Electronic Supplementary Information

Reversible room temperature phosphorescence in response to light stimulation based on photochromic copolymer

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b) Solid state absorbance spectra of polymer C7 at various time points post UV irradiation.

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**Figure S5.** a) Photoluminescence spectra of polymer C7 under continuous 365 nm excitation for several time. b) Photoluminescence spectra of polymer C7 at certain time points post UV irradiation.

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Figure S8. FTIR spectrum of polymer C7.

Figure S9. FTIR spectrum of polymer C8.
Figure S10. FTIR spectrum of polymer C9.

Figure S11. Thermogravimetric analysis of polymer C7.

Figure S12. Thermogravimetric analysis of polymer C8.
**Figure S13.** Thermogravimetric analysis of polymer C9.
**General Methods**

All the reagents and solvents were obtained commercially and used as supplied without further purification unless specified otherwise. The UV-Vis absorption spectra of solid sample were obtained on a PerkinElmer Lambda 950 spectrophotometer. The time-resolved photoluminescence spectra and lifetime at room temperature were recorded in air on an Agilent Cary Eclipse spectrophotometer. The photoluminescence quantum yields were measured using a HAMAMATSU absolute PL quantum yield spectrometer (C11347). The integral area ratio of phosphorescence and fluorescence peak is the ratio of phosphorescence and fluorescence quantum yield. Nuclear Magnetic Resonance (NMR) spectra were measured on a Bruker AV-400 spectrometer and processing on MestReNova (Mestralab Research, version: 14.0.0) software. Reversed phase chromatography was performed on SepaBean™ machine (Santai Technology Inc., China) equipped with C18-bonded Sepaflash® columns. GPC was recorded using a Waters Breeze at 25 °C with water as the eluent. The ESI+ mass spectra were tested on a Waters GCT Premier spectrometer.
Chemistry

Scheme 1. Synthetic route of polymers C7, C8 and C9.

\[
\begin{align*}
C1 & \quad \text{Br} \quad \text{Br} \quad \text{Br} \\
C3 & \quad \text{Br} \quad \text{Br} \quad \text{Br} \\
C4 & \quad \text{Br} \quad \text{Br} \\
C7 & \quad \text{CONH}_2 \\
C8 & \quad \text{CONH}_2 \\
C9 & \quad \text{CONH}_2 \\
C2 & \quad \text{Br} \quad \text{Br} \quad \text{Br} \\
C5 & \quad \text{Br} \quad \text{Br} \\
C6 & \quad \text{Br} \quad \text{Br} \\
\end{align*}
\]

a) K$_2$CO$_3$, Pd(PPh$_3$)$_4$, Dioxane/H$_2$O, reflux; b) 6-Bromo-1-hexene, DMF, 100°C; c) Acrylamide, AIBN, DMF, 70°C; d) Benzyl bromide, Acetonitrile, reflux.

**4-bromo-7-(4-pyridyl)-2,1,3-benzothiadiazole (C1).** The mixture of 4-pyridylboronic acid (244 mg, 2 mmol), 4,7-dibromobenzothiadiazole (647 mg, 2.2 mmol), Pd(PPh$_3$)$_4$ (116 mg, 0.1 mmol), and K$_2$CO$_3$ (832 mg, 6 mmol) in 1,4-dioxane/ H$_2$O (3/1, v/v, 20 mL) was heated to reflux under a nitrogen atmosphere for 18 h. After cooling to room temperature, the reaction was extracted with DCM (3 × 20 ml). The organic phase was combined and dried over sodium sulfate. Then the solvent was removed under reduce pressure. The residue was purified by flash column chromatography on silica gel to yield yellow solid (234 mg, 40%). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.77 (d, $J$ = 5.2 Hz, 1H), 7.97 (d, $J$ = 7.5 Hz, 1H), 7.85 (d, $J$ = 5.2 Hz, 1H), 7.68 (d, $J$ = 7.6 Hz, 1H). HRMS(El): $m/z$ [M]$^+$, calcd for C$_{16}$H$_{10}$N$_4$S: 290.0626; found: 374.0337.
Compound C3. Compound C1 (58 mg, 0.2 mmol) and 6-bromo-1-hexene (65 mg, 0.053 mL, 0.4 mmol) was dissolved in anhydrous DMF (1 mL). The reaction was stirred at 100 °C overnight. After cooling to room temperature, the mixture was poured into diethyl ether (10 mL). Participate was separated and purified by reversed phase chromatography on C18-bonded silica gel to yield white solid (87 mg, 96%). 

\[ ^1H\text{ NMR (400 MHz, } \text{CD}_3\text{OD}) \delta 9.10 (d, } J = 7.0 \text{ Hz, 2H), 8.87 (d, } J = 7.0 \text{ Hz, 2H), 8.26 – 8.16 (m, 2H), 5.90 – 5.76 (m, 1H), 5.06 (dd, } J = 17.1, 1.8 \text{ Hz, 1H), 5.02 – 4.97 (m, 1H), 4.69 (t, } J = 7.6 \text{ Hz, 2H), 2.23 – 2.05 (m, 4H), 1.60 – 1.49 (m, 2H); ^13C\text{ NMR (101 MHz, } \text{CD}_3\text{OD}) \delta 155.3, 153.8, 153.0, 145.7, 138.9, 133.6, 133.1, 128.4, 127.4, 120.2, 115.9, 62.4, 34.1, 31.9, 26.5. HRMS(ESI+): m/z [M-Br]^+ \text{, calcd for C}_{17}\text{H}_{17}\text{BrN}_{3}S^+ : 374.0327; found: 374.0337.}

Polymer C7. Compound C3 (23 mg, 0.05 mmol), acrylamide (178 mg, 2.5 mmol) and 2,2'-azobis(2-methylpropionitrile) (AIBN, 7 mg) was heat at 70 °C under a nitrogen atmosphere in DMF (1 mL) for 12 h. After cooling to room temperature, the reaction was poured into MeOH (10 mL) to participate the polymer solid. The participate was filter off and washed with MeOH and dried to yield a white solid. GPC (H_2O): Mn (PDI) = 5888 Da (2.318).

4,7-di(4-pyridyl)-2,1,3-benzothiadiazole (C2). The mixture of 4-pyridylboronic acid (537 mg, 4.4 mmol), 4,7-dibromobenzothiadiazole (588 mg, 2 mmol), Pd(PPh_3)_4 (232 mg, 0.2 mmol), and K_2CO_3 (1108 mg, 8 mmol) in 1,4-dioxane/ H_2O (3/1, v/v, 20 mL) was heated to reflux under a nitrogen atmosphere for 18 h. After cooling to room temperature, the reaction was extracted with DCM (3 × 30 ml). The organic phase was combined and dried over sodium sulfate. Then the solvent was removed under reduce pressure. The residue was purified by flash column chromatography on silica gel to yield yellow solid (445 mg, 77%). 

\[ ^1H\text{ NMR (400 MHz, CDCl}_3\text{) } \delta 8.75 (d, } J = 6.2 \text{ Hz, 4H), 7.94 (d, } J = 6.2 \text{ Hz, 4H), 7.93 (s, 2H).}

Compound C4. Compound C2 (48 mg, 0.165 mmol) and 6-bromo-1-hexene (107 mg, 0.088 mL, 0.66 mmol) was dissolved in anhydrous DMF (1 mL). The reaction was stirred at 100 °C overnight. After cooling to room temperature, the mixture was poured into diethyl ether (10 mL). Participate was separated and purified by reversed phase chromatography on C18-bonded silica gel to yield white solid (93 mg, 91%). 

