Supporting Information

Polyurethanes prepared from isocyanate triphenylamine: Synthesis and Optical, Electrochemical, Electrochromic and Memory Properties

Xiaotong Wu[a,1], Yanshuang Wu[b,1], Chunyu Zhang[a], Haijun Niu[a,*], Lei Lei[b,*], Chuanli Qin[a], Cheng Wang[a], Xuduo Bai[a], Wen Wang[c]

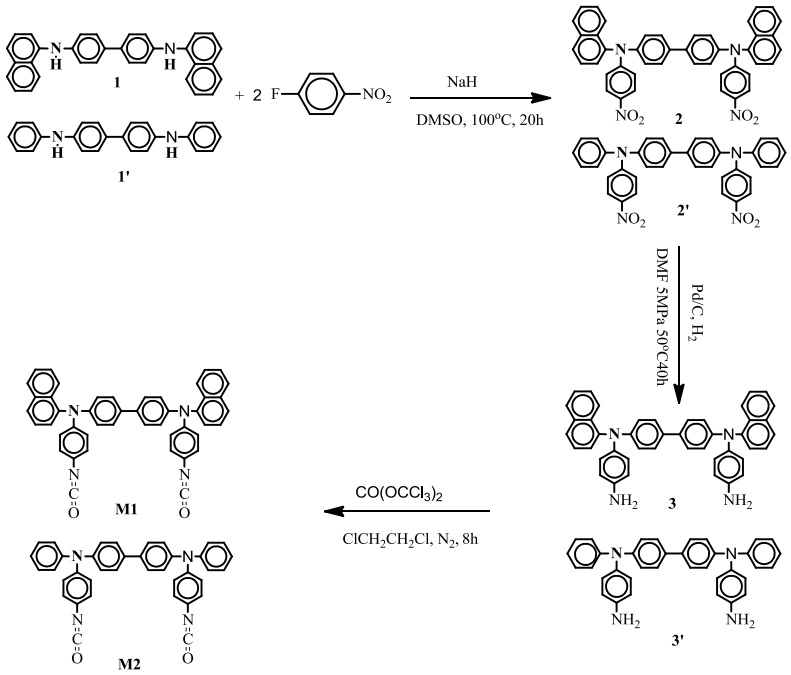
a Key Laboratory of Functional Inorganic Material Chemistry, Ministry of Education; Department of Macromolecular Science and Engineering, School of Chemistry and Chemical Engineering, Heilongjiang University, Harbin 150086, P R China

b Department of Histology and Embryology, Harbin Medical University, Harbin,150081, Heilongjiang Province, China.

c School of Material Science and Engineering, Harbin Institute of Technology, Harbin 150080, P R China

*corresponding author, email: haijunniu@hotmail.com (Haijun Niu); leiys2002@yahoo.com (Lei Lei)

1. These authors contributed equally to this work



Scheme S1 Synthesis routes of M1 and M2.

M1: FT-IR spectrum (KBr pellet, cm-1): 2261 (N=C=O stretching). ^{1}H-NMR (400 MHz, DMSO-d6, ppm): 6.84 (d, 4H, ArH ortho to N), 6.96 (d, 4H, ArH ortho to NCO), 7.12 (m, 3H, ArH of Ph), 7.24 (m, 2H, ArH ortho to N in Ph). ^{13}C-NMR (100 MHz, DMSO-d6, ppm): 120.0, 121.6, 123.2, 123.8, 125.0, 125.4, 126.2, 130.0, 139.8, 136.2, 141.4, 146.8, 148.0, 152.8 (carbon of benzene ring), 127.2 (N=C=O).

M2: FT-IR spectrum (KBr pellet, cm-1): 2268 (N=C=O stretching). ^{1}H-NMR (400 MHz, DMSO-d6, ppm): 6.83 (d, 4H, ArH ortho to N), 6.97 (d, 4H, ArH ortho to NCO), 7.13 (m, 3H, ArH of Ph), 7.25 (m, 2H, ArH ortho to N in Ph). ^{13}C-NMR (100 MHz, DMSO-d6, ppm): 117.7, 120.0, 121.2, 123.1, 124.2, 129.0, 131.0, 136.0, 142.0, 143.6, 147.9 (carbon of benzene ring), 127.6 (N=C=O).

PU (M1)-a: FT-IR spectrum (KBr pellet, cm^{-1}): 3230 (N-H stretching), 1658 (C=O stretching), 1014 (N-CO-O stretching band), 1538 (C-N stretching and N-H bending), 1275(C-N-H combination), 1593, 1505, 756 (aromatic ring of benzene). ^{1}H-NMR (400 MHz, DMSO-d$_6$,

ppm): 7.95 (d, NH-COO), 6.75 (m, aromatic ring of benzene N), 7.67-7.21 (m, aromatic ring of TPA). ^{13}C-NMR (100 MHz, DMSO-d_6, ppm): 92.0 (^{v}C), 115.9, 120.1, 123.2, 123.8, 125.0, 126.0, 127.2, 128.2, 129.0, 131.8, 135.9, 138.2, 142.2, 146.2, 147.8, 151.0, 153.0, 152.7 (carbon of benzene ring), 158.1 (C=O).

PU (M1)-b: FT-IR spectrum (KBr pellet, cm^{-1}): 3285 (N-H stretching), 1660 (C=O stretching), 1014 (N-CO-O stretching band), 1538 (C-N stretching and N-H bending), 1272 (C-N-H combination), 1593, 1505, 755 (aromatic ring of benzene). ^{1}H-NMR (400 MHz, DMSO-d_6, ppm): 7.95 (d, NH-COO), 6.64 (m, aromatic ring of benzene N), 7.61-7.22 (m, aromatic ring of TPA). ^{13}C-NMR (100 MHz, DMSO-d_6, ppm): 31.2 (-CH_3), 40.1(^{v}C), 115.0, 120.2, 121.9, 123.6, 123.9, 126.1, 128.0, 130.1, 133.9, 141.5, 141.8, 142.2, 146.2, 147.9, 148.4, -155.8 (carbon of benzene ring), 152.1 (C=O).

PU (M1)-c: FT-IR spectrum (KBr pellet, cm^{-1}): 3261 (N-H stretching), 1659 (C=O stretching), 1014 (N-CO-O stretching band), 1536 (C-N stretching and N-H bending), 1262 (C-N-H combination), 1594, 1502, 775 (aromatic ring of benzene). ^{1}H-NMR (400 MHz, DMSO-d_6, ppm): 7.95 (d, NH-COO), 6.79 (m, aromatic ring of benzene N), 7.51-7.21 (m, aromatic ring of TPA). ^{13}C-NMR (100 MHz, DMSO-d_6, ppm): 116.0, 120.2, 123.5, 126.1, 127.2, 128.1, 129.0, 131.9, 133.9, 156.4 (carbon of benzene ring), 147.8 (C=O)

PU (M1)-d: FT-IR spectrum (KBr pellet, cm^{-1}): 3247 (N-H stretching), 1658 (C=O stretching), 1014 (N-CO-O stretching band), 1542 (C-N stretching and N-H bending), 1278 (C-N-H combination), 1604, 1505, 772 (aromatic ring of benzene). ^{1}H-NMR (400 MHz, DMSO-d_6, ppm): 7.95 (d, NH-COO), 6.88 (m, aromatic ring of benzene N), 7.62-7.58 (m, aromatic ring of TPA). ^{13}C-NMR (100 MHz, DMSO-d_6, ppm): 115.9, 120.0, 122.0, 123.0, 126.2, 127.2,

128.2, 129.2, 131.4, 132.5, 135.6, 141.6, 147.9 (carbon of benzene ring), 153.9 (C=O), 161.9 (^{v}C).

PU (M1)-e: FT-IR spectrum (KBr pellet, cm^{-1}): 3254 (N-H stretching), 1660 (C=O stretching), 1014 (N-CO-O stretching band), 1538 (C-N stretching and N-H bending), 1270 (C-N-H combination), 1593, 1508, 747 (aromatic ring of benzene). ^{1}H-NMR (400 MHz, DMSO-d_6, ppm): 7.95 (d, NH-COO), 6.87 (m, aromatic ring of benzene N), 7.43-7.26 (m, aromatic ring of TPA). ^{13}C-NMR (100 MHz, DMSO-d_6, ppm): 115.8, 120.2, 122.1, 123.6, 123.8, 126.1, 127.8, 129.0, 130.0, 133.9, 135.9, 136.2, 140.0, 143.8, 146.8, 147.8, 149.9 (carbon of benzene ring), 152.1 (C=O), 156.2 (^{v}C).

PU (M2)-a: FT-IR spectrum (KBr pellet, cm^{-1}): 3253 (N-H stretching), 1660 (C=O stretching), 1015 (N-CO-O stretching band), 1538 (C-N stretching and N-H bending), 1273(C-N-H combination), 1593, 1505, 755 (aromatic ring of benzene). ^{1}H-NMR (400 MHz, DMSO-d_6, ppm): 7.95 (d, NH-COO), 6.74 (m, aromatic ring of benzene N), 7.53-7.23 (m, aromatic ring of TPA). ^{13}C-NMR (100 MHz, DMSO-d_6, ppm): 90.2 (C-O), 115.1, 120.0, 123.0, 124.0, 127.0, 128.0, 131.0, 132.0, 135.2, 144.1, 147.2, 151.2, 158.0, 162.1 (carbon of benzene ring), 169.9 (C=O).

PU (M2)-b: FT-IR spectrum (KBr pellet, cm^{-1}): 3261 (N-H stretching), 1662 (C=O stretching), 1002 (N-CO-O stretching band), 1544 (C-N stretching and N-H bending), 1270 (C-N-H combination), 1593, 1507, 751 (aromatic ring of benzene). ^{1}H-NMR (400 MHz, DMSO-d_6, ppm): 7.95 (d, NH-COO), 6.68 (m, aromatic ring of benzene N), 7.56-7.21 (m, aromatic ring of TPA). ^{13}C-NMR (100 MHz, DMSO-d_6, ppm): 31.2 (-CH_3), 39.4(^{p}C), 115.5, 120.0, 120.2, 121.8, 124.0, 127.0, 129.0, 131.0, 134.8, 140.4, 141.8, 143.6, 148.2, 156.0 (carbon of

benzene ring), 152.1 (C=O).

PU (M2)-c: FT-IR spectrum (KBr pellet, cm^{-1}): 3255 (N-H stretching), 1660 (C=O stretching), 1027 (N-CO-O stretching band), 1536 (C-N stretching and N-H bending), 1265 (C-N-H combination), 1592, 1493, 752 (aromatic ring of benzene). ^{1}H-NMR (400 MHz, DMSO-d_6, ppm): 7.95 (d, NH-COO), 6.79 (m, aromatic ring of benzene N), 7.38-7.34 (m, aromatic ring of TPA). ^{13}C-NMR (100 MHz, DMSO-d_6, ppm): 115.1, 120.1, 120.6, 124.2, 127.5, 128.0, 129.2, 131.2, 132.0, 135.4, 143.0, 147.5, 156.4 (carbon of benzene ring), 152.1 (C=O).

PU (M2)-d: FT-IR spectrum (KBr pellet, cm^{-1}): 3258 (N-H stretching), 1659 (C=O stretching), 1099 (N-CO-O stretching band), 1536 (C-N stretching and N-H bending), 1276 (C-N-H combination), 1604, 1505, 751 (aromatic ring of benzene). ^{1}H-NMR (400 MHz, DMSO-d_6, ppm): 7.95 (d, NH-COO), 6.88 (m, aromatic ring of benzene N), 7.62-7.28 (m, aromatic ring of TPA). ^{13}C-NMR (100 MHz, DMSO-d_6, ppm): 45.5 (^{p}C), 115.5, 120.0, 120.5, 122.2, 124.0, 127.0, 128.4, 162.1 (carbon of benzene ring), 152.2 (C=O).

