (b) H-H COSY spectra of diamine compound **3** in DMSO-d_6.

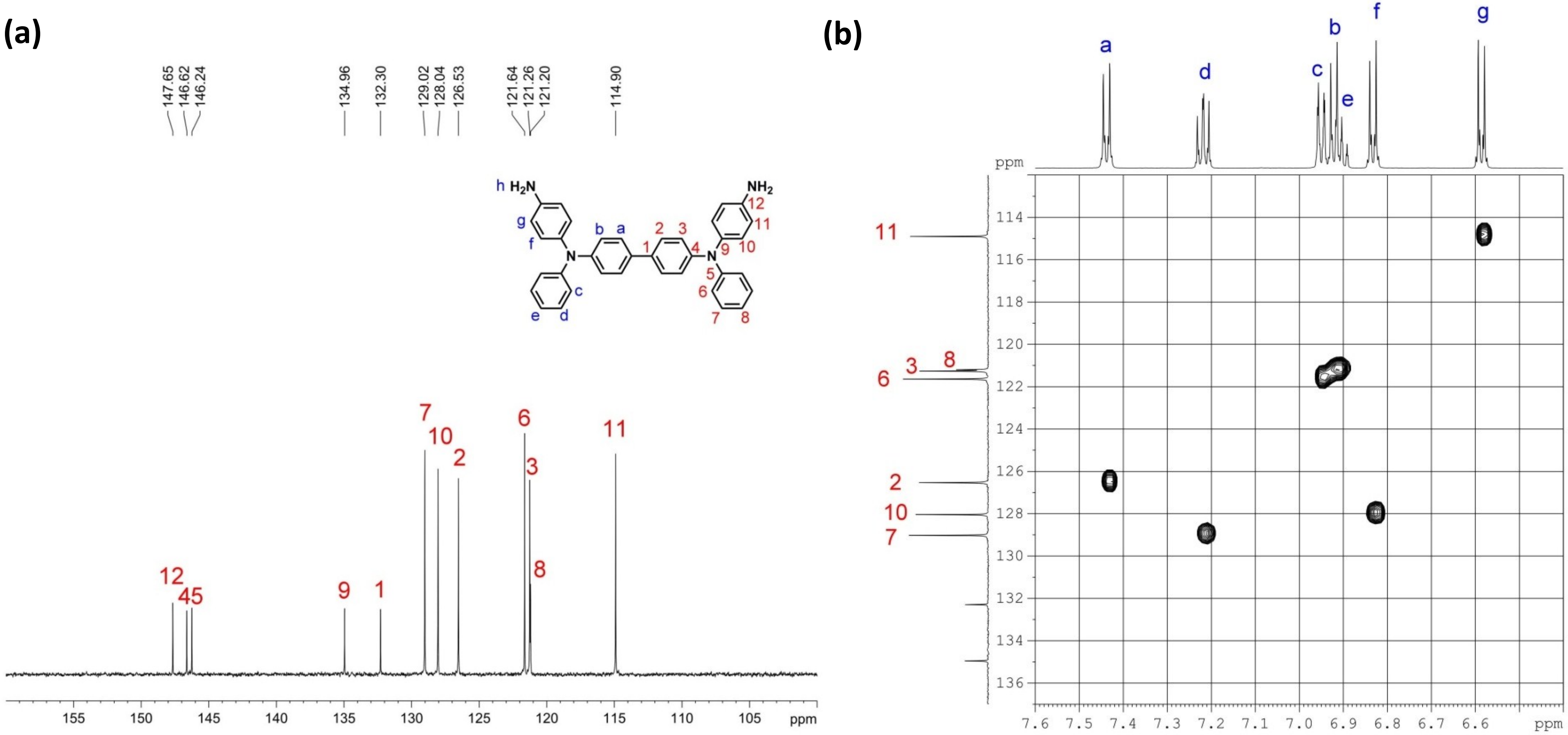

Figure S8. (a) ^{13}C NMR and (b) C-H HMQC spectra of diamine compound **3** in DMSO-d_6.