\[ ^1H\text{ NMR (400 MHz, } \text{CD}_3\text{OD}) \delta 9.17 (d, } J = 7.0 \text{ Hz, 4H), 8.95 (d, } J = 6.9 \text{ Hz, 4H), 8.56 (s, 2H), 5.92 – 5.77 (m, 2H), 5.08 (dd, } J = 17.1, 1.8 \text{ Hz, 2H), 5.03 – 4.98 (m, 2H), 4.73 (t, } J = 7.6 \text{ Hz, 4H), 2.25 – 2.07 (m, 8H), 1.63 – 1.51 (m, 4H); ^13C\text{ NMR (101 MHz, } \text{CD}_3\text{OD}) \delta 154.2, 153.5, 145.9, 138.9, 132.4, 131.2, 129.0, 115.9, 62.6, 34.1, 31.9, 26.5. HRMS(ESI+): m/z [M-2Br]^2+, calcd for C_{28}\text{H}_{32}\text{N}_{4}S^2+: 228.1168; found: 228.1170.}

Polymer C8. The polymer C8 was synthesized follow a similar method as polymer C7. Polymer C8 was achieved as a white solid. GPC (H_2O): Mn (PDI) = 4770 Da (2.410).

Compound C5. Compound C4 (290 mg, 1.0 mmol) and benzyl bromide (171 mg, 0.119 mL, 1 mmol) were dissolved in acetonitrile (30 mL). The mixture was heated to reflux overnight. After cooling to room temperature, the solvent was removed under reduced pressure. The residue was purified by flash column chromatography on silica gel to yield yellow solid (216 mg, 47%). 

\[ ^1H\text{ NMR (400 MHz, } \text{CD}_3\text{OD}) \delta 9.20 (d, } J = 6.4 \text{ Hz, 2H), 8.96 (d, } J = 6.3 \text{ Hz, 2H), 8.73 (d, } J = 4.6 \text{ Hz, 2H), 8.49 (dd, } J = 7.5, 1.9 \text{ Hz, 1H), 8.23 (dd, } J = 7.5, 2.0 \text{ Hz, 1H), 8.16 (d, } J = 4.4 \text{ Hz, 2H), 7.61 (d, } J = 7.0 \text{ Hz,}

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2H), 7.54 – 7.48 (m, 3H), 5.93 (s, 2H); $^{13}$C NMR (101 MHz, CD$_3$OD) $\delta$ 154.7, 154.3, 154.2, 150.5, 146.1, 145.7, 135.6, 134.8, 133.0, 131.1, 130.8, 130.19, 130.1, 128.7, 128.4, 125.6, 65.2. HRMS(ESI+): m/z [M-Br]$^+$, calcd for C$_{23}$H$_{17}$N$_4$S$: 381.1174; found: 381.1177.

**Compound C6.** The compound C6 was synthesized similar as compound C3. The compound C6 was achieved as white solid. $^1$H NMR (400 MHz, CD$_3$OD) $\delta$ 9.28 (d, J = 6.7 Hz, 2H), 9.21 (d, J = 6.9 Hz, 2H), 9.01 – 8.94 (m, 4H), 8.59 (s, 2H), 7.68 – 7.60 (m, 2H), 7.57 – 7.45 (m, 3H), 5.98 (s, 2H), 5.93 – 5.79 (m, 1H), 5.08 (dd, J = 17.1, 1.8 Hz, 1H), 5.01 (dd, J = 10.2, 1.7 Hz, 1H), 4.77 (t, J = 7.6 Hz, 2H), 2.27 – 2.16 (m, 2H), 2.19 – 2.09 (m, 2H), 1.64 – 1.52 (m, 2H); $^{13}$C NMR (101 MHz, CD$_3$OD) $\delta$ 154.2, 153.8, 153.4, 145.9, 138.9, 134.7, 132.7, 132.5, 131.2, 131.1, 131.0, 130.8, 130.3, 129.2, 129.0, 115.9, 65.3, 62.5, 34.1, 31.9, 26.5. HRMS(ESI+): m/z [M-2Br]$^{2+}$, calcd for C$_{29}$H$_{28}$N$_4$S$: 232.1012; found: 232.1006.