PU (M2)-e: FT-IR spectrum (KBr pellet, cm^{-1}): 3259 (N-H stretching), 1660 (C=O stretching), 1005 (N-CO-O stretching band), 1543 (C-N stretching and N-H bending), 1270 (C-N-H combination), 1592, 1509, 748 (aromatic ring of benzene). ^{1}H-NMR (400 MHz, DMSO-d_6, ppm): 7.95 (d, NH-COO), 6.88 (m, aromatic ring of benzene N), 7.52-7.26 (m, aromatic ring of TPA). ^{13}C-NMR (100 MHz, DMSO-d_6, ppm): 115.1, 121.0, 127.0, 128.0, 129.2, 136.8, 140.0, 152.4, -163.0 (carbon of benzene ring), 156.0 (C=O).

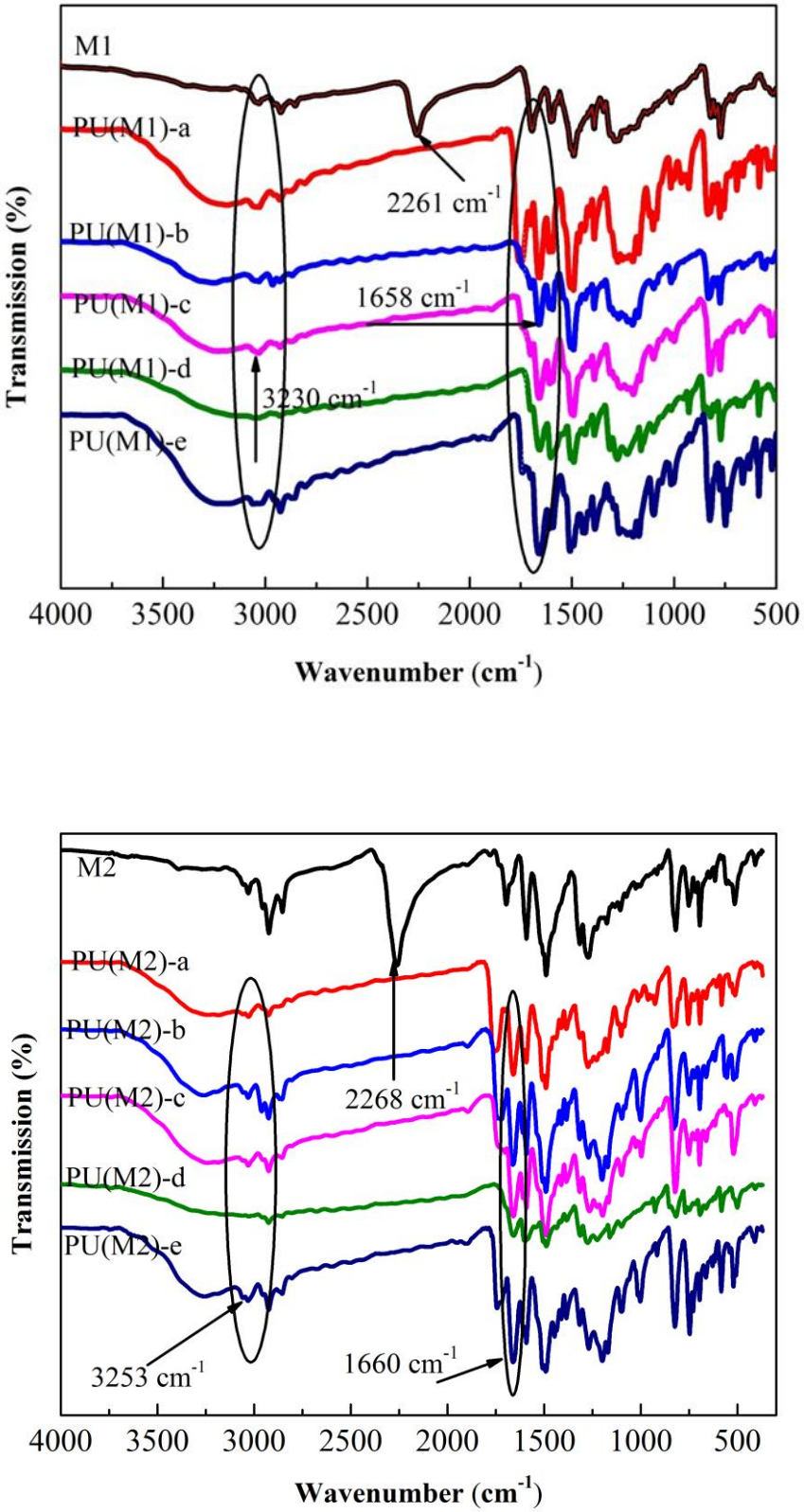
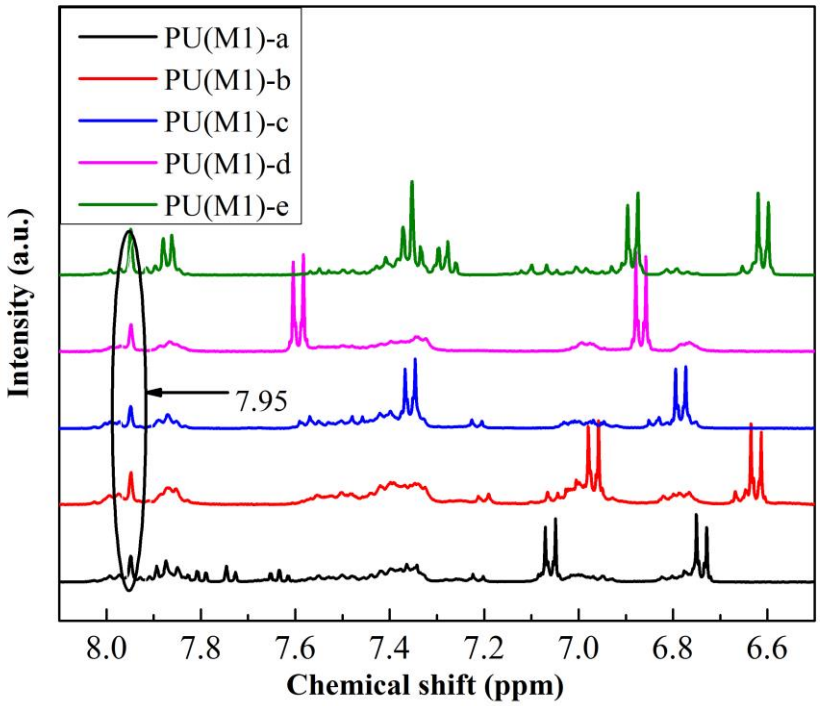
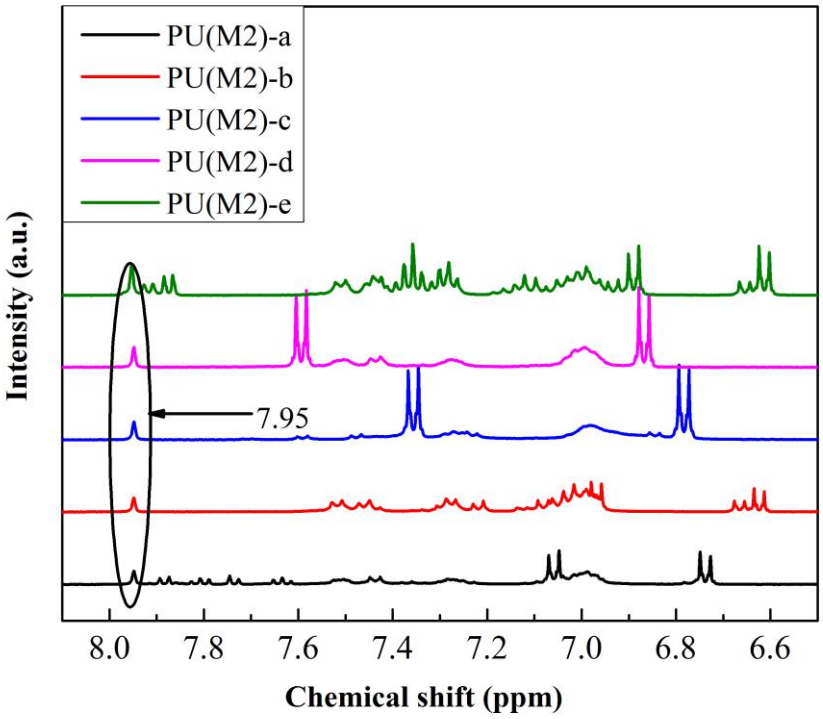
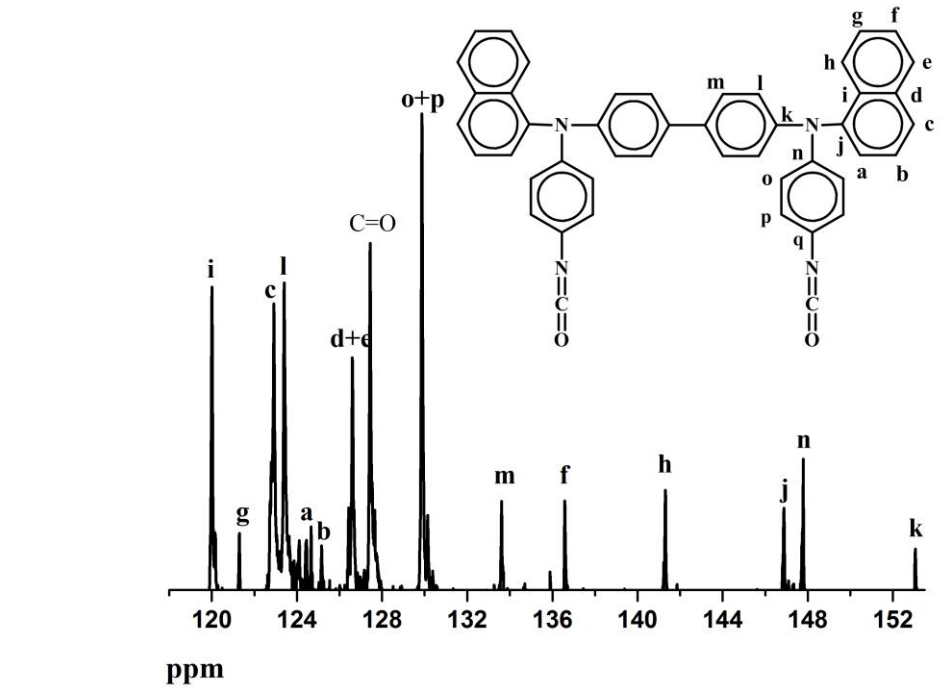
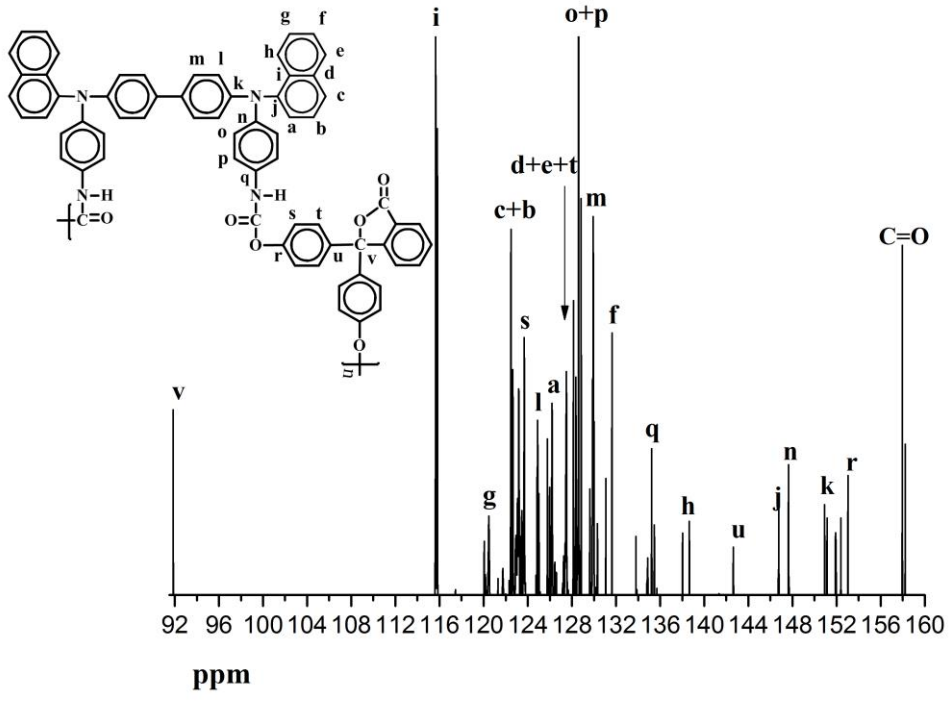