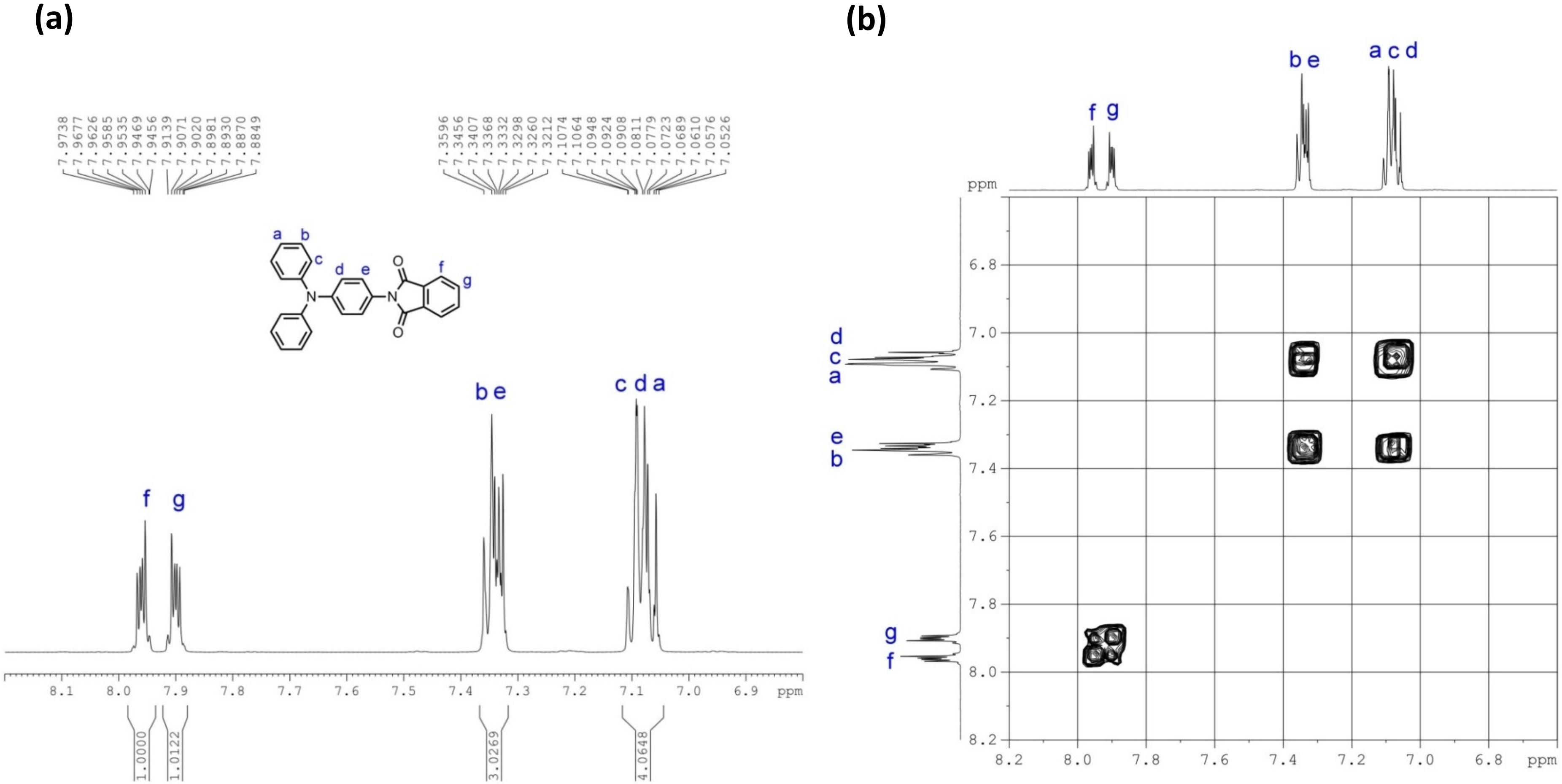

Figure S9. (a) ^{1}H NMR and (b) H-H COSY spectra of model compound $\mathbf{M_1}$ in DMSO-d_6.

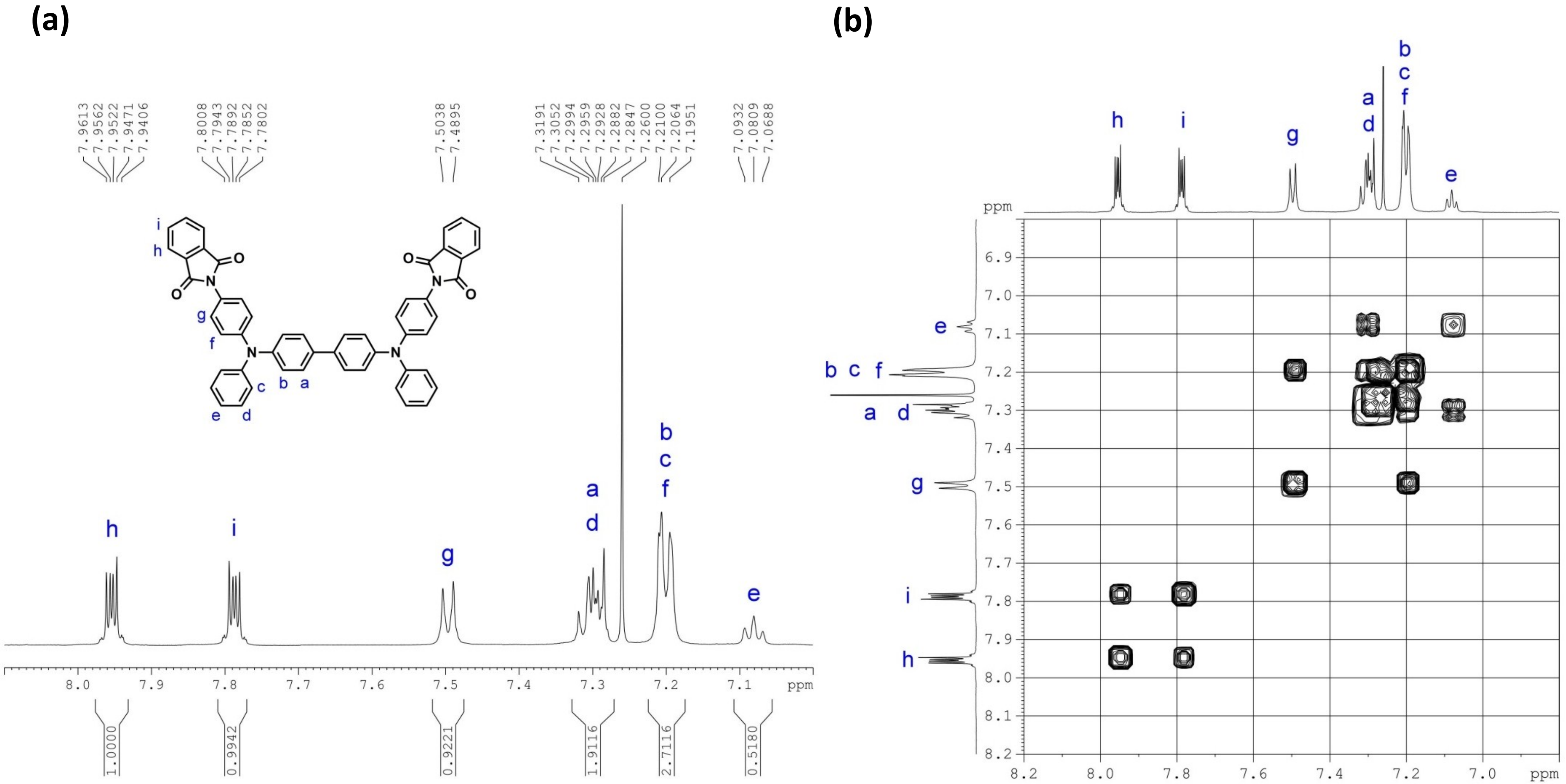

Figure S10 (a) ^{1}H NMR and (b) H-H COSY spectra of model compound $\mathbf{M_2}$ in $CDCl_3$.

