Electronic Supplementary Information

Copolyfluorenes Containing Pendant Bipolar Groups: Synthesis, Optoelectronic Properties and Applications

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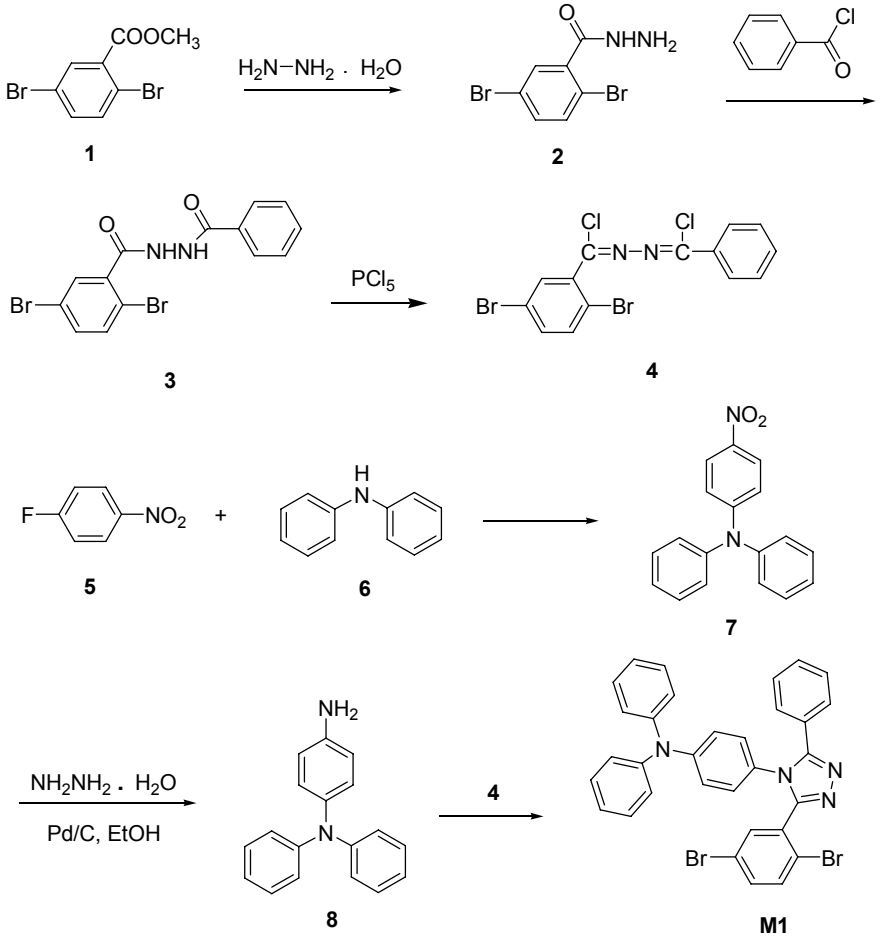
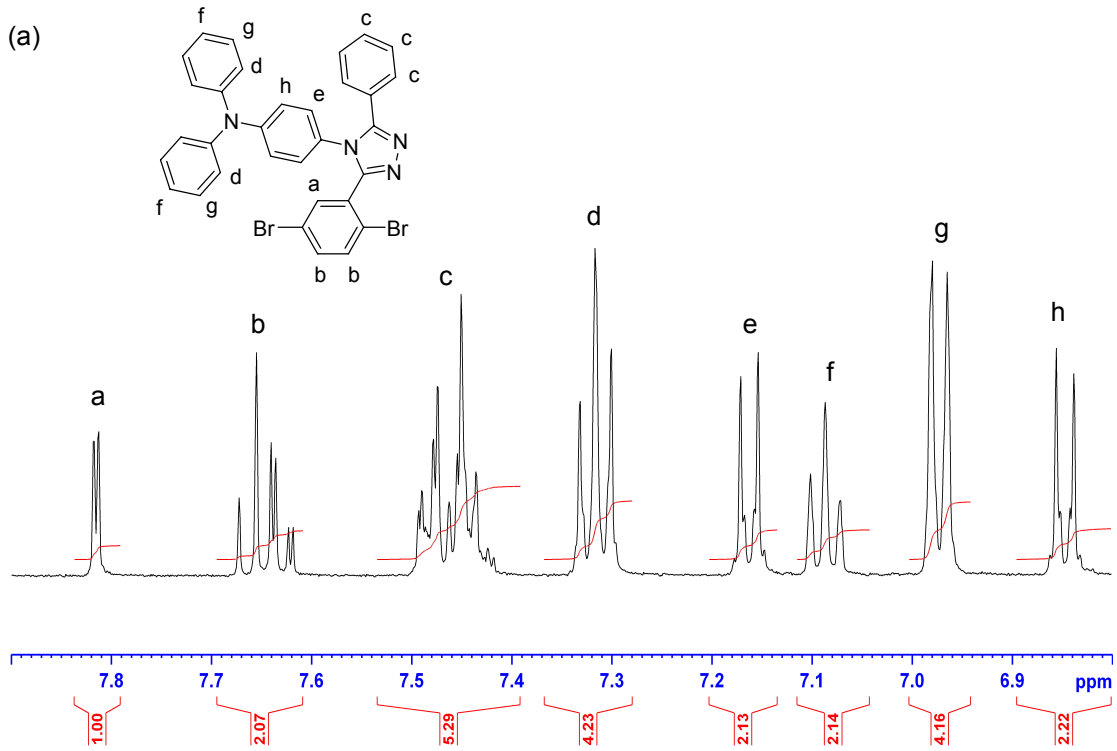
Synthesis of Compounds 3 and 4.

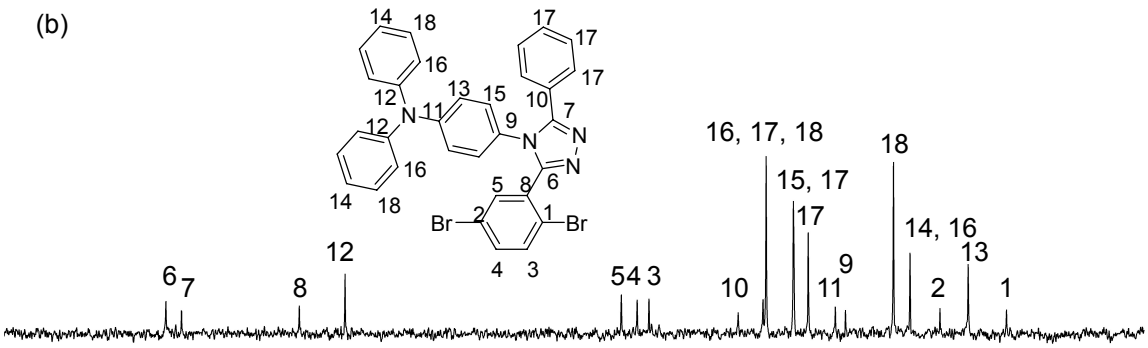
1-(2,5-dibromobenzoyl)-2-benzoylhydrazine (3). To a two-neck glass reactor were added with 2,5-dibromobenzohydrazide [**2**: 0.58 g, 2 mmol], benzoyl chloride (0.29 g, 2.1 mmol), and 10 ml of N-methylpyrrolidone (NMP). The mixture was stirred at 45 ^{o}C for 24 h, poured into a large amount of distilled water. The appearing precipitates were collected by filtration and recrystallized from DMSO and water to afford **3** (68%). mp > 250 ^{o}C. ^{1}H NMR (DMSO-d_6, ppm): δ 10.69 (s, 1H, -NH-), 10.50 (s, 1H, -NH-), 7.94~7.91 (m, 2H, Ar-H), 7.69~7.54 (m, 4H, Ar-H), 7.52~7.50 (m, 2H, Ar-H). FTIR (KBr pellet, cm^{-1}): ν 3185 (-CONH-), 3016, 2839, 2695, 1795, 1600, 1495, 1456, 1169, 1065 (C-Br), 1006, 849. Anal. Calcd. (%) for $C_{14}H_{10}Br_2N_2O_2$: C, 42.24; H, 2.53; N, 7.04. Found: C, 42.33; H, 2.57; N, 7.20.

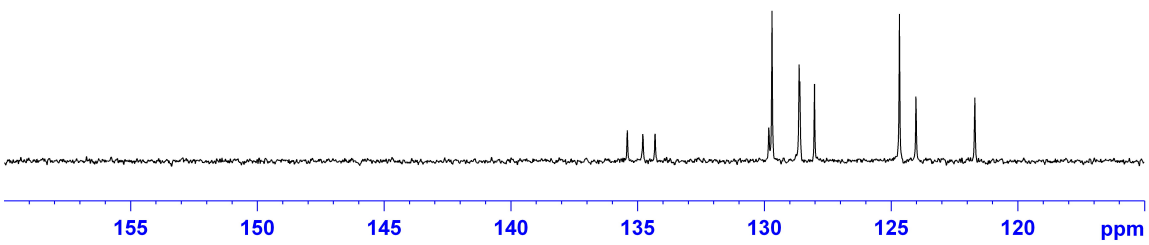
Scheme 1. Synthesis of Monomer M1



1-((2,5-dibromophenyl)chloromethylene)-2-(chloro(phenyl)methylene)hydrazine (4). The mixture of **3** (0.8 g, 2 mmol), phosphorus pentachloride (0.96 g, 4.62 mmol), and 10 ml of toluene was stirred at 120 ^{o}C for 3 h under nitrogen atmosphere. After stripping off toluene under vacuum, the solid residue was washed twice with deionized water, dried *in vacuo*, and then recrystallized from ethanol and dichloromethane to afford **4** (77%). mp: 118-120 ^{o}C. ^{1}H NMR (DMSO-d_6, ppm): δ 8.07~7.98 (m, 3H, Ar-H), 7.79~7.47 (m, 5H, Ar-H). FTIR (KBr pellet, cm^{-1}): ν 3177, 3086, 2811, 2297, 1912, 1787, 1596, 1577 (-N=N-), 1483, 1393, 1223, 1072 (C-Br), 1010, 926, 827. Anal. Calcd. (%) for $C_{14}H_8Br_2Cl_2N_2$: C, 38.66; H, 1.85; N, 6.44. Found: C, 38.65; H, 1.84; N, 6.61.


(a)
a
b
c
d
e
f
g
h
7.8
7.7
7.6
7.5
7.4
7.3
7.2
7.1
7.0
6.9
ppm
1.00
2.07
5.29
4.23
2.13
2.14
4.16
2.22


(b)
6
7
8
12
54
3
10
16, 17, 18
15, 17
17
11
9
18
14, 16
2
13
1


(c)
155
150
145
140
135
130
125
120
ppm

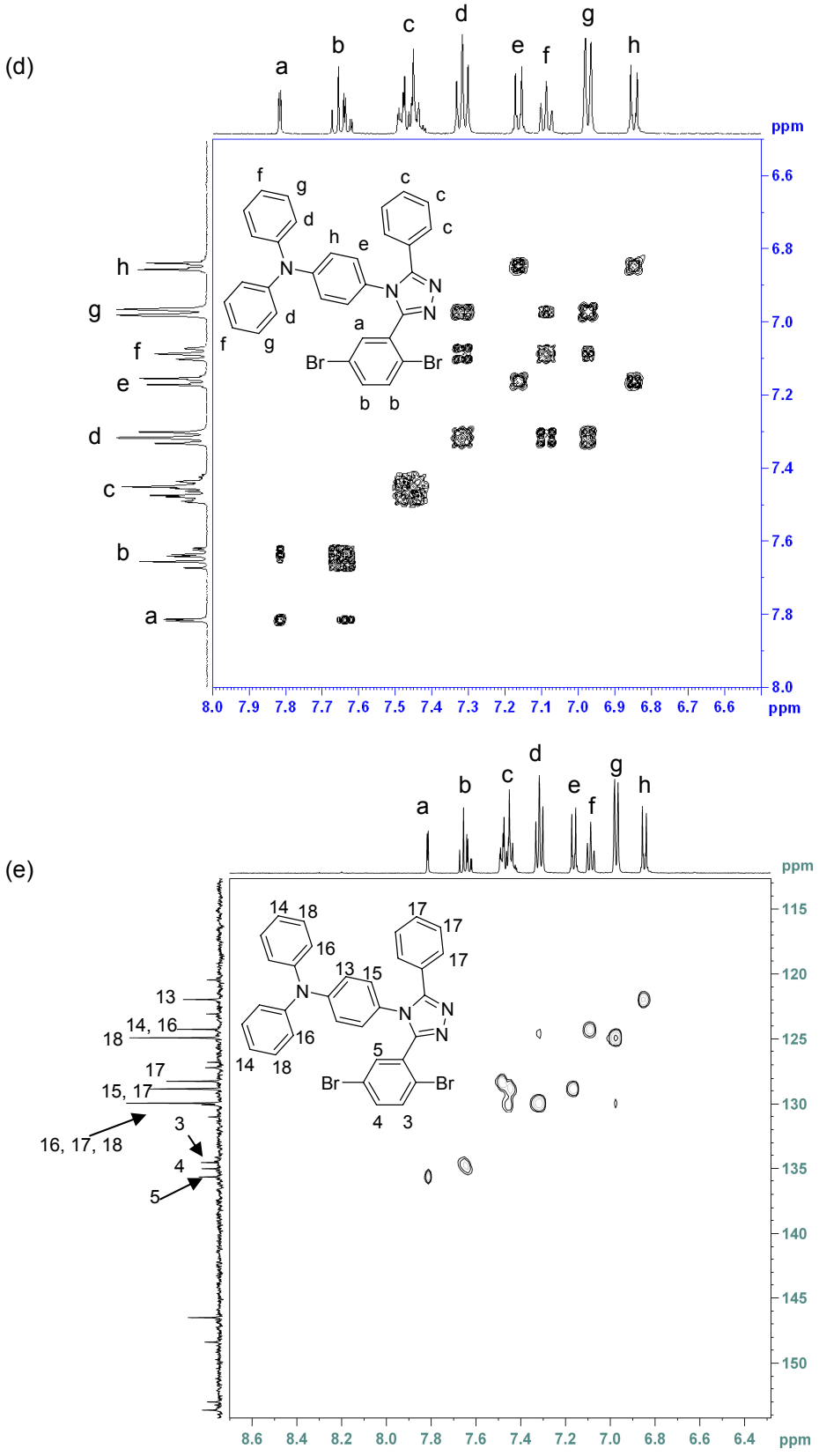


Figure S1. (a) ^{1}H NMR and (b) ^{13}C NMR and (c) DEPT135 and (d) H-H COSY and (e) C-H

HMQC spectra of **M1** in $CDCl_3$.