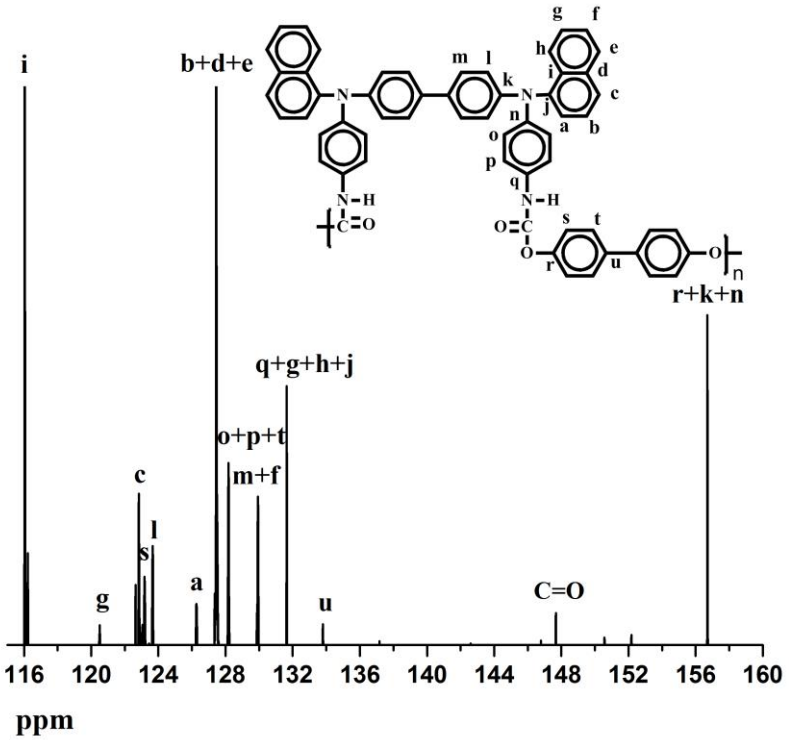
Fig. S1 FT-IR spectra of M1, M2, PUs (M1) and PUs (M2).

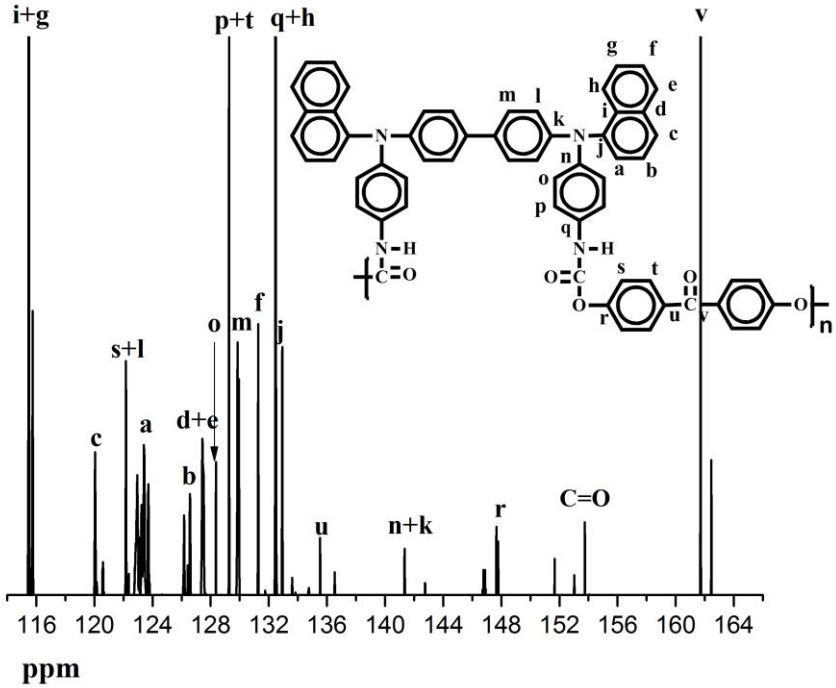

PU(M1)-a
PU(M1)-b
PU(M1)-c
PU(M1)-d
PU(M1)-e
7.95
Intensity (a.u.)
8.0
7.8
7.6
7.4
7.2
7.0
6.8
6.6
Chemical shift (ppm)

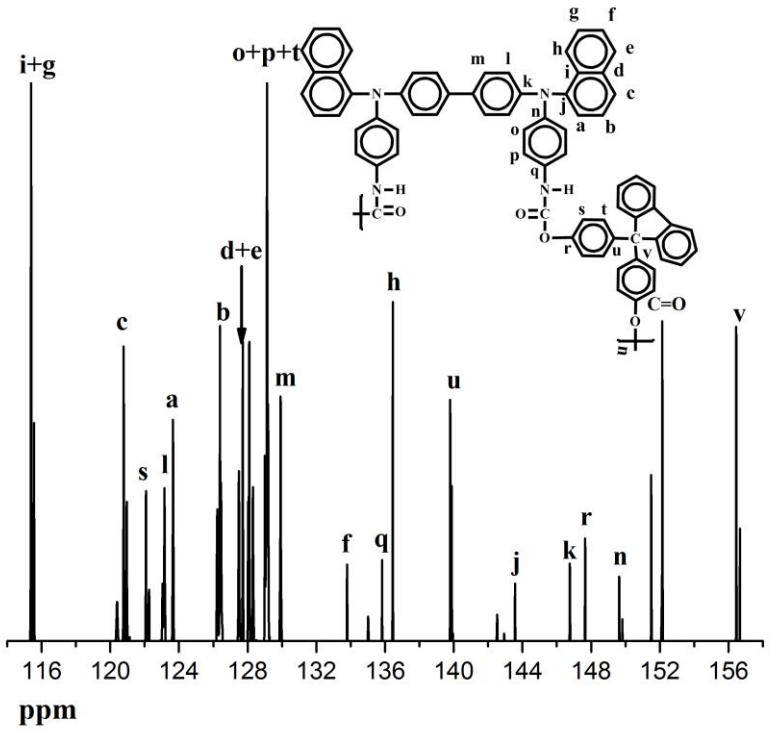

PU(M2)-a
PU(M2)-b
PU(M2)-c
PU(M2)-d
PU(M2)-e
7.95
Intensity (a.u.)
8.0
7.8
7.6
7.4
7.2
7.0
6.8
6.6
Chemical shift (ppm)

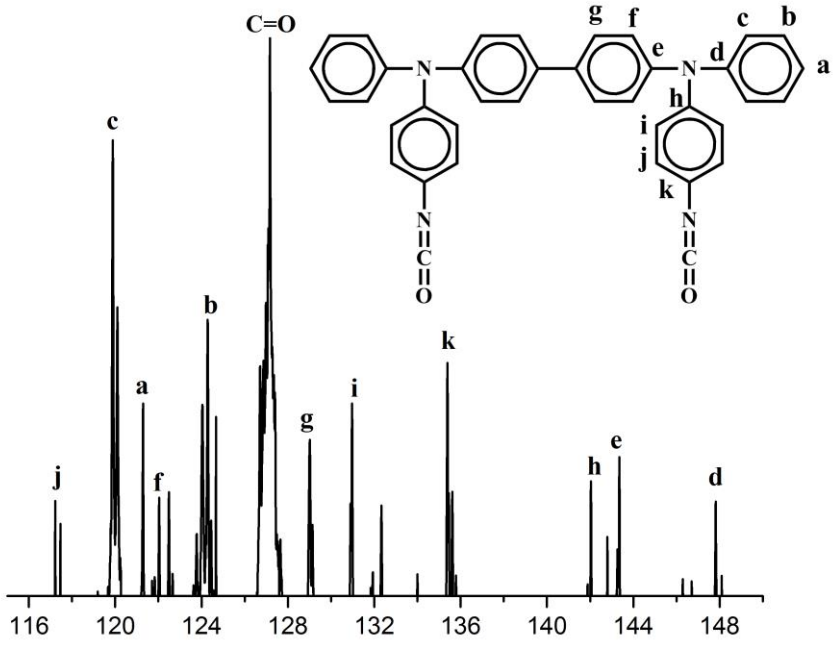

o+p
C=O
i
c
l
d+e
g
a
b
m
f
h
j
n
k
120
124
128
132
136
140
144
148
152
ppm

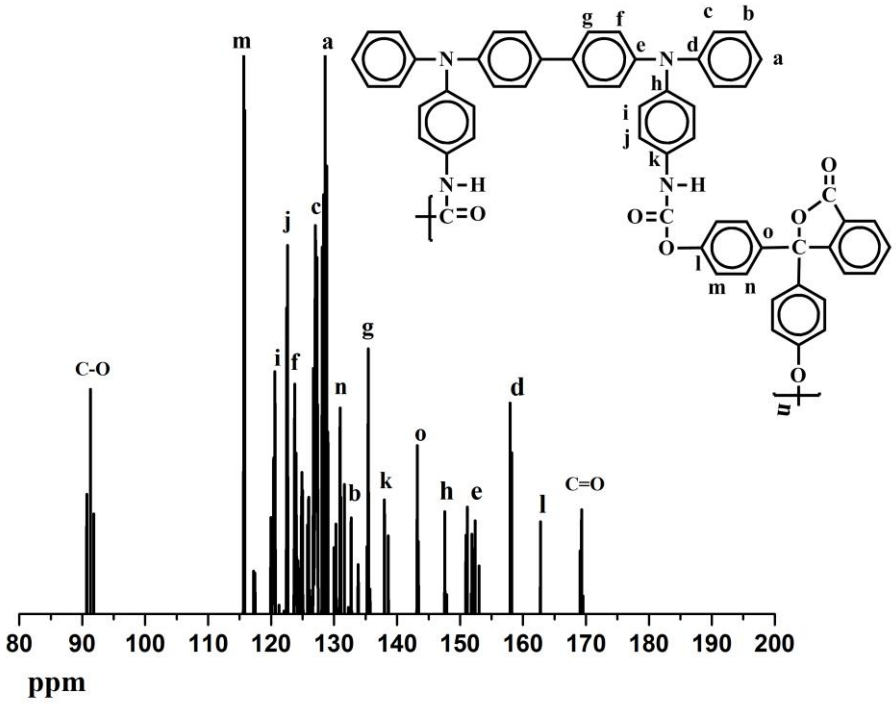

i
o+p
d+e+t
c+b
m
C=O
s
f
a
l
q
n
r
k
g
h
j
u
v
92
96
100
104
108
112
116
120
124
128
132
136
140
144
148
152
156
160
ppm


i
b+d+e
r+k+n
q+g+h+j
o+p+t
m+f
c
l
s
a
g
u
C=O
116 120 124 128 132 136 140 144 148 152 156 160
ppm