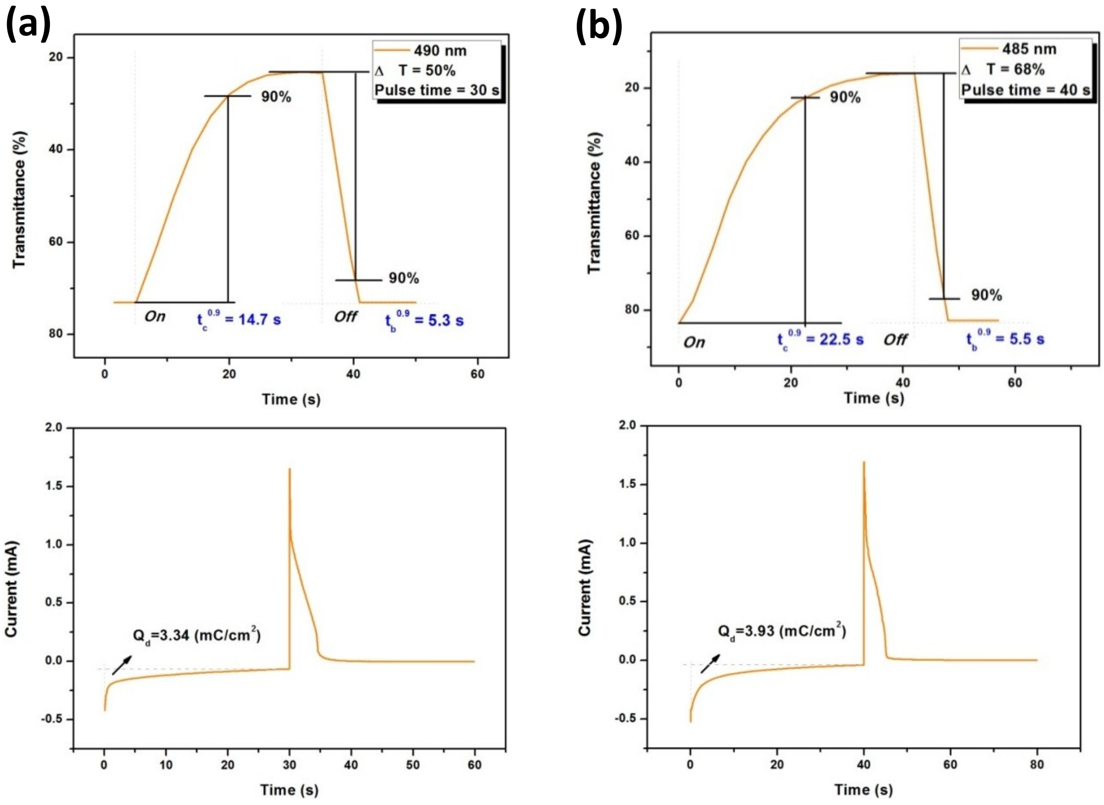

Figure S11 Current monitored and optical transmittance changes of the film on the ITO-glass slide in 0.1 M Bu_4NClO_4/CH_2Cl_2 while the potential was switched: (a) **PI**-**E** film (thickness: 200 ± 100 nm) between 0.0 V and 1.0 V at 485 nm with a pulse time of 30 s and (b) **PI**-**C** film (thickness: 200 ± 30 nm) between 0.0 V and 1.0 V at 490 nm with a pulse time of 40 s.