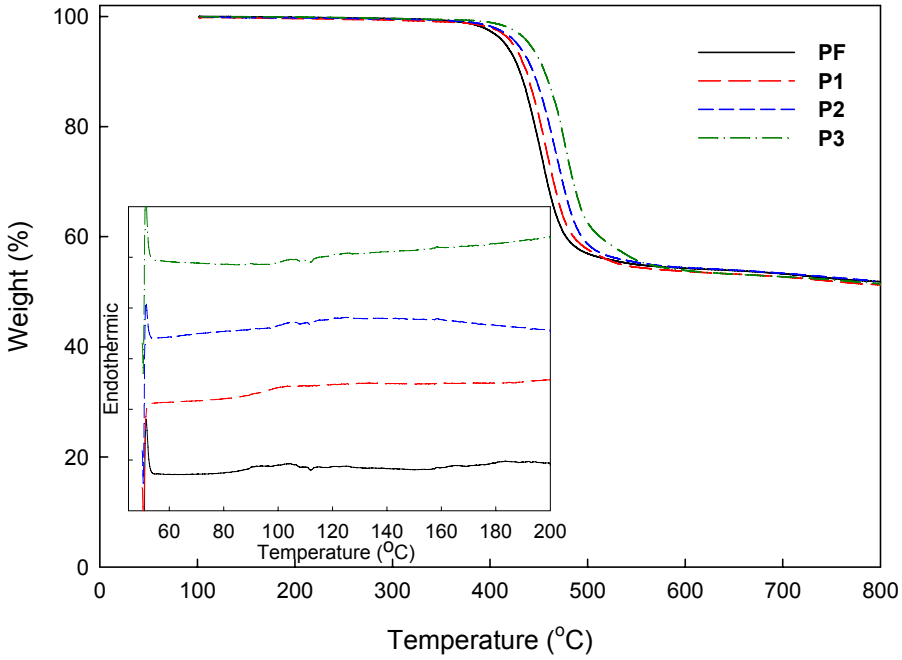


Figure S2. TGA thermograms of **PF** and **P1-P3** recorded at a heating rate of 20 °C /min. Inset: DSC traces of **PF** and **P1-P3** recorded at a heating rate of 10 °C /min.

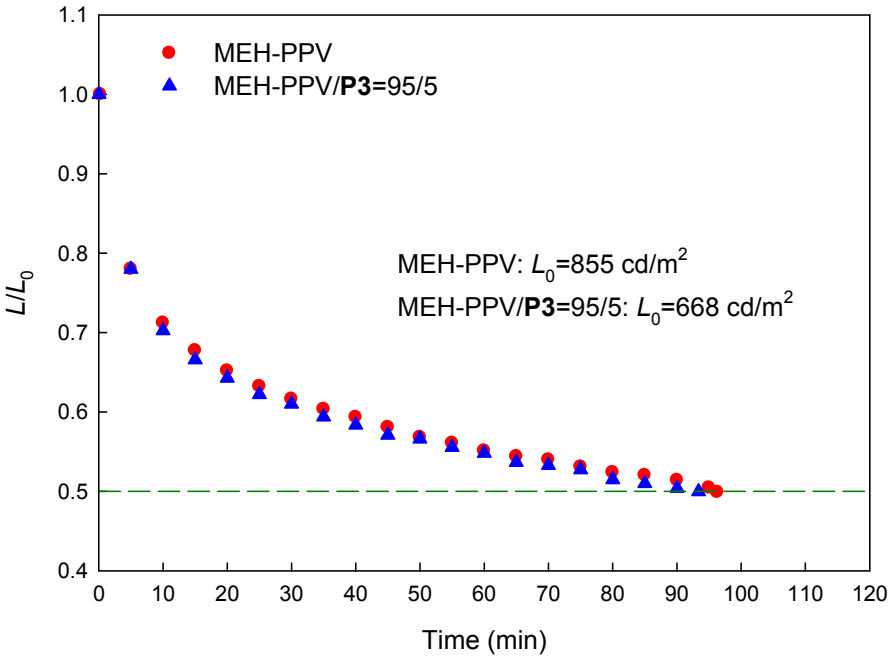


Figure S3. Half-decay lifetime ($t_{1/2}$) characteristics of PLEDs using blends of MEH-PPV and **P3** (0 and 5 wt%) as emitting layer. Device structure: ITO/PEDOT:PSS/MEH-PPV + **P3** (90~110 nm)/Ca(50 nm)/Al(100 nm).

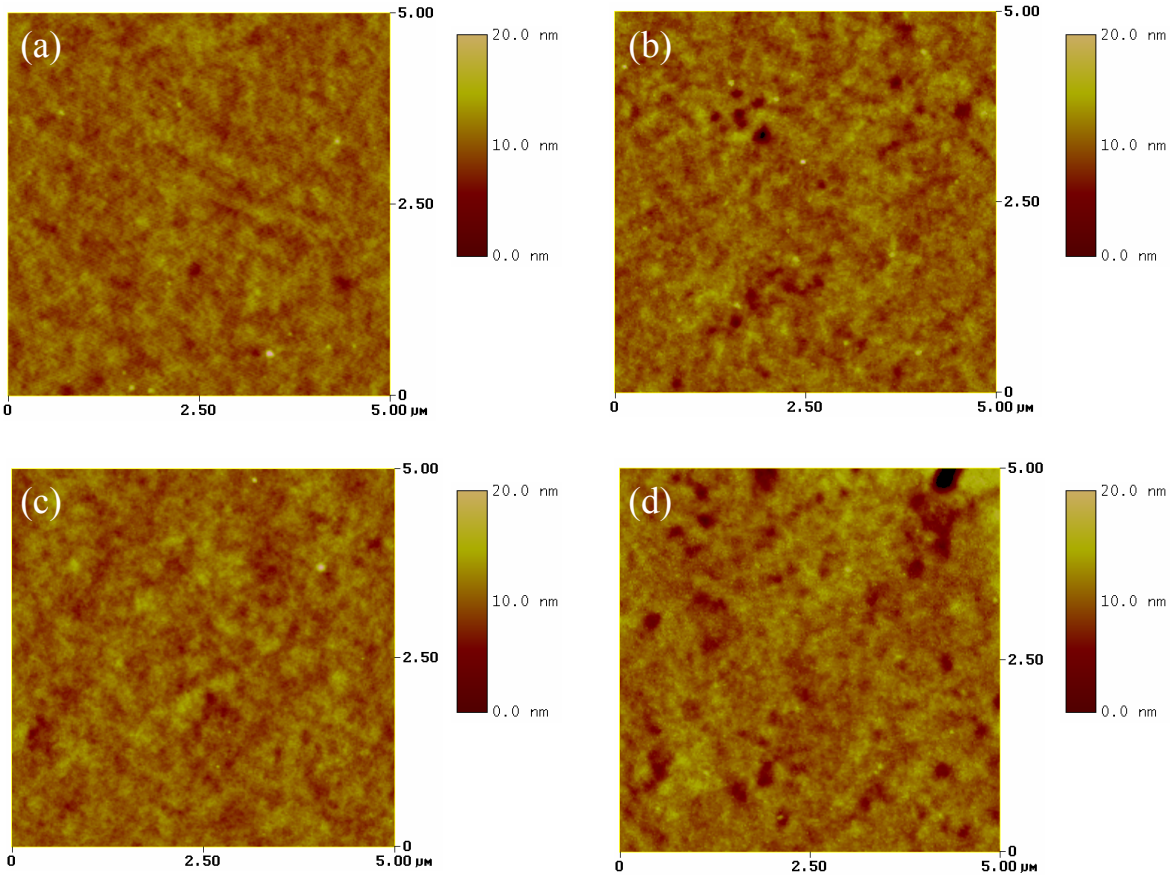


Figure S4. AFM images of (a) MEH-PPV before annealing, RMS roughness = 0.93 nm (b) MEH-PPV after annealing in vacuum at 90 °C for 24 h, RMS roughness = 1.21 nm (c) blend (MEH-PPV/**P3** = 95/5) before annealing, RMS roughness = 1.01 nm (d) blend (MEH-PPV/**P3** = 95/5) after annealing in vacuum at 90 °C for 24 h, RMS roughness = 1.46 nm. (Scan size: 5×5 µm)