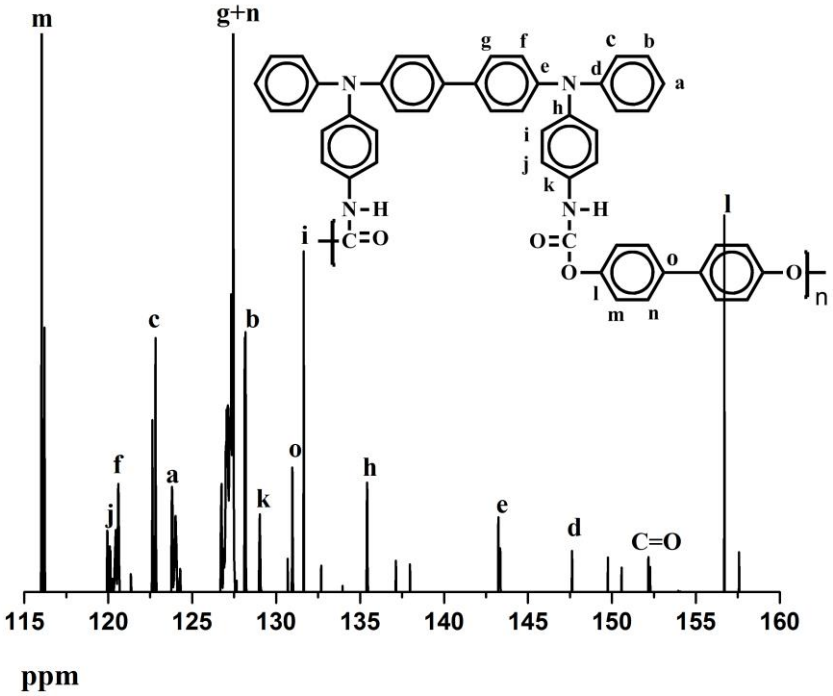

i+g
p+t
q+h
v
s+l
o
m
f
j
c
a
d+e
b
u
n+k
r
C=O
116 120 124 128 132 136 140 144 148 152 156 160 164
ppm


i+g
o+p+t
d+e
c
b
a
s
l
m
h
u
f
q
j
k
r
n
C=O
v
116
120
124
128
132
136
140
144
148
152
156
ppm


C=O
c
b
a
j
f
g
i
k
h
e
d
116
120
124
128
132
136
140
144
148


m
a
g
f
c
b
d
e
h
i
j
k
l
o
n
C-O
C=O
80
90
100
110
120
130
140
150
160
170
180
190
200
ppm

ii


m
g+n
f
c
b
a
i
j
k
l
o
h
e
d
C=O
115
120
125
130
135
140
145
150
155
160
ppm

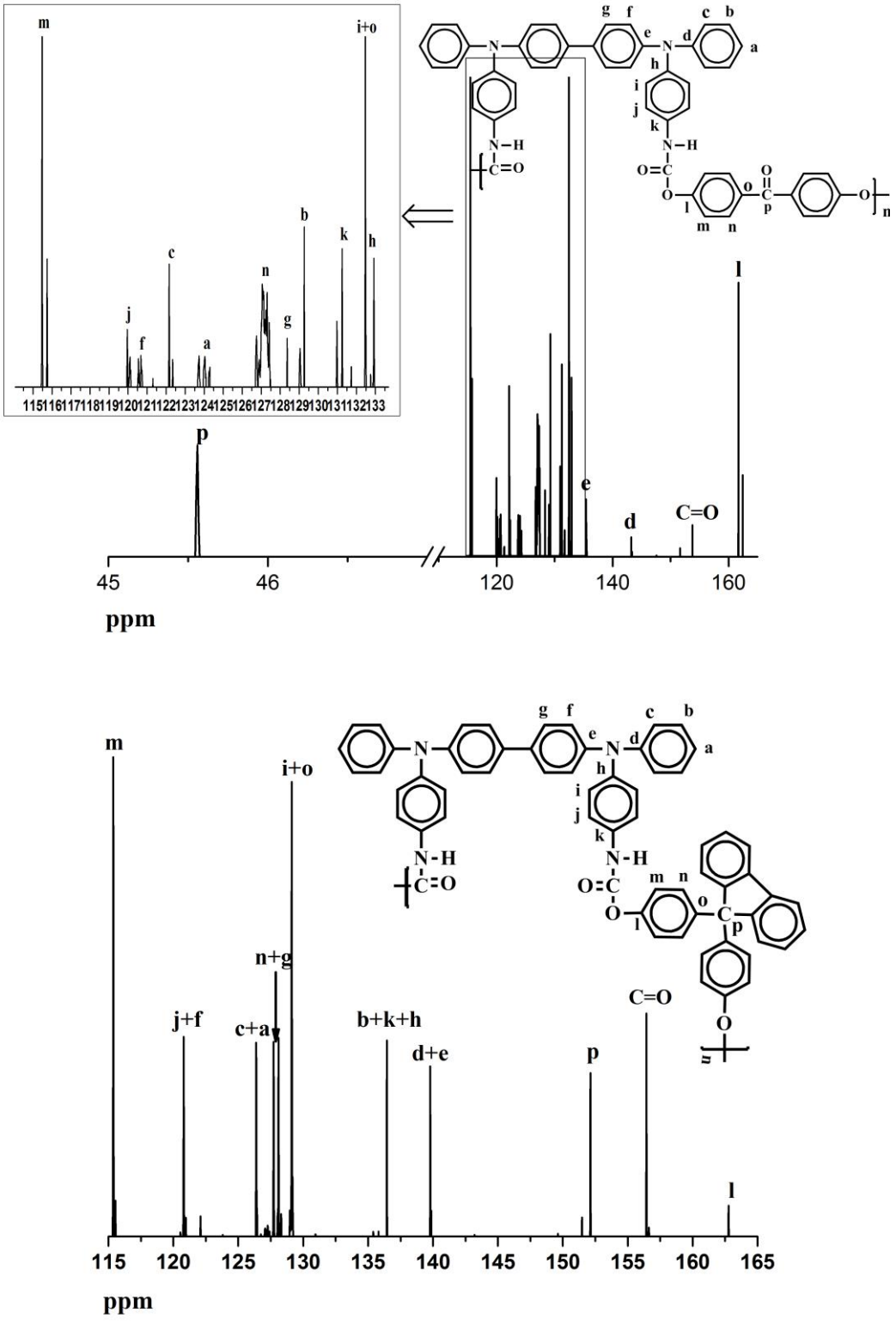


Fig. S2 ^{1}H and ^{13}C NMR spectras of PUs (M1) and PUs (M2) in DMSO-d_6.

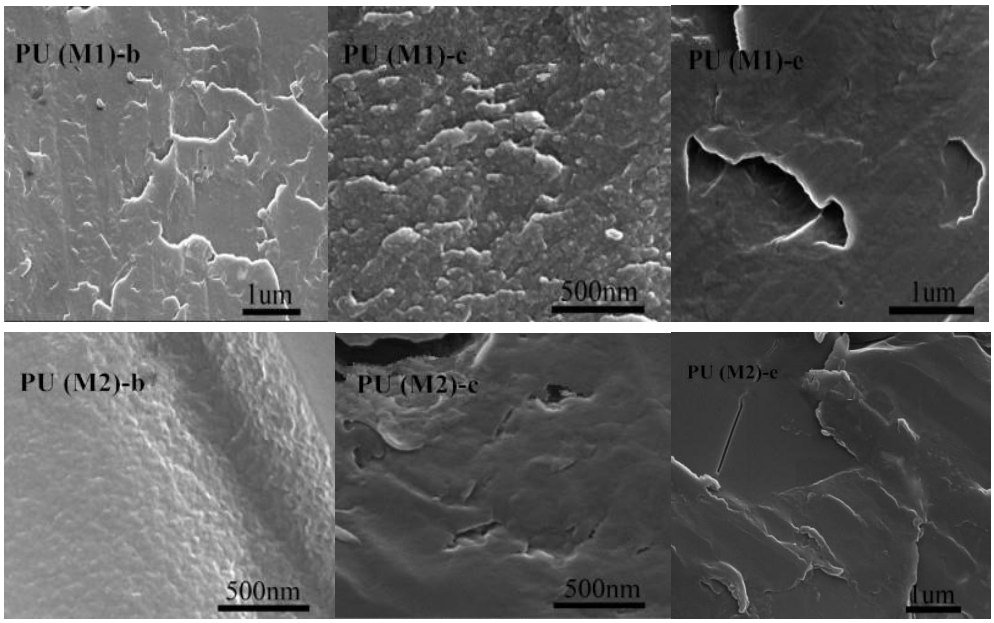
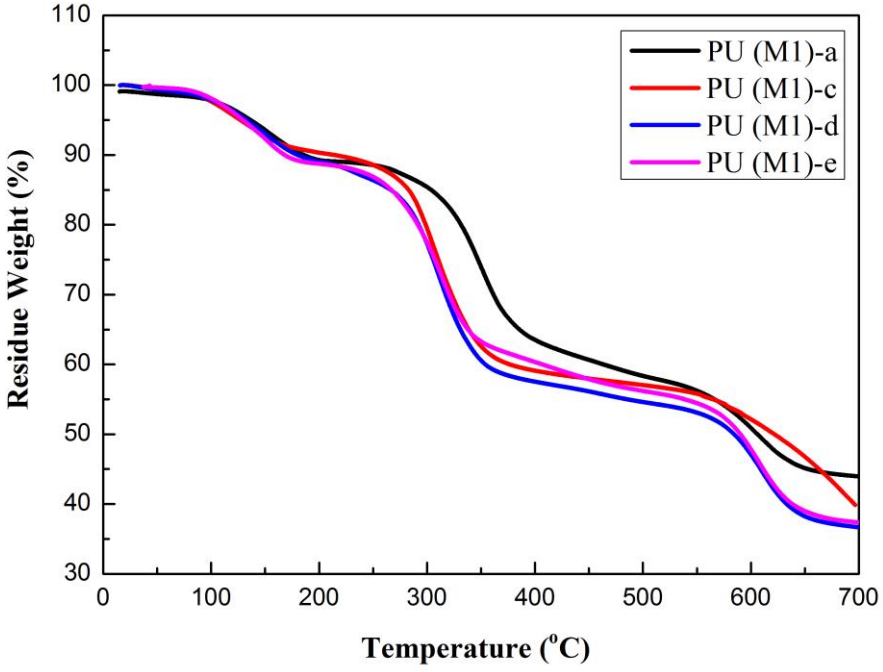


Fig. S3 SEM images of other PUs (M1) and PUs (M2).



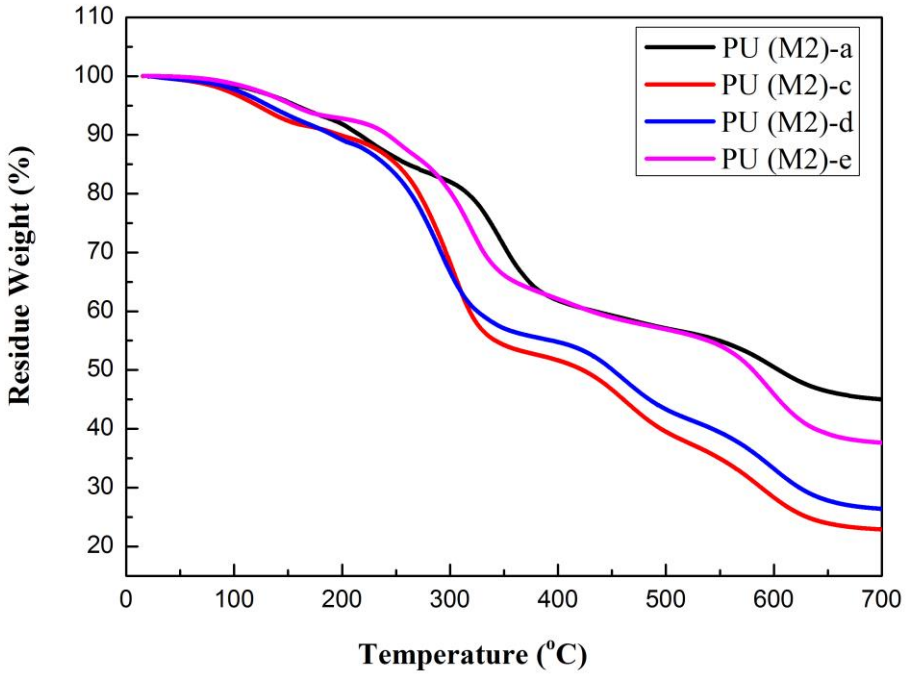


Fig. S4 TGA traces of the PUs (M1) and PUs (M2).

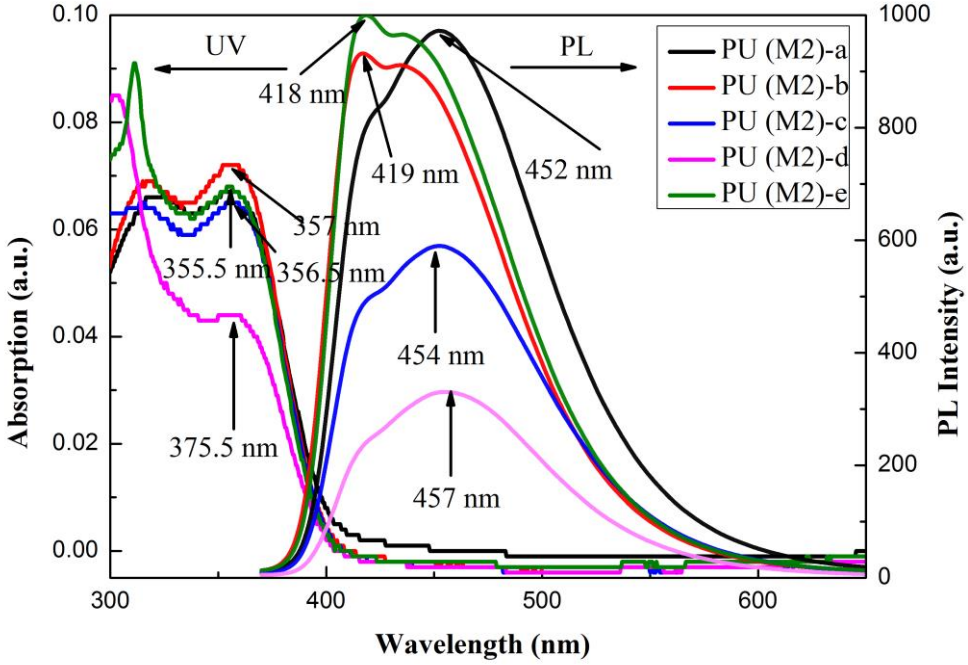
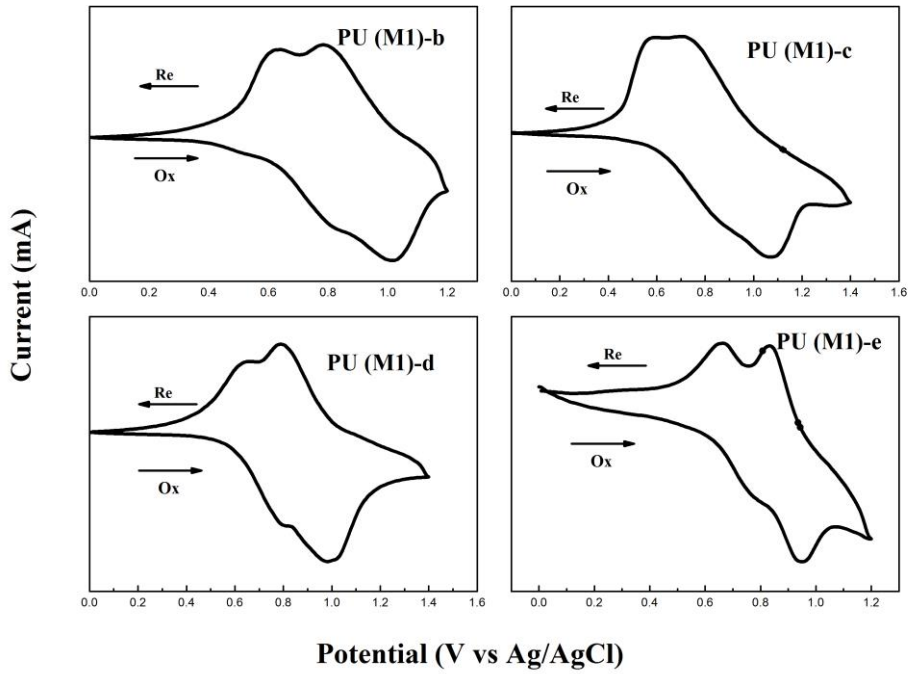


Fig. S5 UV-vis absorption and PL spectra of PUs (M2) with a concentration of DMSO (conc.: 10^{-8} M).

Table S1 Molecular weights of the PUs.

	M_n	M_w	M_z	M_w/M_n	n
PU(M1)-a	10400	15500	21400	1.49	10
PU(M1)-b	11900	13200	14800	1.11	13
PU(M1)-c	12500	13600	14900	1.09	14
PU(M1)-d	11700	13100	15000	1.12	13
PU(M1)-e	11400	12100	13000	1.06	11
PU(M2)-a	13100	15200	18700	1.16	14
PU(M2)-b	10600	13200	16600	1.27	13
PU(M2)-c	10900	17100	26400	1.57	14
PU(M2)-d	10400	11000	12200	1.09	13
PU(M2)-e	10200	10400	10500	1.04	11



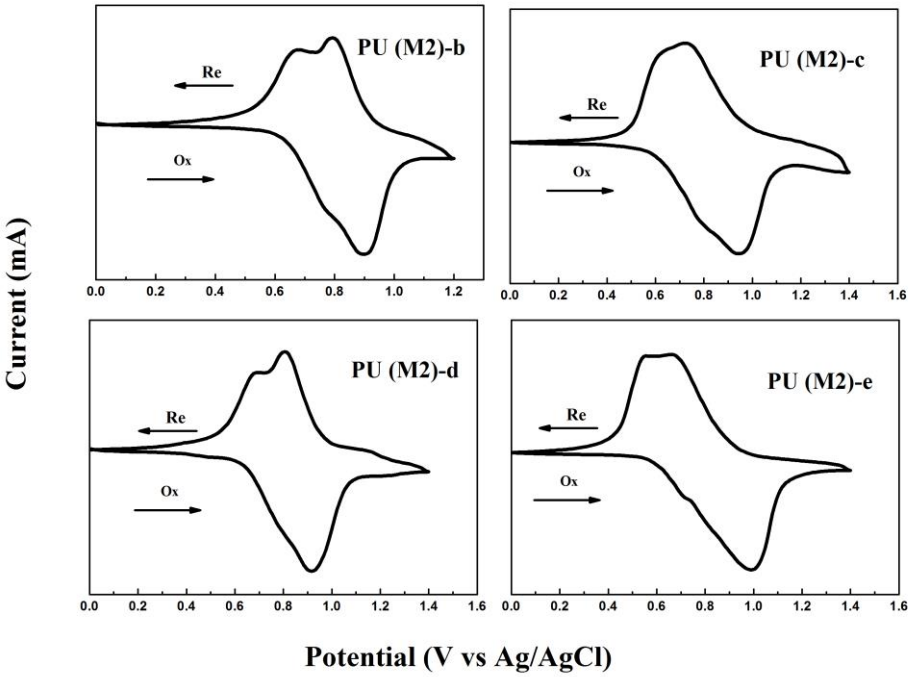


Fig. S6 CVs for PUs (M1) and PUs (M2) in 0.1 M $LiClO_4/CH_3CN$ at the scanning rate of 50 mV/s.

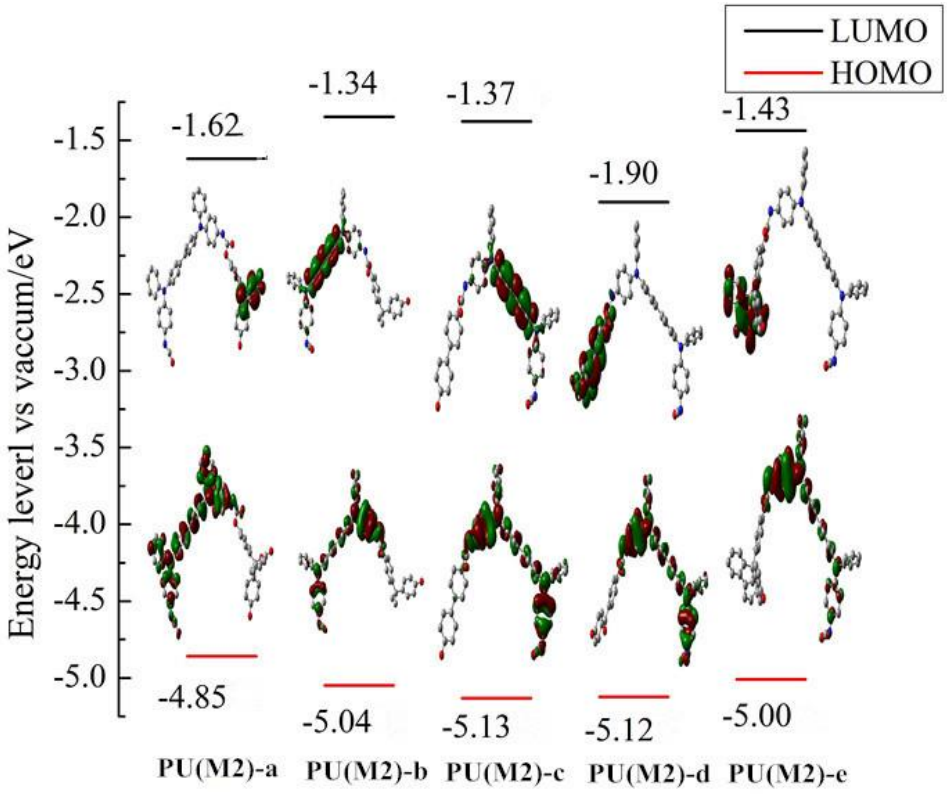
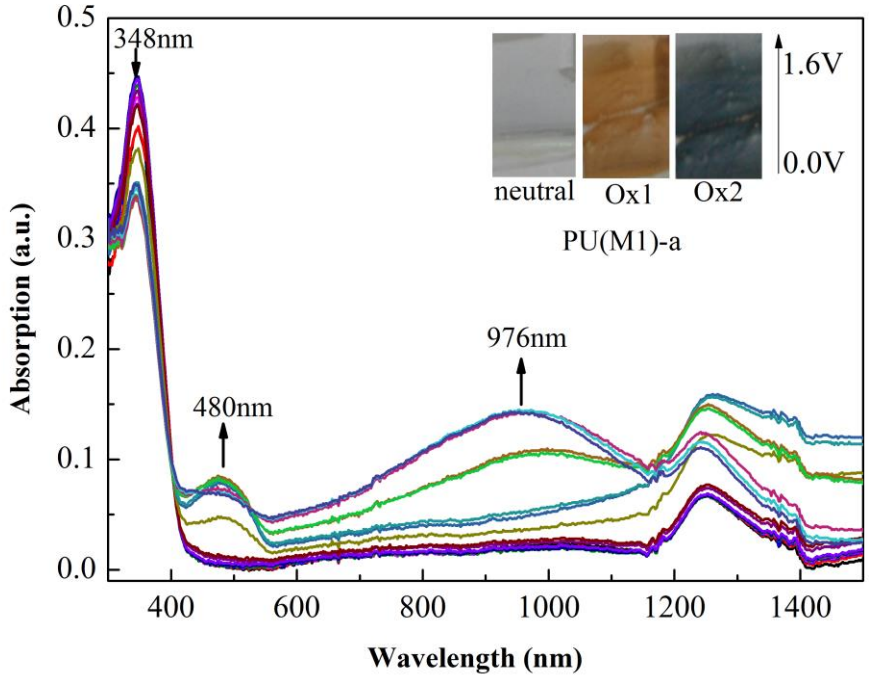
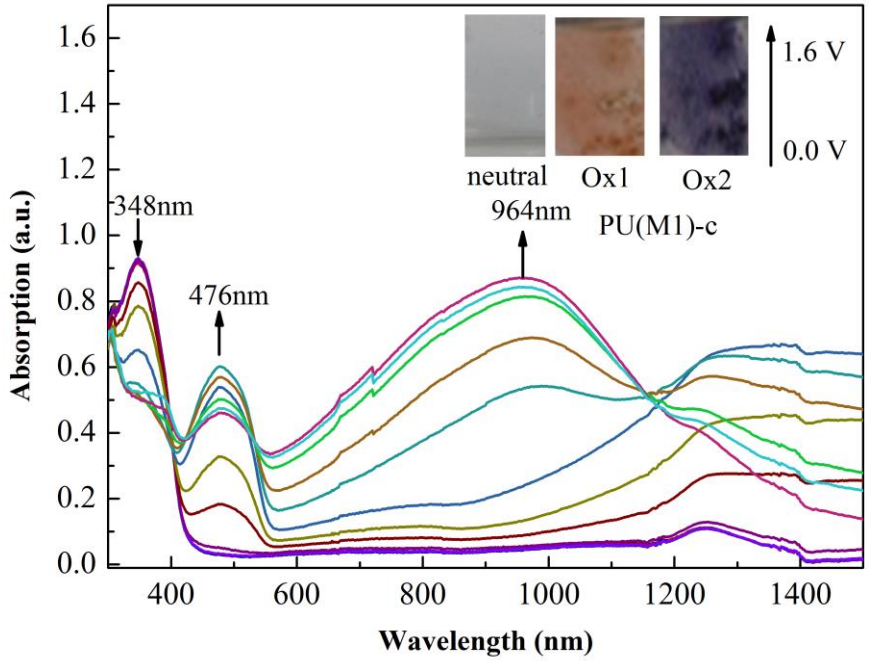
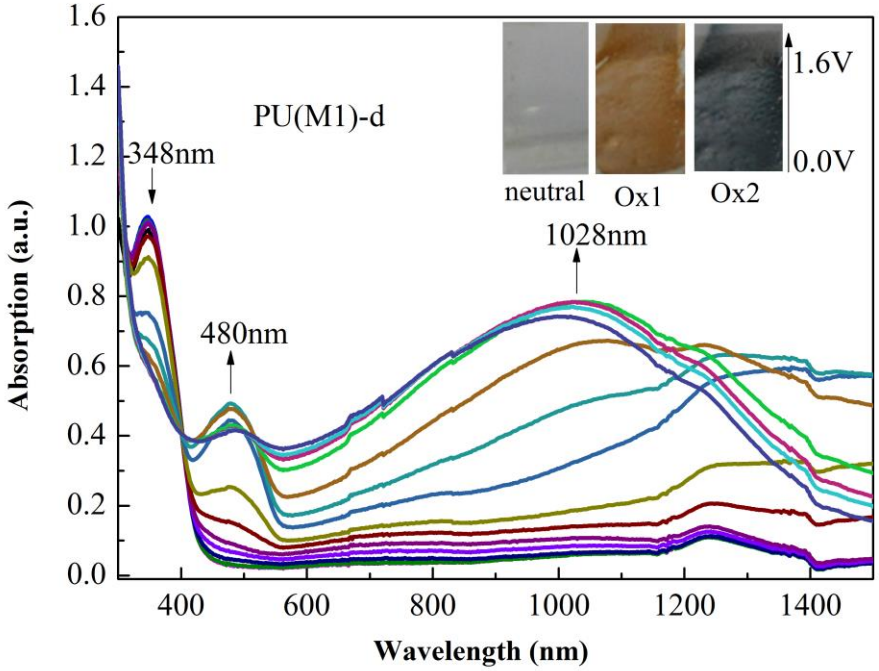
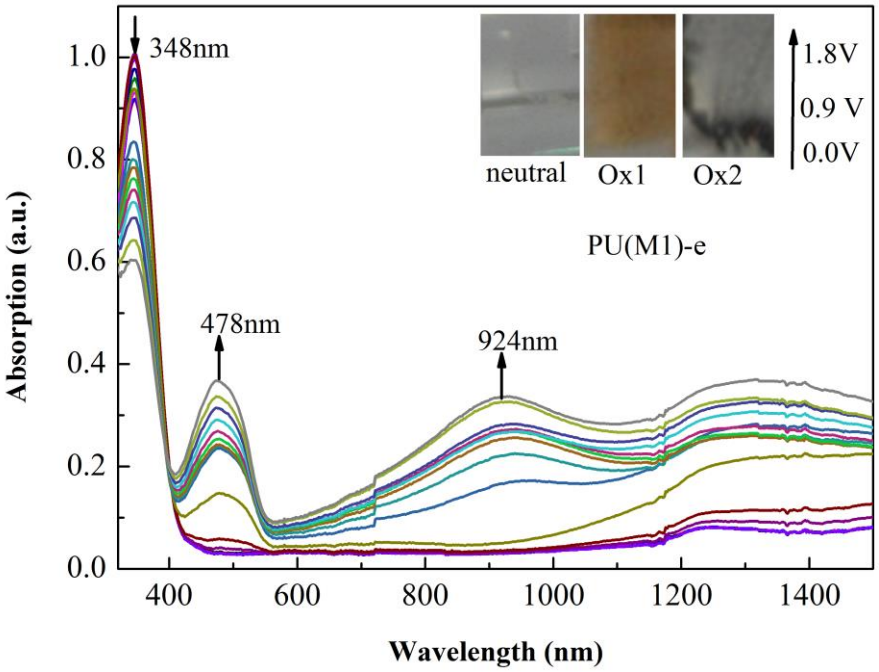


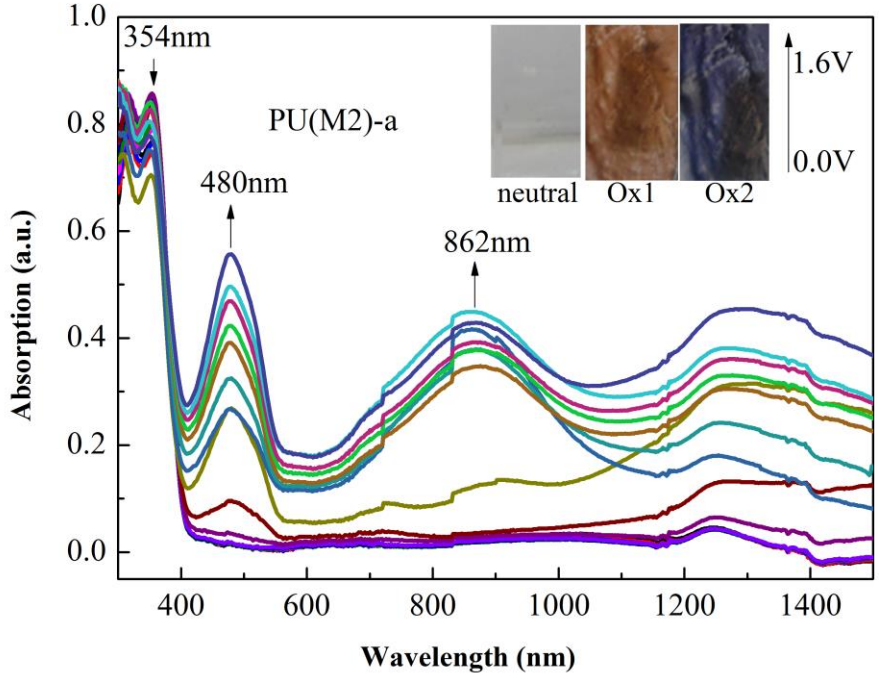
Fig. S7 Pictorial representations of the electron density in the frontier molecular orbitals of repetition units for PUs (M2).

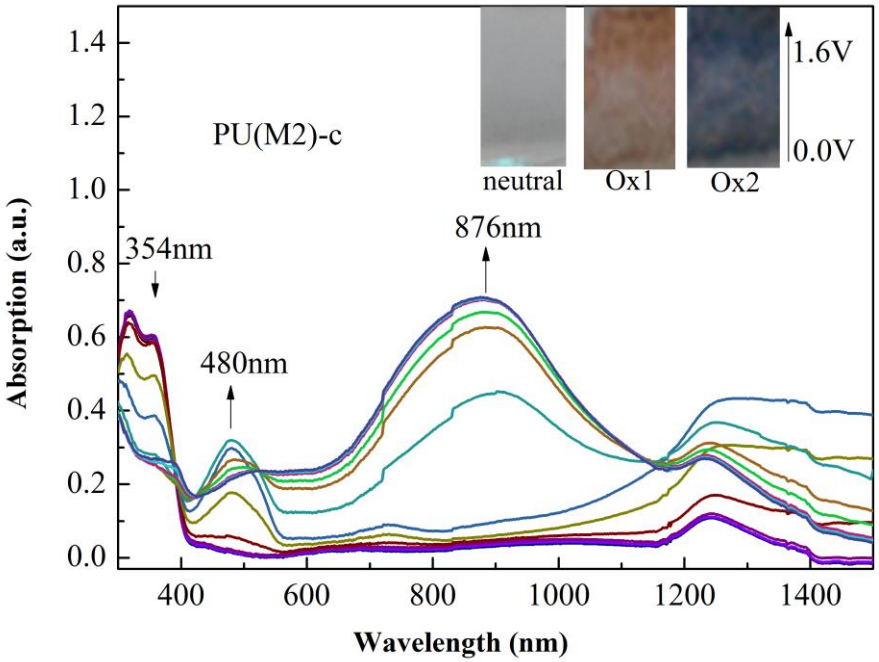


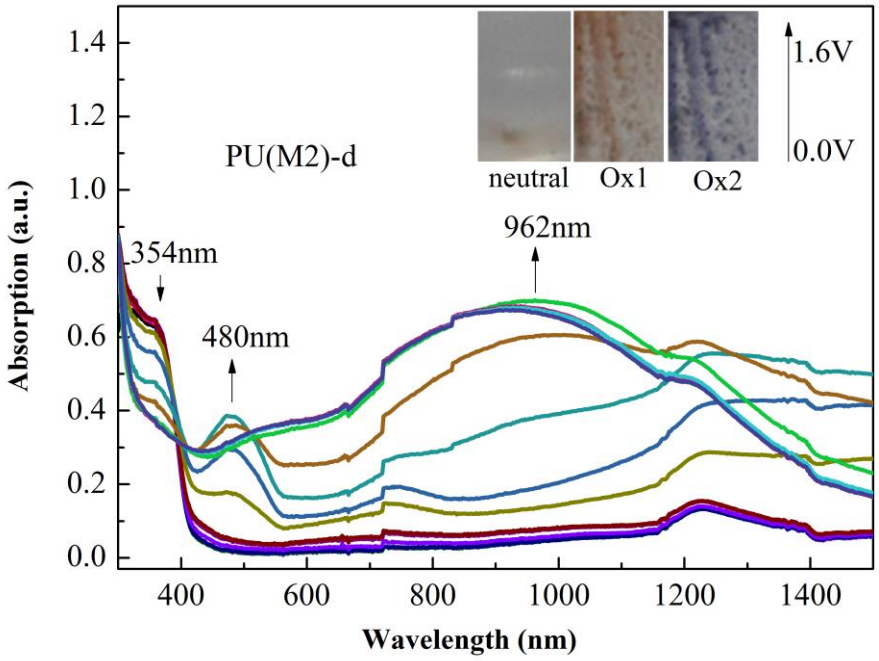

Absorption (a.u.)
Wavelength (nm)
348nm
476nm
964nm
PU(M1)-c
neutral
Ox1
Ox2
1.6 V
0.0 V


Absorption (a.u.)
Wavelength (nm)
PU(M1)-d
348nm
480nm
1028nm
neutral
Ox1
Ox2
1.6V
0.0V


348nm
478nm
924nm
1.8V
0.9 V
0.0V
neutral
Ox1
Ox2
PU(M1)-e
Absorption (a.u.)
Wavelength (nm)
1.0
0.8
0.6
0.4
0.2
0.0
400
600
800
1000
1200
1400


