Supporting Information for

A Highly Electroluminescent Molecular Square

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1. Material and General Procedures.

All of the chemicals were obtained from commercial sources and used without further purification. All of the reactions and manipulations were carried out under N_2 with the use of standard inert-atmosphere and Schlenk techniques. Solvents used in reactions were dried by standard procedures. UV-Visible spectra were obtained using a Shimadzu UV-2410PC spectrophotometer. Circular dichroism (CD) spectra were recorded on a Jasco J-710 spectropolarimeter. The IR spectra were recorded from KBr pellets on a Nicolet Magna-560 FT-IR spectrometer. Fluorescence studies were carried out using Shimadzu RF-5301PC fluorimeter. FAB-MS spectra were taken at Mass Spectrometry Facility at Michigan State University while MALDI-TOF mass spectra were taken at Duke University. NMR spectra were recorded on a Varian XL-400 and a Bruker NMR 400 DRX spectrometer. ^{1}H-NMR spectra were recorded at 400 MHz and referenced to the proton resonance resulting from incomplete deuteration of the deuterated dichloromethane (5.32 ppm). $^{13}C\{^1H\}$ NMR spectra were recorded at 100 MHz, and all of the chemical shifts are reported downfield in ppm relative to the carbon resonance of the methyl group of dichloromethane-d_2 (53.8 ppm).

UV-vis absorption spectra of thin films of **2a** and **3a** were measured using a Perkin-Elmer Lambda 9 UV/vis/NIR spectrophotometer. PL and EL spectra were recorded with an Oriel InstaSpec IV spectrograph with a charge coupled device (CCD) detector.

The EL devices were fabricated on ITO-coated glass substrates that were pre-cleaned and oxygen plasma treated before use. A layer of poly(ethylene dioxythiophene): poly(styrene sulfonate) (PEDOT:PSS, Baytron P from Bayer Co.), 40 nm thick, was formed by spin-coating from its aqueous solution (1.3 wt.%). Blends were made by mixing the PVK host solution (in chlorobenzene) with the guest solutions at specific volume ratios. The EL layer was spin-coated on top of the vacuum dried PEDOT:PSS layer. The nominal thickness of the EL layer was 60 nm. Under a base pressure below 1×10^{-6} torr, a layer of CsF (~1 nm) and subsequently a thicker layer of aluminum were vacuum deposited as cathodes. Current-voltage characteristics were measured with a Hewlett-Packard 4155B semiconductor parameter analyzer. The brightness and efficiencies were measured with a calibrated Si-photodiode.

Ligands $\mathbf{L_1}$-H_2 and $\mathbf{L_2}$-H_2 were synthesized according to our previously published procedures.[1]

2. Detailed Synthetic Procedures and Characterization data.

Self-assembly of [Pt(4,4'-di-tert-butyl-2,2'-dipyridyl)($\mathbf{L_1}$)]$_3$, 1a: To a 100 mL two-necked round bottom flask containing Pt(4,4'-di-tert-butyl-2,2'-dipyridyl)Cl_2 (59.4 mg, 0.11 mmol), CuI (7 mg, 0.036 mmol) and $\mathbf{L_1}$-H_2 (54.2 mg, 0.11 mmol) was added 60 mL of CH_2Cl_2 and followed by 0.3 mL of $NHEt_2$. The mixture was stirred at rt for 72 h. The mixture was passed through a short silica gel column to get rid of CuI. The solvent was removed under reduced pressure to afford the crude product, which was purified by column chromatography using dichloromethane:acetone (50:1 v/v). Yield: 23 mg (29%). ^{1}H NMR (CD_2Cl_2, 400MHz): 9.75 (d, J=6Hz, 1H), 8.80 (d, J=1.6Hz, 1H), 8.12 (s, 1H), 7.74 (dd, J=1.6Hz and J=6Hz, 1H), 7.56 (s, 1H), 6.99 (d, J=8.8Hz, 1H), 6.95 (dd, J=8.8Hz and J=1.6Hz, 1H), 1.92 (s, 3H), 1.53 (s, 9H). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 100 MHz): 169.53, 164.54, 156.66, 151.97, 147.14, 134.28, 132.03, 131.76, 130.19, 128.43, 127.29, 127.06, 125.39, 125.07, 121.55, 119.76, 98.70, 96.58, 36.24, 29.87, 20.87. IR: ν(-CH_3) 2959.99 cm^{-1} (m); ν(-C≡C-) 2107.28 cm^{-1} (m); MALDI-TOF MS: m/z 2848.19 (calcd m/z 2847.4 for $[M+H]^+$). Anal. Calcd for $C_{138}H_{117}Cl_6O_{12}N_6Pt_3$, **1a**•4$CH_2Cl_2$: C, 53.53; H, 3.86; N, 2.64 ; Found: C, 53.36 ; H, 4.47; N, 2.48.