**Polymer C9.** The polymer C9 was synthesized follow a similar method as polymer C7. Polymer C9 was achieved as a white solid. GPC (H$_2$O): Mn (PDI) = 3567 Da (1.835).
\[ \text{H NMR (400 MHz, Chloroform-d)} \delta \]

- \( 8.77 (d, J = 5.2 \text{ Hz}, 1H) \)
- \( 7.97 (d, J = 7.5 \text{ Hz}, 1H) \)
- \( 7.85 (d, J = 5.2 \text{ Hz}, 1H) \)
- \( 7.68 (d, J = 7.6 \text{ Hz}, 1H) \)

\[ \text{H NMR (400 MHz, Chloroform-d)} \delta \]

- \( 8.75 (d, J = 6.2 \text{ Hz}, 4H) \)
- \( 7.94 (d, J = 6.2 \text{ Hz}, 4H) \)
- \( 7.93 (s, 2H) \)
**PROTON** MeOD {D:\data\research\new\2019-11-6} nmr

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NMR (400 MHz, Methanol-d$_4$) δ 9.10 (d, J = 7.0 Hz, 2H), 8.87 (d, J = 7.0 Hz, 2H), 8.26 – 8.16 (m, 2H), 5.90 – 5.76 (m, 3H), 5.06 (q, J = 17.1, 1.8 Hz, 1H), 5.02 – 4.97 (m, 1H), 4.69 (s, 0.5 Hz, 2H), 2.25 – 2.05 (m, 4H), 1.60 – 1.49 (m, 2H).

**C$^{13}$CPD** MeOD {D:\data\research\new\2019-11-6} nmr

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C$^{13}$NMR (101 MHz, MeOD) δ 155.3, 153.8, 153.0, 145.7, 154.9, 133.6, 133.1, 128.4, 127.7, 126.2, 115.9, 62.4, 34.1, 31.9, 28.5.
\[ \text{NMR} (400 \text{ MHz}, \text{Methanol-}d_4) \delta 9.17 (d, J = 7.0 \text{ Hz}, 4H), 8.95 (d, J = 6.9 \text{ Hz}, 4H), 8.56 (s, 2H), 5.92 – 5.77 (m, 2H), 5.08 (dd, J = 17.1, 1.8 \text{ Hz}, 2H), 5.03 – 4.98 (m, 2H), 4.73 (t, J = 7.6 \text{ Hz}, 4H), 2.25 – 2.07 (m, 8H), 1.63 – 1.51 (m, 4H). \]
1H NMR (400 MHz, Methanol-d$_4$): δ 9.20 (d, J = 6.4 Hz, 2H), 8.96 (d, J = 6.5 Hz, 2H), 8.73 (d, J = 4.6 Hz, 2H), 8.49 (d, J = 7.5, 3.9 Hz, 1H), 8.23 (d, J = 7.5, 3.0 Hz, 1H), 8.16 (d, J = 4.4 Hz, 2H), 7.61 (d, J = 7.0 Hz, 2H), 7.44 – 7.36 (m, 3H), 5.93 (s, 2H).

13C NMR (101 MHz, MeOD): δ 154.7, 154.3, 154.2, 150.5, 146.1, 145.7, 135.6, 134.8, 135.6, 131.1, 130.8, 130.10, 130.1, 128.7, 129.4, 128.6, 65.2.
$^{1}H$ NMR (400 MHz, Methanol-$d_4$) δ 9.28 (d, $J = 6.7$ Hz, 2H), 9.21 (d, $J = 6.9$ Hz, 2H), 9.01 – 8.94 (m, 4H), 8.59 (s, 2H), 7.68 – 7.60 (m, 2H), 7.57 – 7.45 (m, 3H), 6.98 (s, 2H), 5.93 – 5.79 (m, 2H), 2.27 – 2.16 (m, 2H), 2.19 – 2.09 (m, 3H), 1.64 – 1.52 (m, 2H).

$^{13}$C NMR (101 MHz, MeOD) δ 154.2, 153.8, 153.4, 145.9, 138.9, 134.7, 132.7, 132.5, 131.0, 130.8, 130.3, 129.2, 129.0, 128.3, 62.5, 63.1, 26.8.
HRMS (ESI+) spectra of C1.

HRMS (EI+) spectra of C2.
HRMS (ESI+) spectra of C3.

HRMS (ESI+) spectra of C4.
HRMS (ESI+) spectra of C5.

HRMS (ESI+) spectra of C6.