354nm
480nm
862nm
1.6V
0.0V
neutral
Ox1
Ox2
PU(M2)-a
Absorption (a.u.)
Wavelength (nm)
1.0
0.8
0.6
0.4
0.2
0.0
400
600
800
1000
1200
1400


PU(M2)-c
neutral
Ox1
Ox2
1.6V
0.0V
354nm
480nm
876nm
Absorption (a.u.)
Wavelength (nm)
0.0
0.2
0.4
0.6
0.8
1.0
1.2
1.4
400
600
800
1000
1200
1400


PU(M2)-d
neutral
Ox1
Ox2
1.6V
0.0V
354nm
480nm
962nm
Absorption (a.u.)
Wavelength (nm)
0.0
0.2
0.4
0.6
0.8
1.0
1.2
1.4
400
600
800
1000
1200
1400

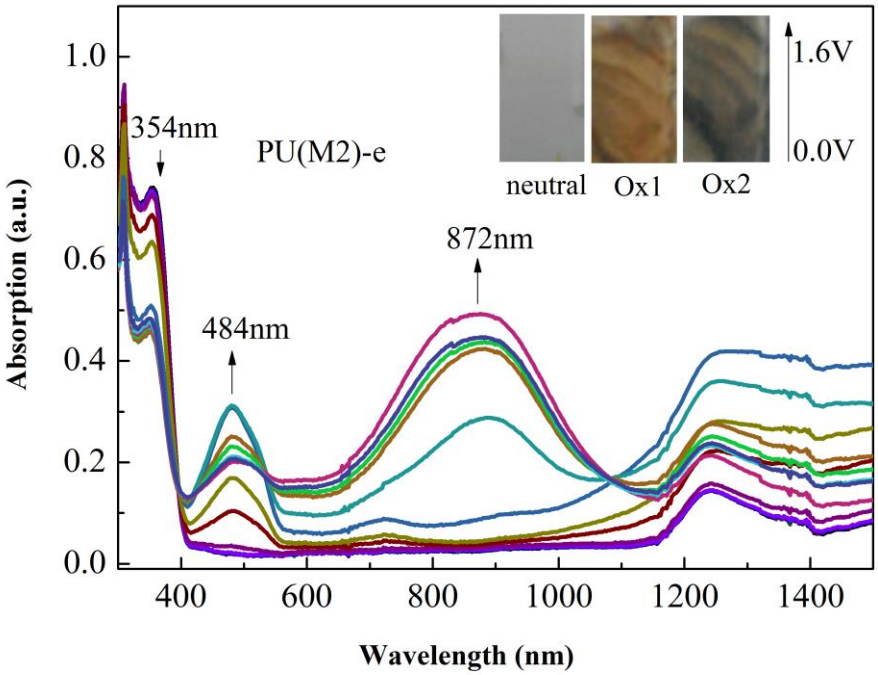


Fig. S8 Electrochromic behaviors of PUs (M1) and PUs (M2) thin film in CH_3CN with 0.1 M $LiCO_4$ as the supporting electrolyte (insets are the pictures of oxidized PUs).

Table S2 Optical and Electrochemical Data Collected for Coloration Efficiency Measurements of polymers.

Polymer code[a]	λ (nm)[b]	δ_{OD}[c]	Q(mC/cm^2)[d]	η(cm^2/C)[e]
PU(M1)-a	480	0.309	1.185	261.1
PU(M1)-b	476	0.135	1.044	129.6
PU(M1)-c	476	0.134	1.300	103.6
PU(M1)-d	480	0.175	1.053	166.5
PU(M1)-e	478	0.267	1.454	182.4
PU(M2)-a	480	0.571	3.418	167.3
PU(M2)-b	480	0.550	2.174	253.1

PU(M2)-c	480	0.372	1.579	235.8
PU(M2)-d	480	0.549	1.927	285.0
PU(M2)-e	484	0.429	1.445	297.4

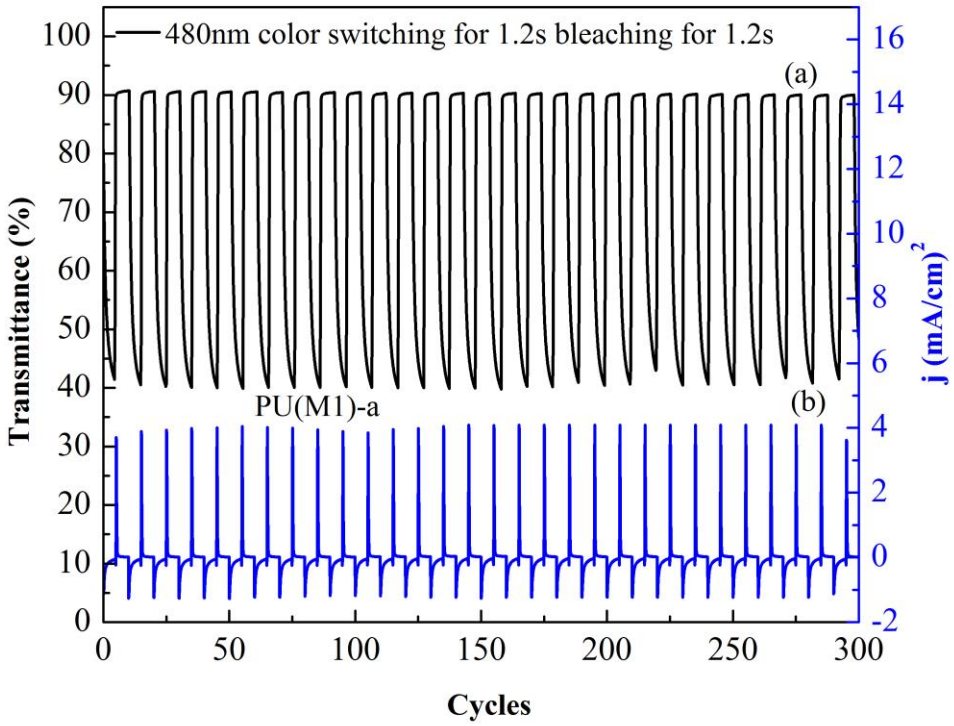
a the voltage 0 to 0.8 V (V vs. Ag/AgCl)

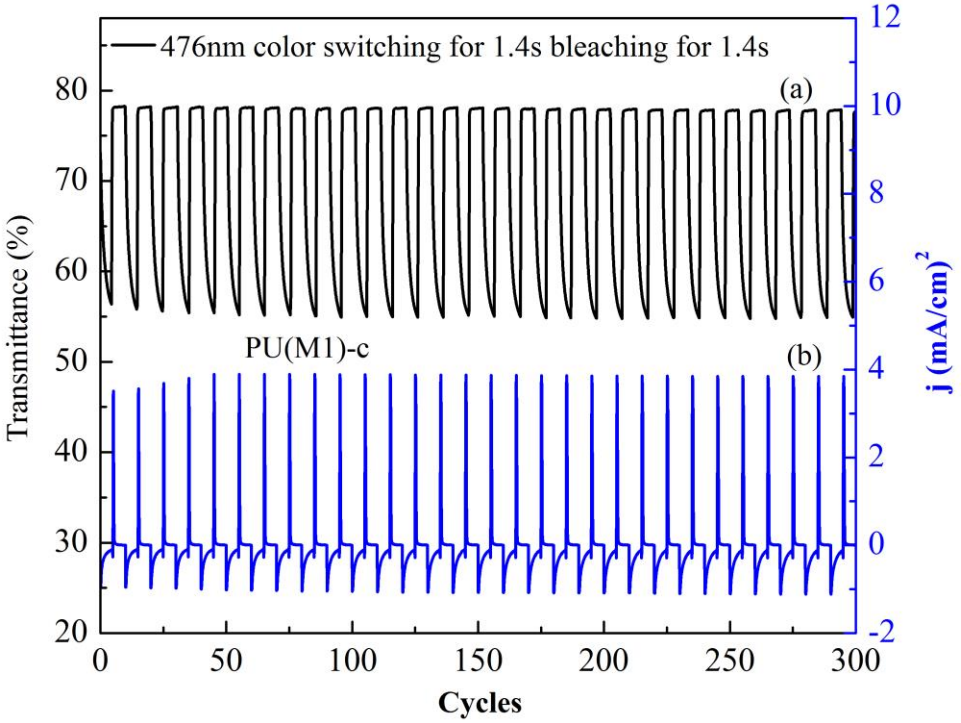
b the given wavelength

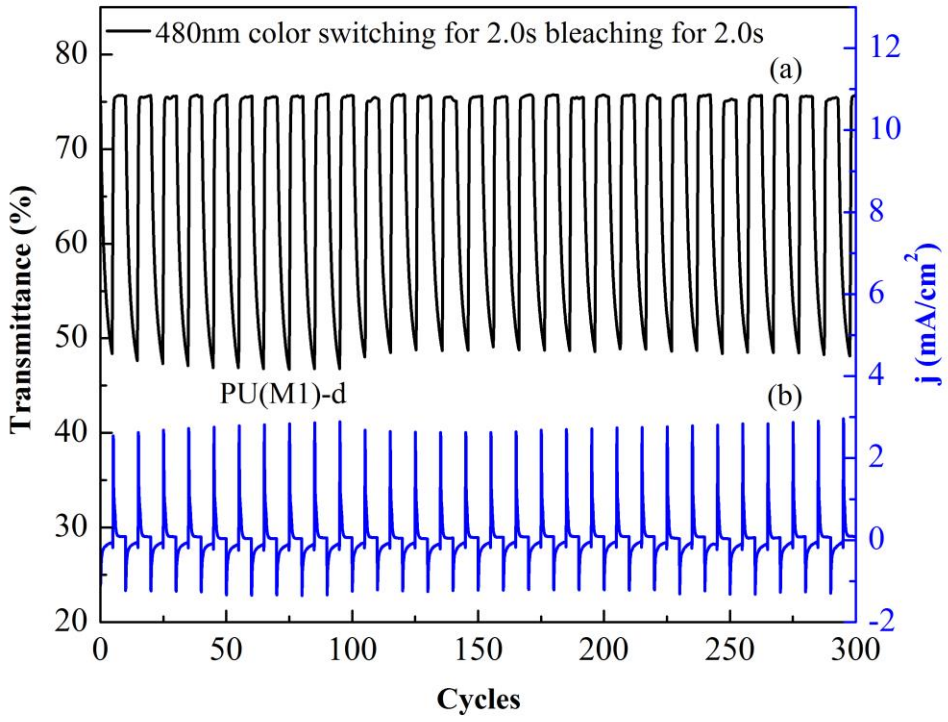
c the change of the optical density

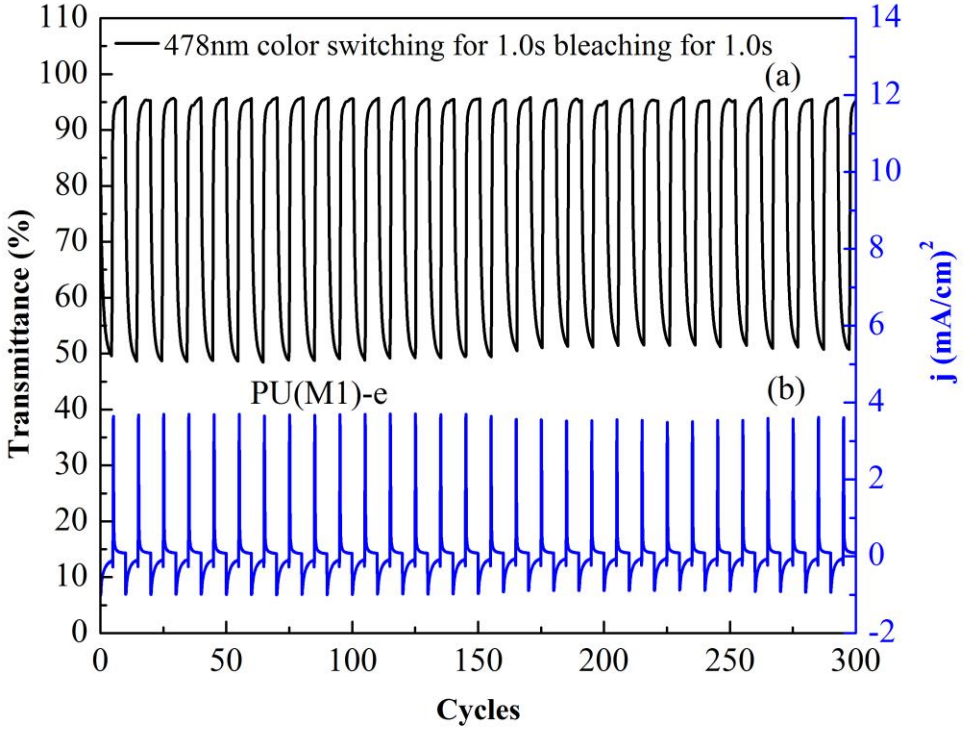
d the amount of injected/ejected charge per unit sample area

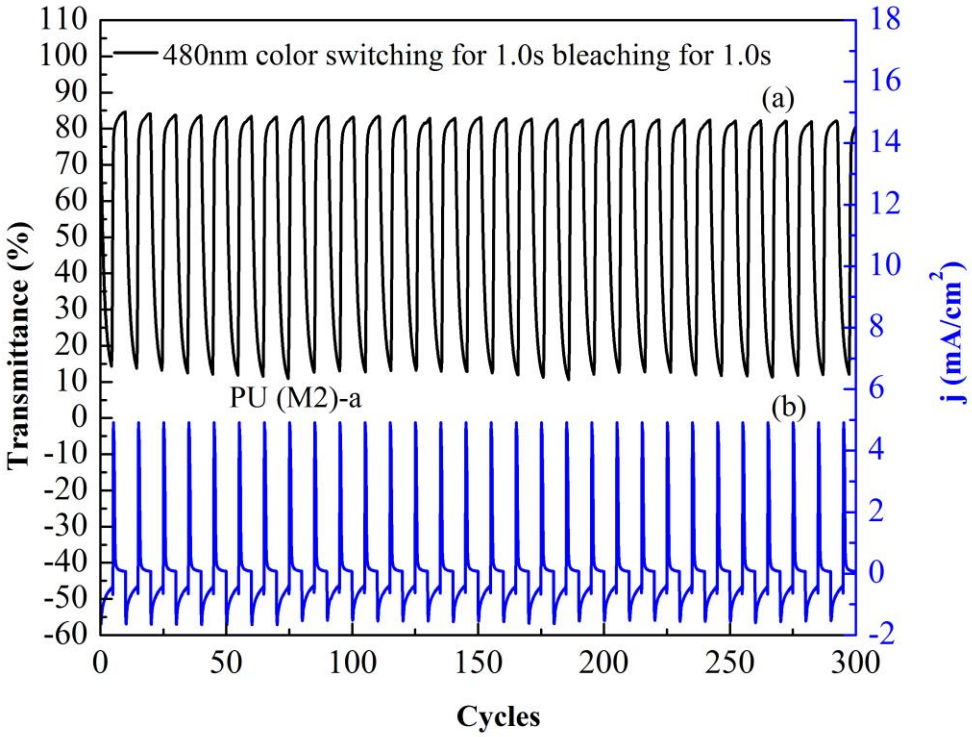
e coloration efficiency $\eta=\delta_{OD}/Q$.

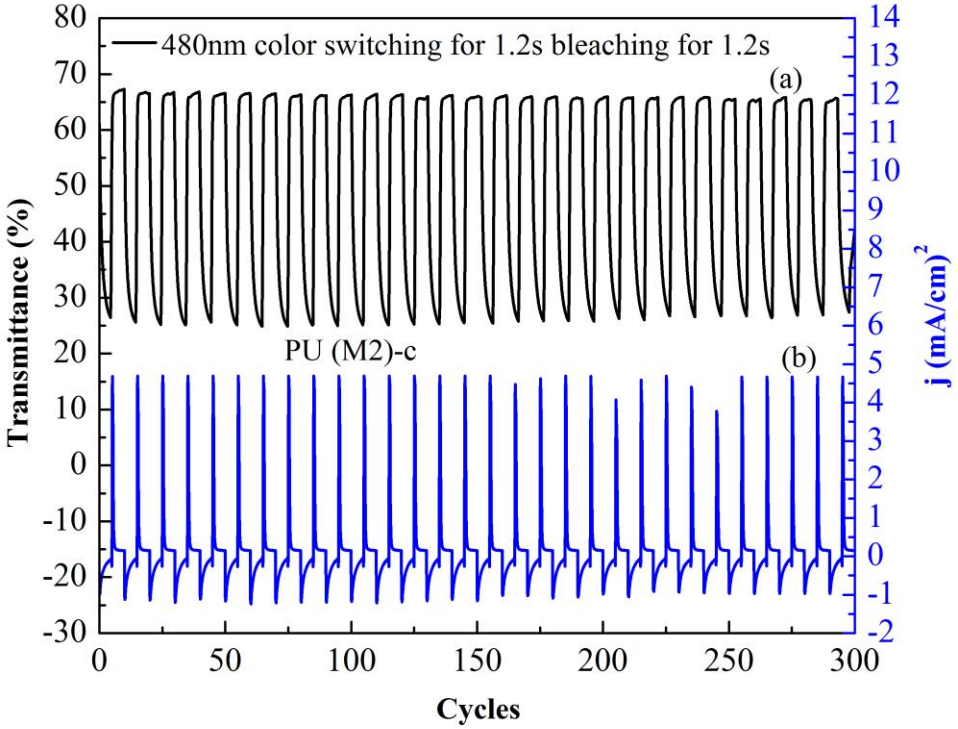


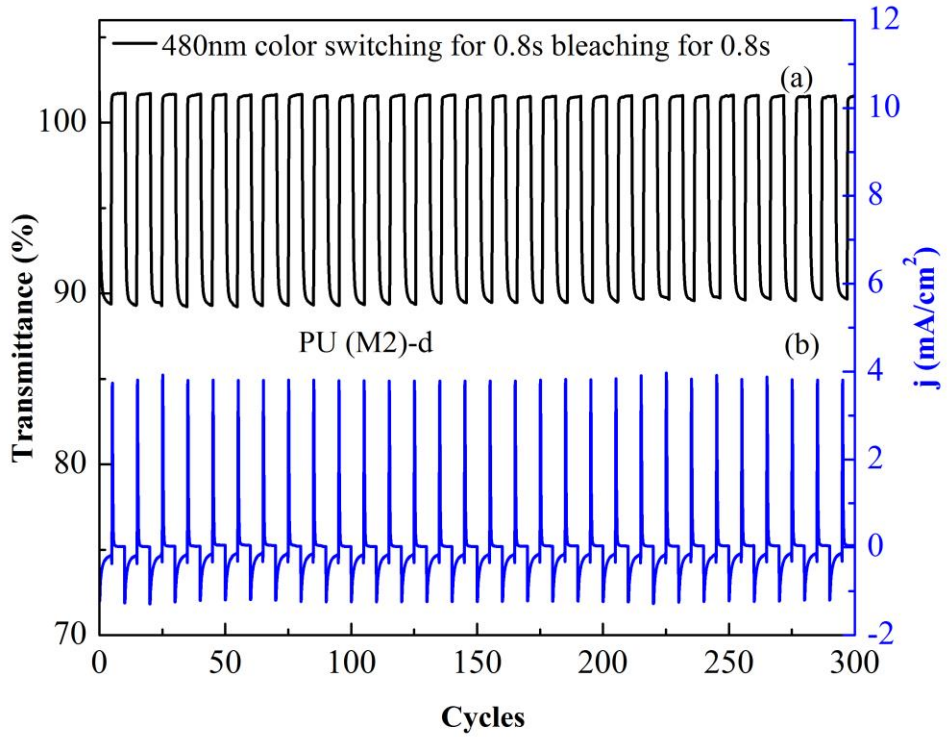

476nm color switching for 1.4s bleaching for 1.4s
(a)
PU(M1)-c
(b)
Transmittance (%)
j (mA/cm)^2
Cycles
80
70
60
50
40
30
20
12
10
8
6
4
2
0
-2
0
50
100
150
200
250
300


480nm color switching for 2.0s bleaching for 2.0s
(a)
PU(M1)-d
(b)
Transmittance (%)
j (mA/cm^2)
Cycles
80
70
60
50
40
30
20
12
10
8
6
4
2
0
-2
0
50
100
150
200
250
300


478nm color switching for 1.0s bleaching for 1.0s
(a)
PU(M1)-e
(b)
Transmittance (%)
j (mA/cm)^2
Cycles


480nm color switching for 1.0s bleaching for 1.0s
(a)
PU (M2)-a
(b)
Transmittance (%)
j (mA/cm^2)
Cycles


480nm color switching for 1.2s bleaching for 1.2s
(a)
PU (M2)-c
(b)
Transmittance (%)
j (mA/cm)^2
Cycles


480nm color switching for 0.8s bleaching for 0.8s
(a)
PU (M2)-d
(b)
Transmittance (%)
j (mA/cm^2)
Cycles

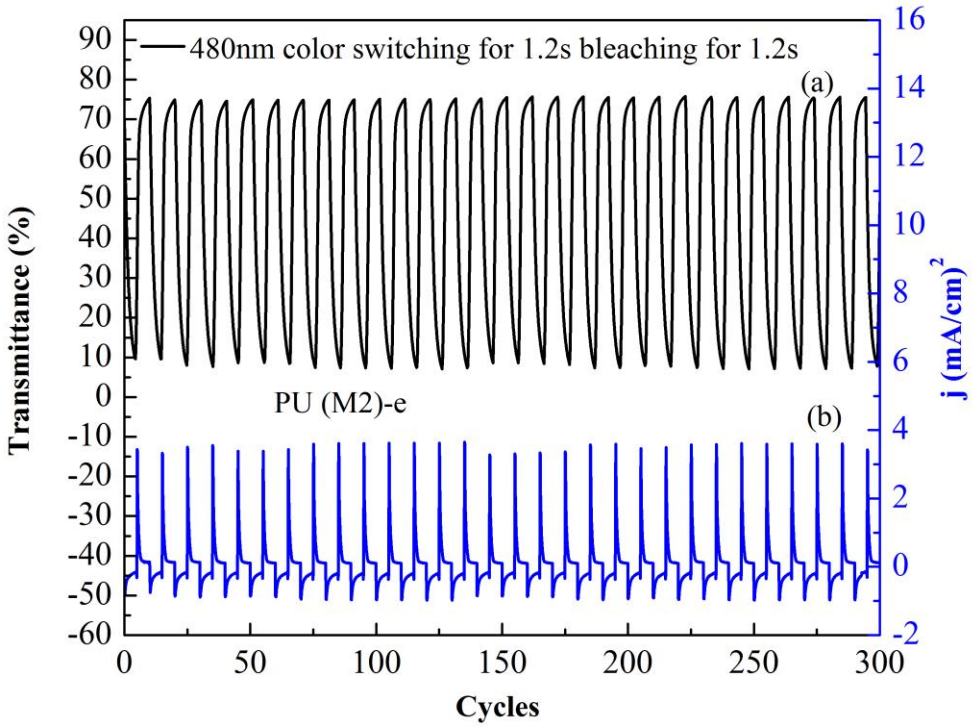


Fig. S9 Optical switching procedures (0.1 M $LiClO_4$ as the supporting electrolyte with a cycle time of 10 s): (a) potential step transmittance of PUs (M1) and PUs (M2) by applying a potential step (0.0-0.8 V). (b) Current consumption of PUs (M1) and PUs (M2).