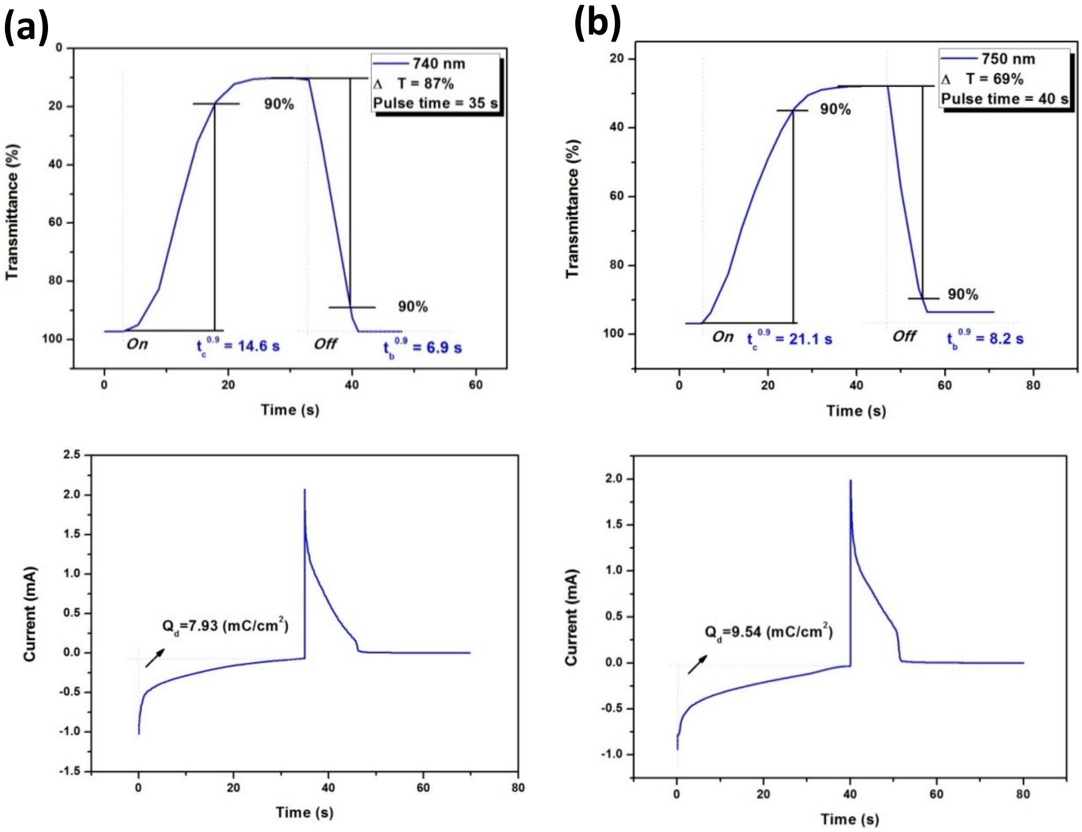

Figure S12 Current monitored and optical transmittance changes of the film on the ITO-glass slide in 0.1 M Bu_4NClO_4/CH_2Cl_2 while the potential was switched: (a) **PI-E** film (thickness: 200 ± 100 nm) between 0.0 V and 1.3 V at 740 nm with a pulse time of 35 s and (b) **PI-C** film (thickness: 200 ± 30 nm) between 0.0 V and 1.3 V at 750 nm with a pulse time of 40 s.

Table S1 Coloration efficiency of polyimide **PI-E**

Cycling times[a]	ΔOD_{490}[b]	Q_d[c] (mC cm^{-2})	CE[d] (cm^2 C^{-1})	Decay (%)[e]
1	0.50	3.34	149	0
10	0.47	3.24	145	2.7
20	0.42	3.00	140	6.0
30	0.39	2.83	138	7.2
40	0.36	2.66	135	9.4
50	0.33	2.51	132	11.1
60	0.30	2.34	128	14.1
70	0.28	2.31	121	18.8
80	0.25	2.16	116	22.1
90	0.22	2.01	110	26.2
100	0.20	1.92	104	30.2

[a] Switching between 0 and 1.0 V (vs. Ag/AgCl).

[b] Optical Density (ΔOD) = $\log[T_{bleached} / T_{colored}]$, where $T_{colored}$ and $T_{bleached}$ are the maximum transmittance in the oxidized and neutral states, respectively.

[c] Q_d is ejected charge, determined from the in situ experiments.

[d] Coloration efficiency (CE) = $\Delta OD/Q_d$.

[e] Decay of coloration efficiency after cyclic scans.

Table S2 Coloration efficiency of polyimide **PI-C**

Cycling times[a]	ΔOD_{485}[c]	Q_d[d] (mC cm^{-1})	CE[e] (cm^2 C^{-1})	Decay (%)[e]
1	0.72	3.93	183	0
10	0.72	3.92	183	0
20	0.71	3.87	183	0
30	0.71	3.90	182	0.5
40	0.71	3.88	182	0.5
50	0.70	3.84	182	0.5
60	0.70	3.86	181	1.1
70	0.70	3.88	180	1.6
80	0.69	3.83	180	1.6
90	0.69	3.85	179	2.2
100	0.69	3.85	179	2.2

[a] Switching between 0 V and 1.0 V (vs. Ag/AgCl).

[b] Optical Density (ΔOD) = $\log[T_{bleached}/T_{colored}]$, where $T_{colored}$ and $T_{bleached}$ are the maximum transmittance in the oxidized and neutral states, respectively.

[c] Q_d is ejected charge, determined from the in situ experiments.

[d] Coloration efficiency (CE) = $\Delta OD/Q_d$.

[e] Decay of coloration efficiency after cyclic scans.