Self-Assembly of [Pt(4,4'-di-tert-butyl-2,2'-dipyridyl)($\mathbf{L_1}$)]$_4$, 2a: 23.4 mg (22.4%

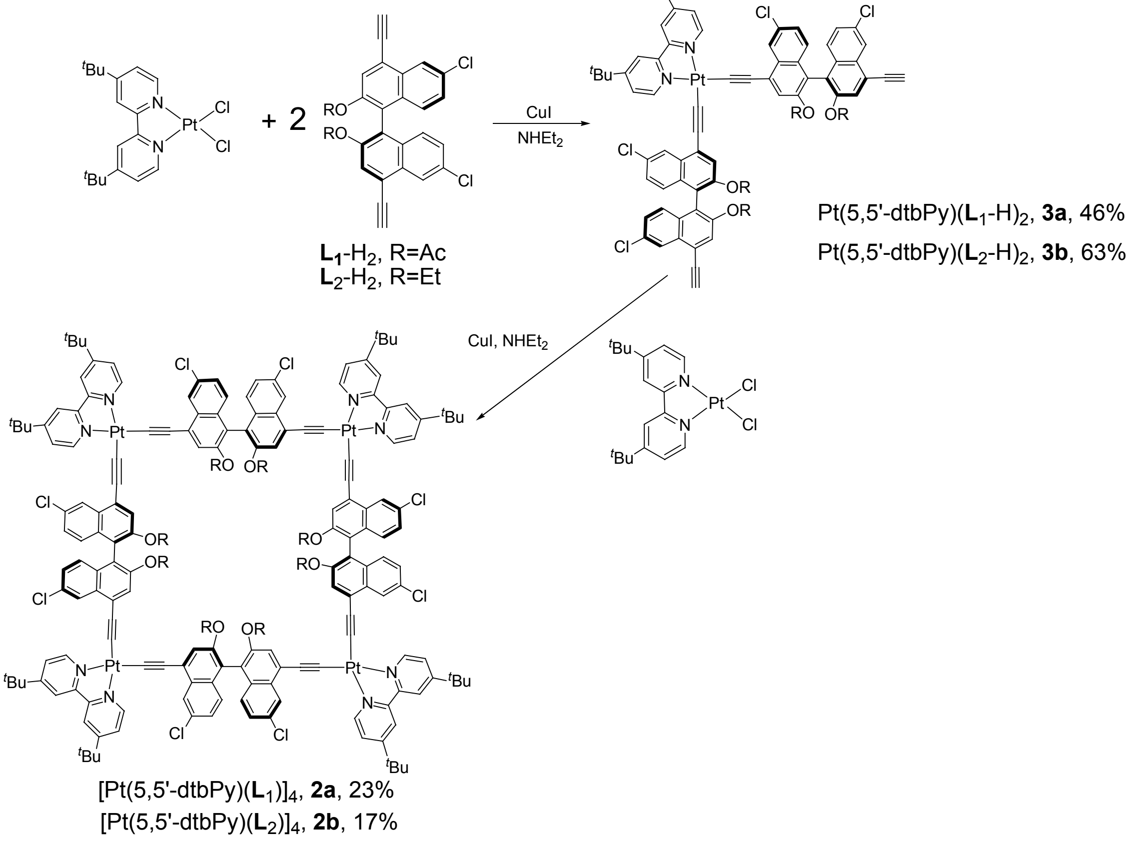
yield) of **2a** was obtained from the above reaction along with **1a**. ^{1}H NMR (CD_2Cl_2, 400MHz): 9.81(d, J=6Hz, 1H), 8.86 (d, J=2.4Hz, 1H), 8.12 (s, 1H), 7.74 (dd, J=1.6Hz and J=6Hz, 1H), 7.65 (s, 1H), 7.19 (dd, J=9.2Hz and J=2.4Hz, 1H), 7.09 (d, J=9.2Hz, 1H), 1.90 (s, 3H), 1.50 (s, 9H). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 100 MHz): 169.40, 164.63, 156.78, 151.62, 147.32, 134.11, 132.19, 132.06, 128.44, 127.65, 127.32, 126.86, 125.98, 125.37, 121.60, 119.76, 98.35, 96.59, 36.25, 30.37, 20.80. IR: ν(-CH_3) 2961.55 cm^{-1} (m); ν(-C≡C-) 2100.63 cm^{-1} (m); MS (FAB): m/z 3796.2 (calcd m/z 3796.2 for $[M+H]^+$). Anal. Calcd for $C_{138}H_{117}Cl_6O_{12}N_6Pt_3$, **2a**•6$CH_2Cl_2$•2Hexane: C, 54.19; H, 4.32; N, 2.50; Found: C, 53.07; H, 4.46; N, 2.56.

Self-Assembly of [Pt(4,4'-di-tert-butyl-2,2'-dipyridyl)(L_2)]$_4$, 2b: To a 100 mL two-necked round bottom flask containing Pt(4,4'-di-tert-butyl-2,2'-dipyridyl)Cl_2 (50.6 mg, 0.09 mmol), CuI (3 mg, 0.015 mmol) and **L**$_2$-H_2 (43.5 mg, 0.09 mmol) was added 60 mL of CH_2Cl_2 and followed by 0.3 mL of $NHEt_2$. The mixture was stirred at rt for 72 h. The mixture was passed through a short column to get rid of CuI. The solvent was removed under reduced pressure to afford the crude product, which was purified by column chromatography using dichloromethane:acetone (100:1 v/v). Yield: 15 mg (17%). ^{1}H NMR ($CDCl_3$, 400MHz): 9.94(d, J=6Hz, 1H), 8.80 (s, 1H), 8.02 (s, 1H), 7.71 (s, 1H), 7.67 (d, J=4.4Hz, 1H), 7.09 (s, 2H), 4.00 (m, 2H), 1.47 (s, 9H), 1.00 (m, 3H). ^{13}C NMR (CD_2Cl_2, 100 MHz): 164.52, 156.80, 154.76, 151.60, 132.79, 131.58, 129.70, 127.68, 127.07, 126.72, 126.55, 125.33, 119.71, 118.78, 99.26, 94.60, 65.48, 36.25, 30.38, 15.20. IR: ν(-CH_3) 2963.93 cm^{-1} (m); ν(-C≡C-) 2099.48 cm^{-1} (m); MALDI-TOF MS: m/z 3684.57 (calcd m/z 3684.29 for $[M+H]^+$). Anal. Calcd for $C_{138}H_{117}Cl_6O_{12}N_6Pt_3$, **2b**•3Hexane•$CH_2Cl_2$: C, 60.53 ; H, 5.33 ; N, 2.78 ; Found: C, 59.84; H, 5.53; N, 2.41.

Synthesis of [Pt(4,4'-di-tert-butyl-2,2'-dipyridyl)(L_1-H)$_2$], 3a: To a 100 mL two-necked round bottom flask containing Pt(4,4'-di-tert-butyl-2,2'-dipyridyl)Cl_2 (114.4 mg, 0.21 mmol), CuI (10 mg, 0.05 mmol) and **L**$_1$-H_2 (417.5 mg, 0.84 mmol) was added 40 mL of CH_2Cl_2 and followed by 0.1 mL of $NHEt_2$. The mixture was stirred at rt for 2 h. The mixture was passed through a short column to get rid of CuI. The solvent was removed under reduced pressure to afford the crude product, which was purified by column chromatography using dichloromethane:acetone (100:1 v/v). Yield: 140 mg (46.4%). ^{1}H NMR ($CDCl_3$, 400 MHz):

9.82(d, J=4Hz, 1H), 8.92 (d, J=2.8Hz, 1H), 8.40 (d, J=2.4Hz, 1H), 8.06 (d, J=2.4Hz, 1H), 7.68 (m, 3H), 7.21 (m, 3H), 6.98 (d, J=2.4Hz, 1H), 3.59 (s, 1H), 1.90 (s, 3H), 1.86 (s, 3H), 1.49 (s, 9H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz): 169.08, 168.94, 164.04, 156.24, 151.41, 146.61, 146.20, 133.81, 133.13, 132.40, 131.96, 131.12, 128.50, 127.82, 127.59, 127.38, 127.00, 125.69, 125.48, 125.16, 124.95, 124.13, 120.58, 120.06, 118.93, 98.51, 83.81, 80.26, 35.94, 30.29, 20.56. IR: ν(-C≡*CH*) 3294.82 cm^{-1} (m); ν(-*CH*$_3$) 2965.24 cm^{-1} (m); ν(-*C*≡*C*-) 2101.43 cm^{-1} (m); MALDI-TOF MS: m/z 1436.88 (calcd m/z 1437.13 for $[M+H]^+$). Anal. Calcd for $C_{138}H_{117}Cl_6O_{12}N_6Pt_3$, **3a**•3$CH_2Cl_2$: C, 54.69; H, 3.58; N, 1.66; Found: C, 53.98; H, 3.70; N, 1.99.

Scheme S1. Directed-Assembly of 2a and 2b



Synthesis of [Pt(4,4'-di-tert-butyl-2,2'-dipyridyl)(L_2-H)$_2$], 3b: To a 50 mL two-necked round bottom flask containing Pt(4,4'-di-tert-butyl-2,2'-dipyridyl)Cl_2 (160 mg, 0.3 mmol), CuI (10 mg, 0.05 mmol) and **L**$_2$-H_2 (551.4 mg, 1.2 mmol) was added 20 mL of CH_2Cl_2 and followed by 0.4 mL of $NHEt_2$. The mixture was stirred at rt for 0.5 h. The mixture was passed through a short column to get rid of CuI. The solvent was removed under reduced pressure to afford the crude product, which was purified by column chromatography using dichloromethane. Yield: 258 mg (62.3%). ^{1}H NMR ($CDCl_3$, 400MHz): 9.98(d, J=6Hz, 1H), 8.82 (d, J=2.4Hz, 1H), 8.30 (d, J=2.0Hz, 1H), 8.04 (d, J=2.0Hz, 1H), 7.71 (s, 1H), 7.66 (dd, J=6Hz and J=2.0Hz, 1H), 7.63 (s, 1H), 7.12 (m, 3H), 6.94 (d, J=9.2Hz, 1H), 4.00 (m, 2H), 3.53 (s, 1H), 1.47 (s, 9H), 1.04 (m, 3H). $^{13}C\{_1H\}$ NMR ($CDCl_3$, 100 MHz): 163.85, 156.22, 153.88, 153.76, 151.19, 132.36, 131.88, 131.18, 130.51, 130.08, 129.26, 127.65, 127.44, 126.82, 126.65, 126.55, 124.77, 122.80, 121.25, 119.70, 119.20, 119.02, 117.00, 99.25, 93.58, 83.55, 81.27, 65.27, 64.73, 60.30, 53.40, 35.80, 30.16, 14.85. IR: ν(-C≡CH) 3285.18 cm^{-1} (m); ν($-CH_3$) 2962.73 cm^{-1} (m); ν(-C≡C-) 2099.63 cm^{-1} (m); MALDI-TOF MS: m/z 1382.19 (calcd m/z 1381.18 for $[M+H]^+$). Anal. Calcd for $C_{138}H_{117}Cl_6O_{12}N_6Pt_3$, **3b**•1.5 CH_2Cl_2: C, 60.31; H, 4.33; N, 1.85; Found: C, 59.12; H, 4.46; N, 2.25.

Directed-Assembly of 2a: To a 100 mL two-necked round bottom flask containing Pt(4,4'-di-tert-butyl-2,2'-dipyridyl)(**L**$_1$-H)$_2$ (28.6 mg, 0.02 mmol), CuI (2 mg, 0.01 mmol) and Pt(4,4'-di-tert-butyl-2,2'-dipyridyl)Cl_2 (10.6mg, 0.02mmol) was added 40 mL of CH_2Cl_2 and followed by 0.4 mL of $NHEt_2$. The mixture was stirred at rt for 72 h. The mixture was passed through a short column to get rid of CuI. The solvent was removed under reduced pressure to afford the crude product, which was purified by column chromatography using dichloromethane:acetone (50:1 v/v). