Supplementary Information for

High-Color-Quality White Electroluminescence and Amplified Spontaneous Emission from a Star-Shaped Single-Polymer System with Simultaneous Three-Color Emission

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Experimental

4,7-dibromobenzo[c][1,2,5]thiadiazole (**2**)

White solid, yield 86%. ^{1}H NMR ($CDCl_3$, 400 MHz) δ (ppm): 7.72 (s, 2H). ^{13}C NMR ($CDCl_3$) δ (ppm): 152.95, 132.34, 113.91.

2,2'-(9,9-dihexyl-9H-fluorene-2,7-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (**4**)

White solid, yield 91%. ^{1}H NMR ($CDCl_3$, 400 MHz) δ (ppm): 7.80-7.82 (d, 2H, J = 8.1 Hz), 7.71-7.75 (m, 4H), 1.98-2.02 (m, 4H), 1.39 (s, 24H), 0.99-1.10 (m, 12H), 0.73-0.76 (t, 6H, J = 7.1 Hz), 0.50-0.56 (dd, 4H, J = 7.3 Hz, J = 15.5 Hz). ^{13}C NMR ($CDCl_3$) δ (ppm): 150.47, 143.93, 133.66, 128.92, 119.38, 83.72, 55.19, 40.10, 31.45, 29.63, 24.95, 23.57, 22.58, 14.02.

4,7-bis(4-hexylthiophen-2-yl)benzo[c][1,2,5]thiadiazole (**7**)

Pale-yellow solid, yield 81%. ^{1}H NMR ($CDCl_3$, 400 MHz) δ (ppm): 7.98 (s, 2H), 7.83(s, 2H), 7.04(s, 2H), 2.68-2.71 (t, 4H), 1.67-1.72 (m, 4H), 1.34 (m, 12H), 0.89-0.92 (t, 6H). ^{13}C NMR ($CDCl_3$) δ (ppm): 154.31, 141.72, 132.22, 129.93, 129.25, 127.49, 125.90, 31.60, 30.72, 29.39, 29.14, 22.57, 14.08.

4-(5-bromo-4-hexylthiophen-2-yl)-7-(4-hexylthiophen-2-yl)benzo[c][1,2,5]thiadiazole (**8**)

Red solid, yield 83%. ^{1}H NMR ($CDCl_3$, 400 MHz) δ (ppm): 7.97 (s, 1H), 7.70-7.78 (m, 3H), 7.04 (s, 3H), 2.61-2.71 (m, 4H), 1.65-1.72 (m,4H), 1.34-1.41 (m, 12H), 0.91 (t, 6H). ^{13}C NMR ($CDCl_3$) δ (ppm): 152.48, 152.31, 144.42, 142.99, 138.86, 138.66, 129.18, 127.86, 126.31, 125.33, 124.94, 121.72, 111.36, 31.73, 31.67, 30.67, 30.49, 29.77, 29.72, 29.71, 29.08, 29.00, 22.66, 22.65, 14.14.

3,6-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)-9H-carbazole (**12**)

White solid, yield 66%. ^{1}H NMR ($CDCl_3$, 400 MHz) δ (ppm): 8.70 (s, 2H), 8.05-8.07 (d, 2H, J =

8.4 Hz), 7.83-7.85 (t, 2H, *J* = 7.0 Hz), 7.56-7.58 (d, 2H, *J* = 8.2 Hz), 7.37-7.40(m, 2H) , 1.39 (s, 36H). ^{13}C NMR ($CDCl_3$) δ (ppm): 142.87, 142.86, 139.99, 136.42, 132.36, 128.02, 126.14, 123.39, 109.21, 84.10, 83.61, 24.95.

Tris(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)amine (**15**)

White solid, yield 63%. ^{1}H NMR ($CDCl_3$, 400 MHz), δ (ppm): 7.68-7.70 (d, 6H), 7.07-7.09 (d, 6H), 1.34 (s, 36H). ^{13}C NMR ($CDCl_3$), δ (ppm): 149.80, 135.93, 123.49, 83.68, 24.89.

7,7'-(5,5'-(9-(4-(3-hexyl-5-(7-(4-hexylthiophen-2-yl)benzo[c][1,2,5]thiadiazol-4-yl)thiophen-2-yl) phenyl)-9H-carbazole-3,6-diyl)bis(4-hexylthiophene-5,2-diyl))bis(4-(4-hexylthiophen-2-yl)benzo[c][1,2,5]thiadiazole) (**TM**)

Dark red solid, yield 76%. ^{1}H NMR ($CDCl_3$, 400 MHz) δ (ppm): 8.32 (s, 2H), 8.05-8.07 (d, 3H, *J* = 11.0 Hz), 7.96-7.97 (d, 3H, *J* = 5.0 Hz), 7.74-7.82 (m, 8H), 7.60-7.66 (dd, 4H, *J* = 8.5 Hz, *J* = 16.2 Hz) , 7.53-7.55 (d, 2H, *J* = 8.5 Hz), 7.03 (m, 3H), 2.81-2.85 (m, 6H), 2.67-2.71 (t, 6H, *J* = 7.5 Hz), 1.69-1.80 (m, 12H), 1.29-1.43 (m, 36H), 0.86-0.92 (m, 18H). ^{13}C NMR ($CDCl_3$) δ (ppm): 152.64, 152.60, 144.38, 144.32, 140.50, 140.49, 140.40, 140.29, 139.46, 139.13, 138.23, 137.82, 136.89, 136.51, 133.92, 130.59, 130.31, 130.30, 129.07, 128.88, 127.86, 126.83, 126.80, 125.87, 125.66, 125.54, 125.42, 124.99, 123.69, 121.60, 121.41, 121.27, 121.26, 110.09, 110.06, 110.03, 31.76, 30.71, 30.50, 29.40, 29.13, 22.72, 22.70, 14.18, 14.15. MS (MALDI-TOF, m/z): $[M]^+$ Calcd. For $C_{96}H_{103}N_7S_9$: 1643.5; found: 1645.9 ($[M+2H]^+$) Anal. Calcd. for $C_{96}H_{103}N_7S_9$: C 70.16, H 6.32, N 5.97, S 17.56; Found: C 70.12, H 6.49, N 6.19, S17.68.

Table S1. Thermal, electrochemical and photophysical properties of TM.

Sample	T_g [°C]	T_d [°C]	E_{HOMO} [eV]	E_{LUMO} [eV]	E_g [eV]	λ_{abs} [nm]	λ_{em} [nm]
TM	159	407	-5.65	-2.87	2.78	334/486	625

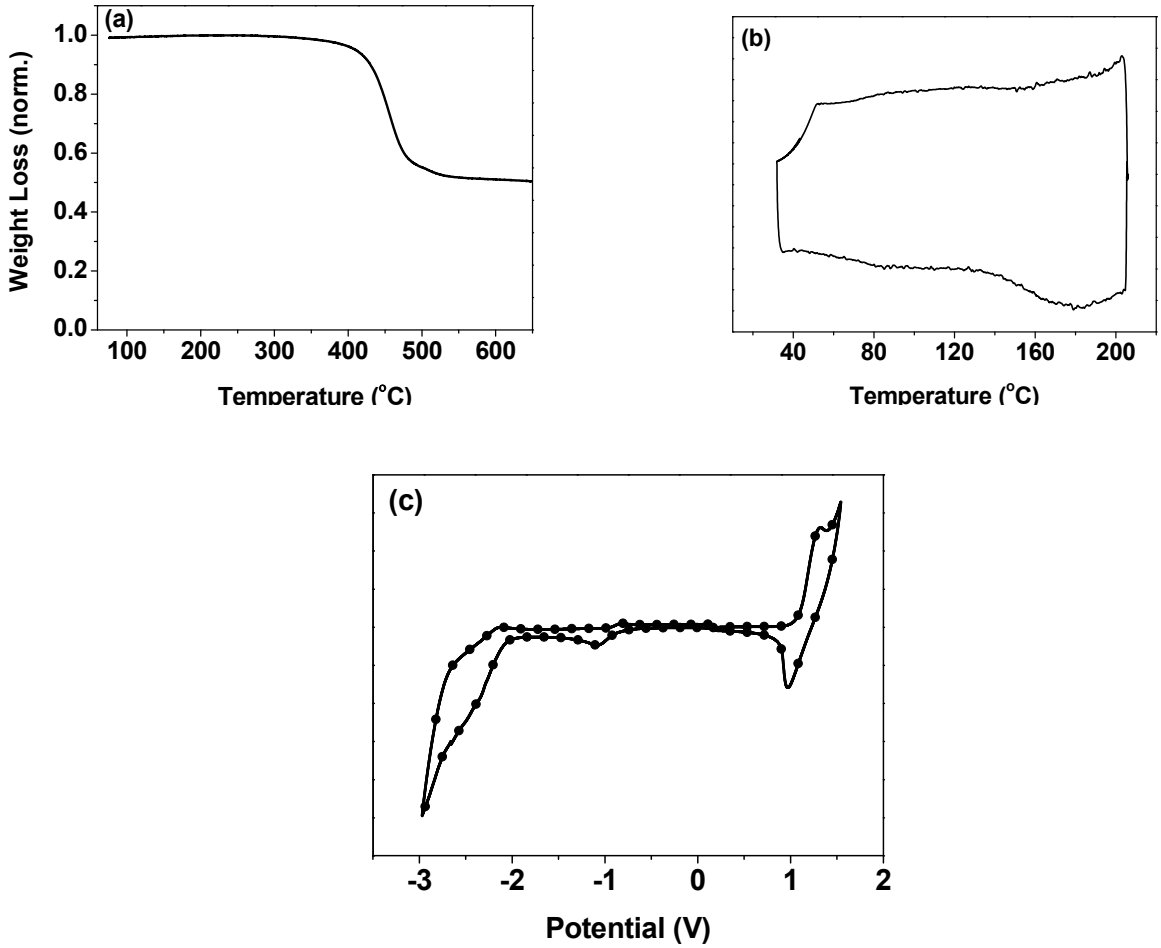

Figure S1. (a, b) Thermal properties and (c) electrochemical properties of TM.

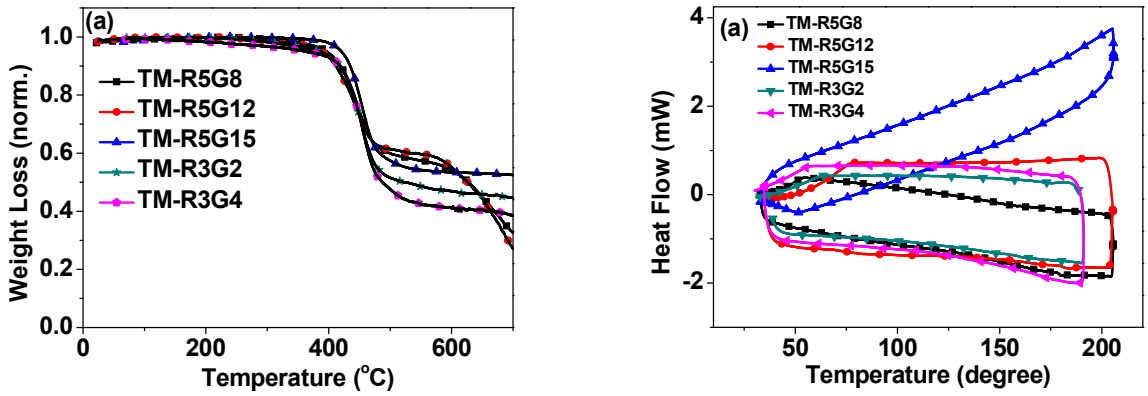

Figure S2. Thermal properties of TM-RxGy: (a) TGA and (b) DSC curves.

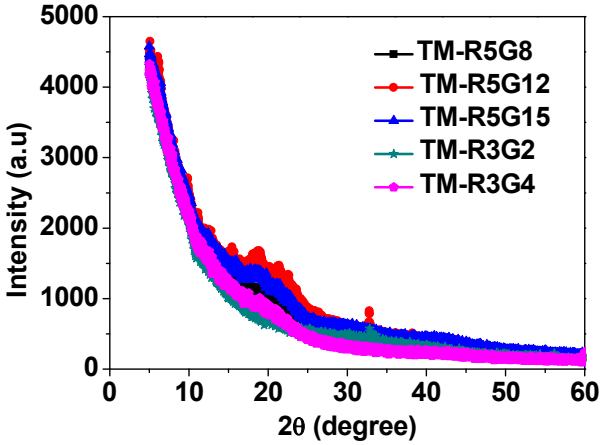

Figure S3. WAXD patterns (0-60°) of TM-RxGy powders. All samples were tested under the same conditions and each pattern was at its original intensity.

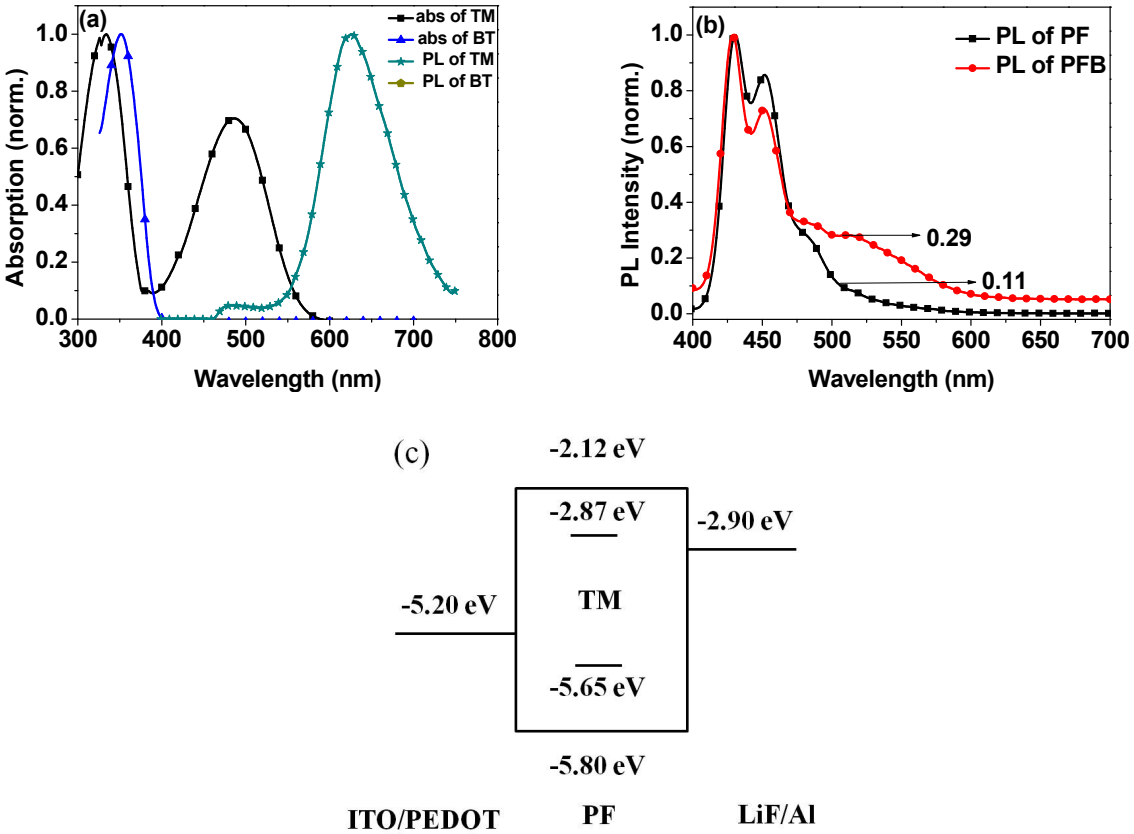

Figure S4. (a) Absorption spectra and PL spectra of TM and BT in dilute solutions; (b) PL spectra of PF and PFB in solid films; (c) Energy levels of TM and PF.

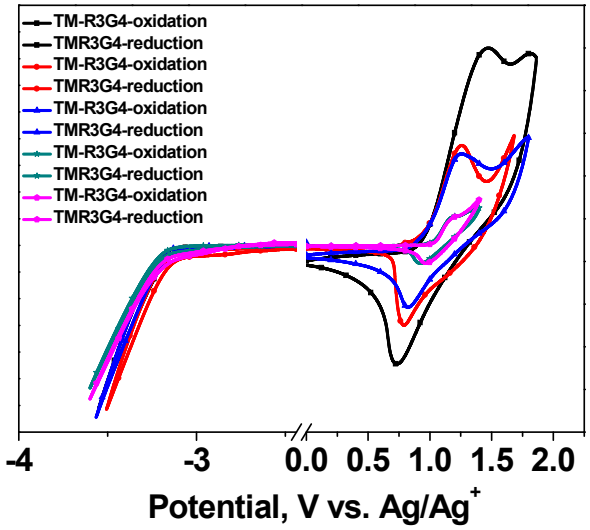

Figure S5. Electrochemical properties of TM-RxGy.

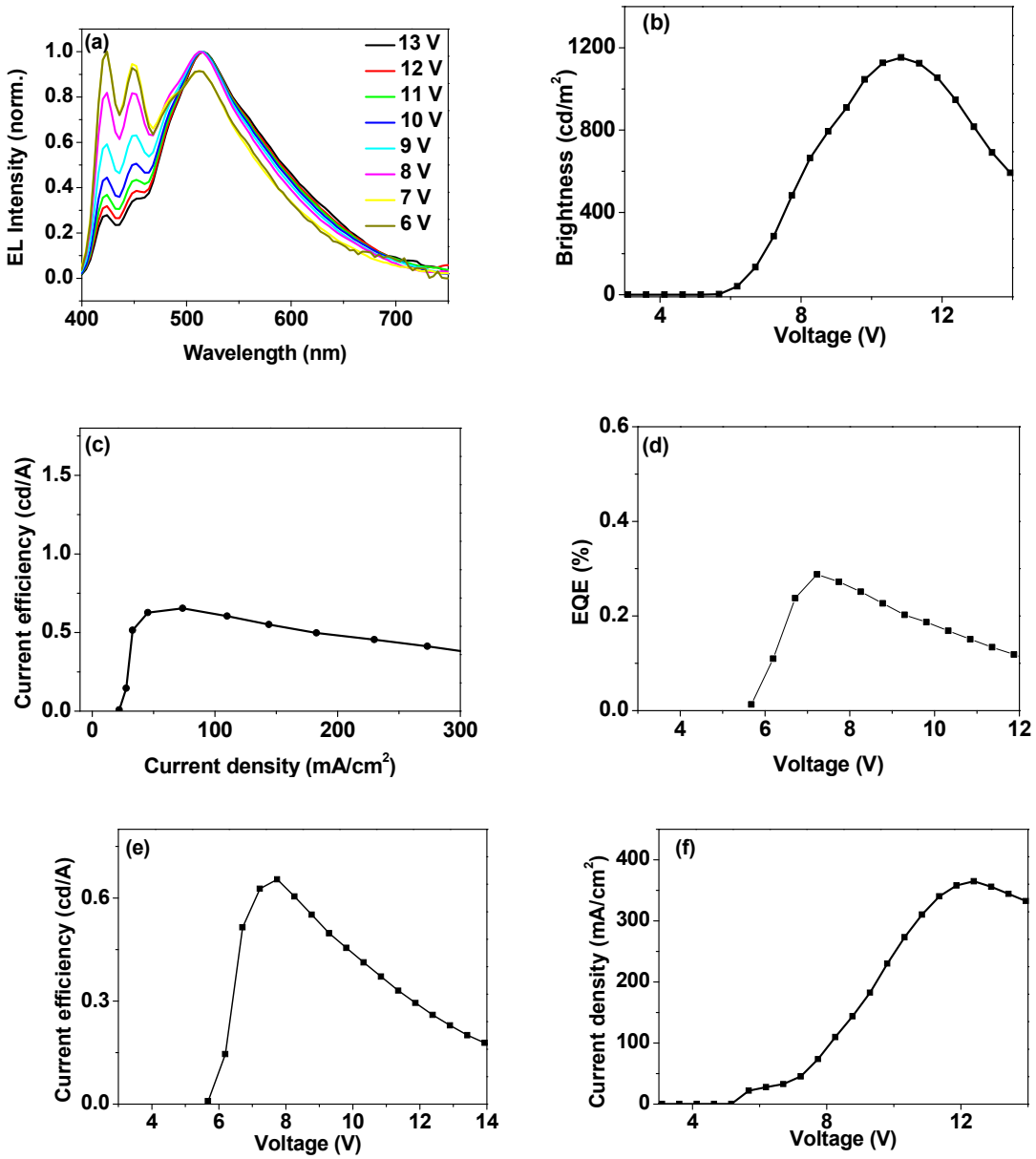

Figure S6. EL characteristics of devices based on 0.03 mol% TM blended into PFB. (a) EL spectra with different voltages; (b) Brightness-voltage characteristics; (c) Current efficiency-current density characteristics; (d) EQE-voltage characteristics; (e) Current efficiency-voltage characteristics; (e) Current density-voltage characteristics.

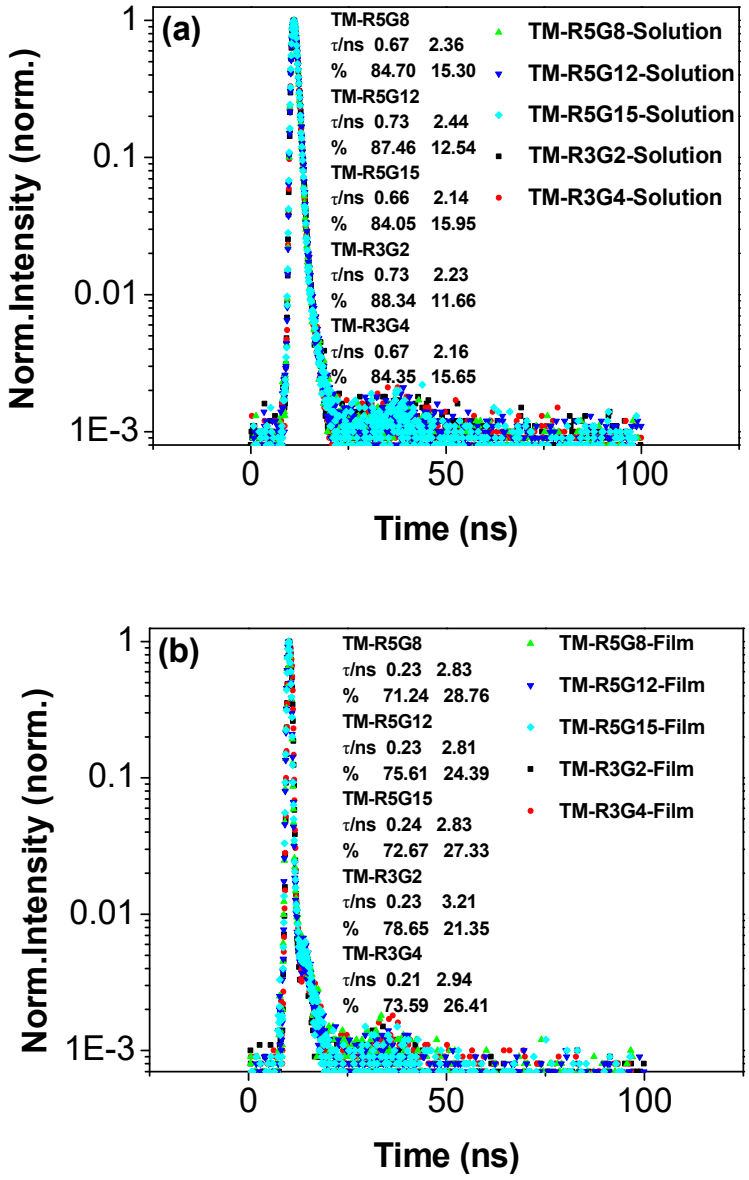

Figure S7. Fluorescence transients of (a) THF solution (10^{-5} M) and (b) films of TM-RxGy measured at the fluorescence band maxima collected at 421 nm and 434 nm, respectively.

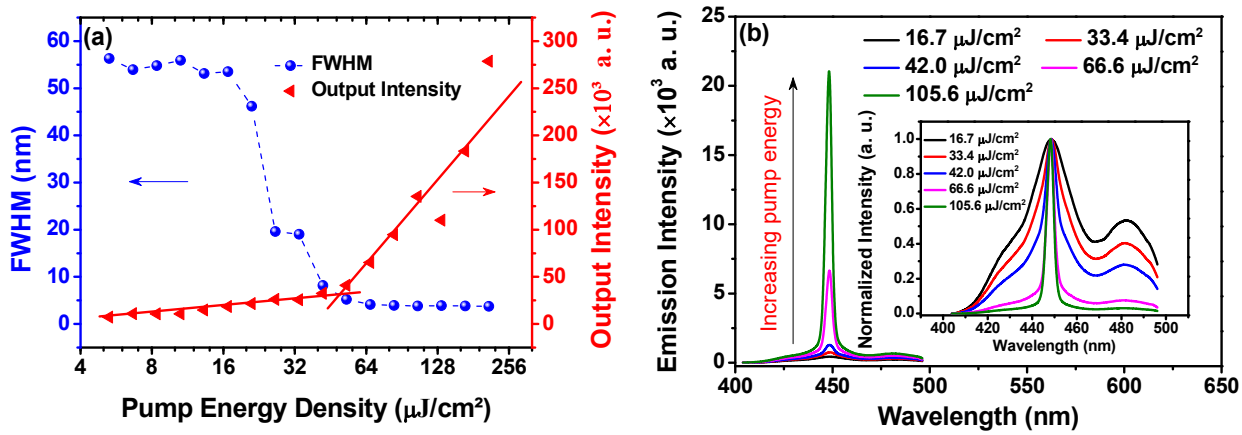

Figure S8. ASE characteristics of PF. (a) The FWHM of the emission spectrum (left, solid spheres) and the corresponding light emission peak intensity (right, solid triangles); (b) The emission spectra for the planar waveguide of PF under laser pumped by different energy, and the corresponding normalized spectra shown in the inset.

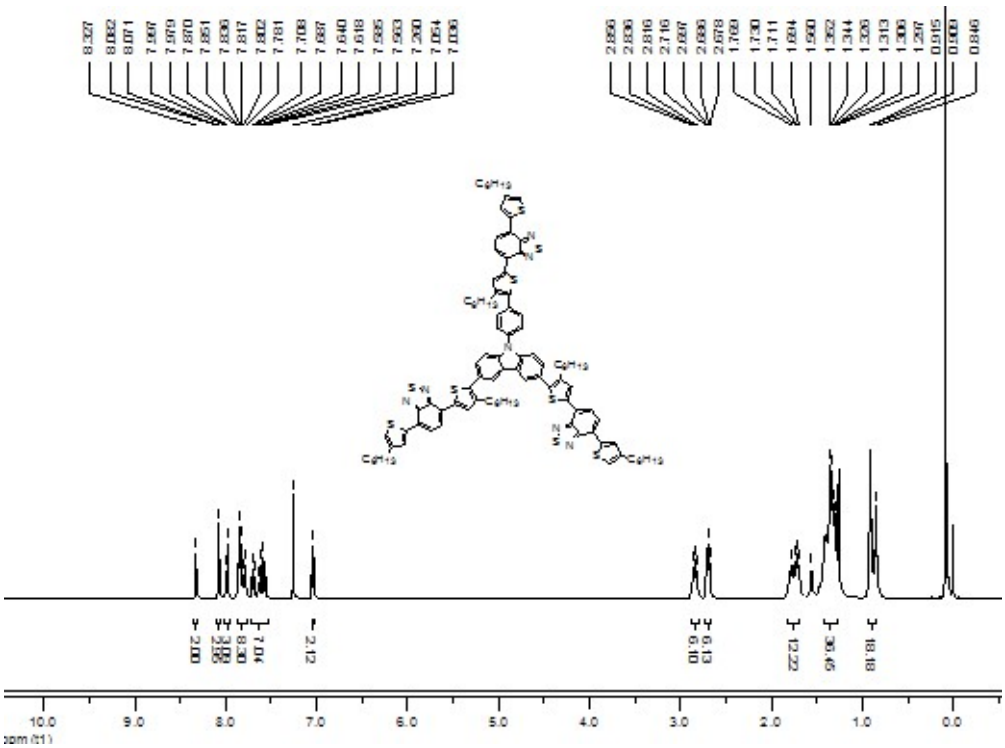

Figure S9. ^{1}H NMR spectrum of TM in $CDCl_3$.

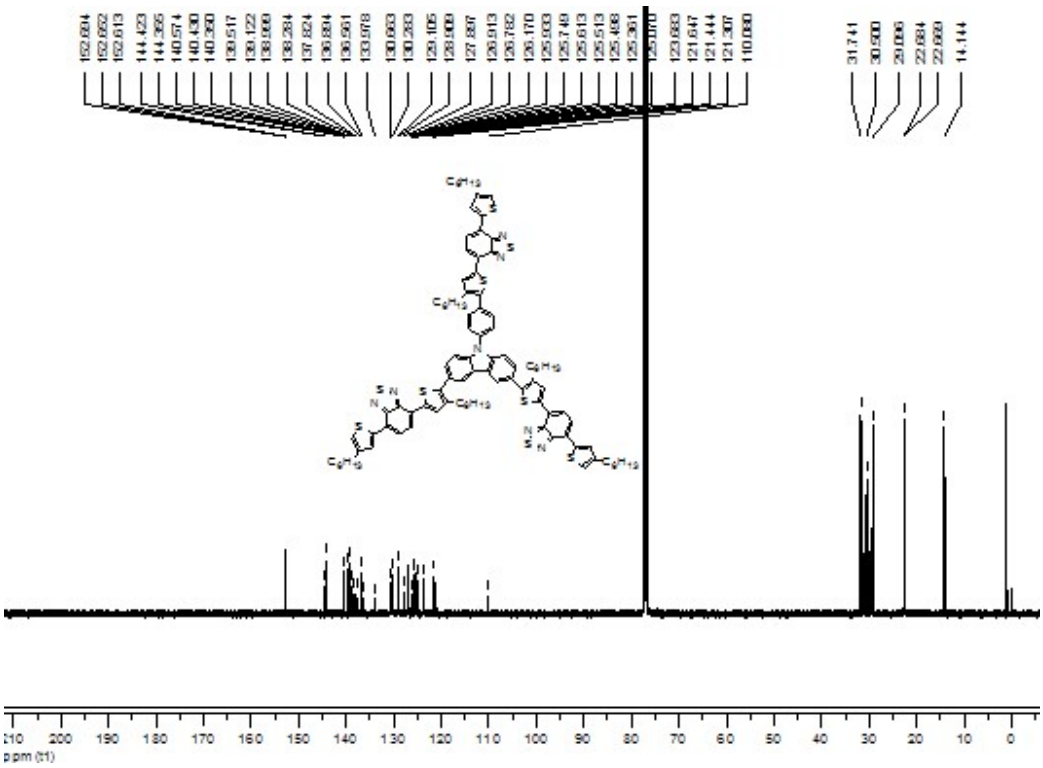

Figure S10. ^{13}C NMR spectrum of TM in $CDCl_3$.

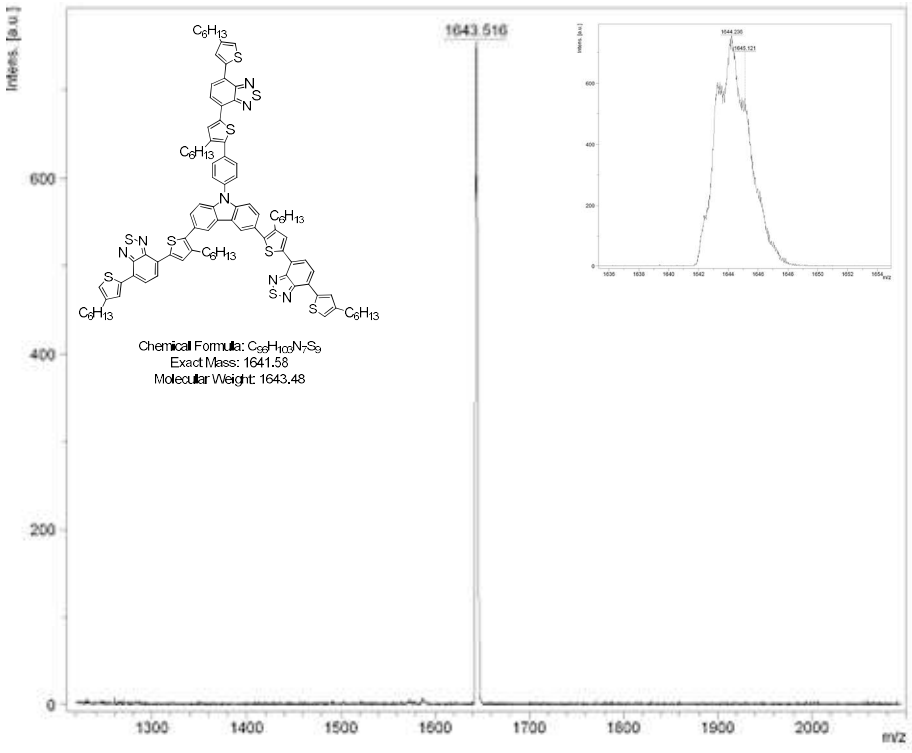

Figure S11. MALDI-TOF mass spectrum of TM.

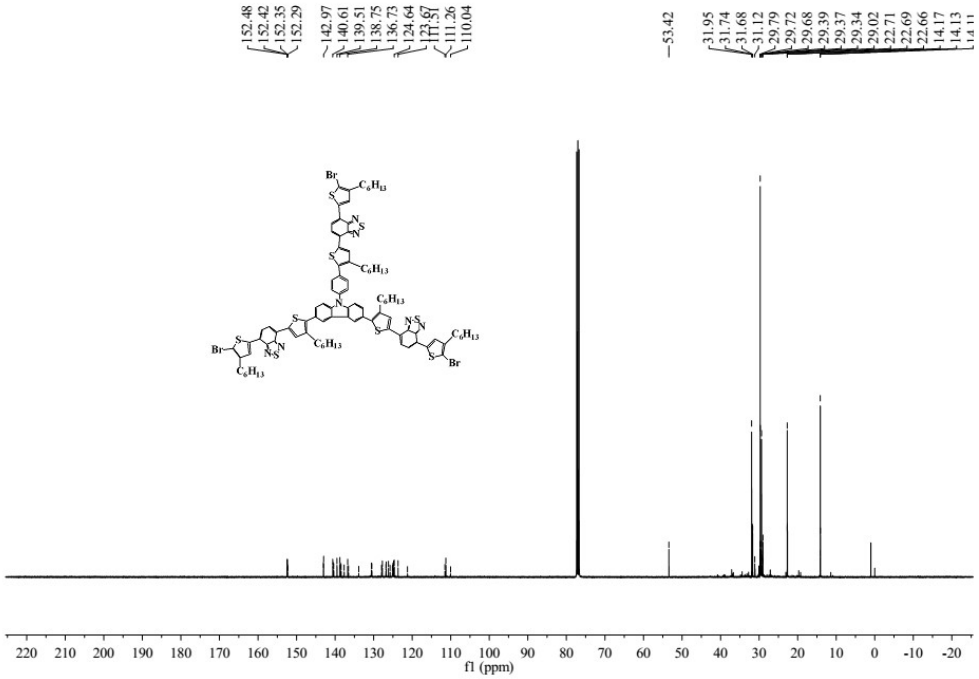

Figure S12. ^{1}H NMR spectrum of TM3Br in $CDCl_3$.

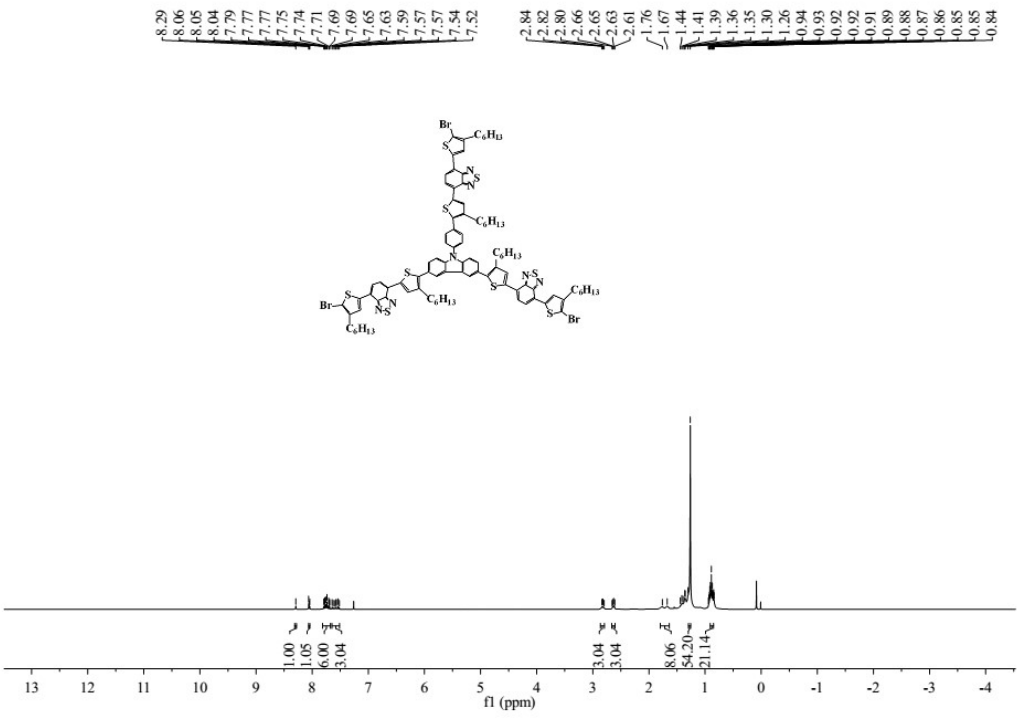

Figure S13. ^{13}C NMR spectrum of TM3Br in $CDCl_3$.

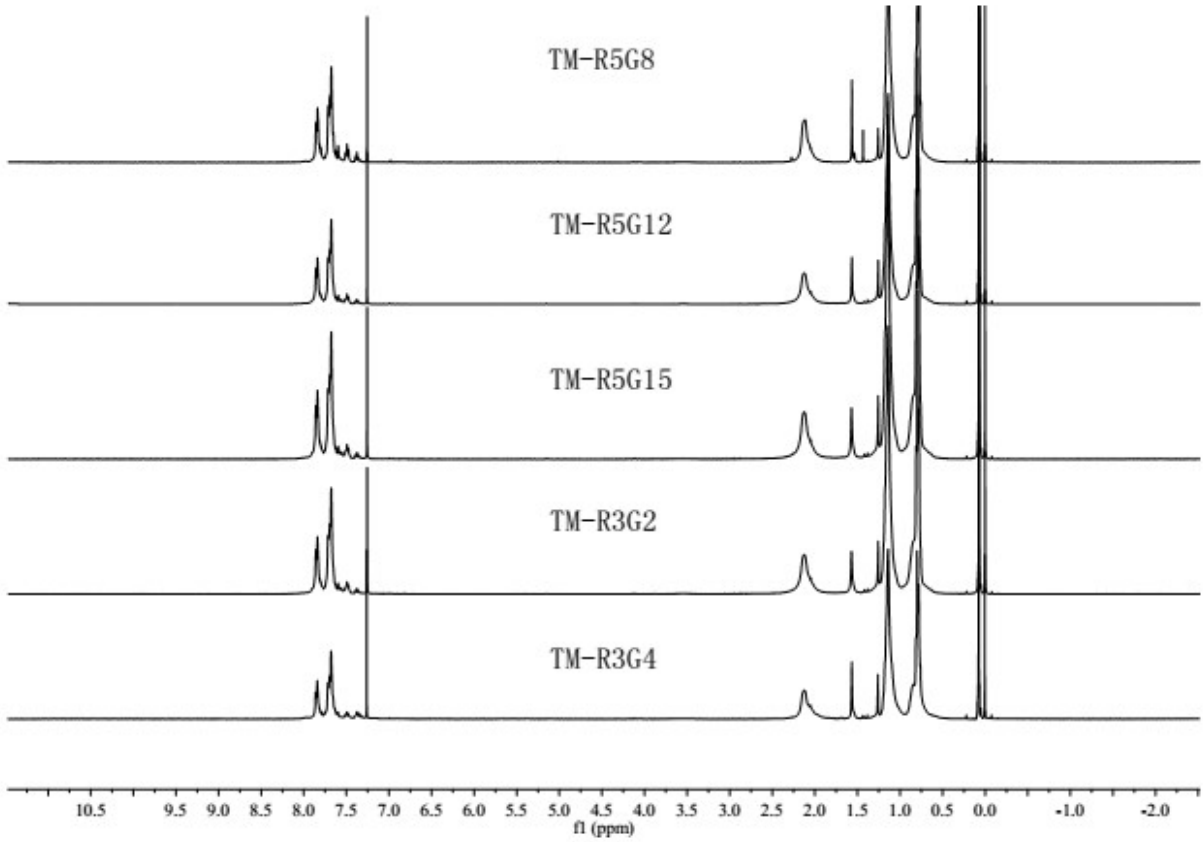

Figure S14 ^{1}H NMR spectra of TM-RxGy.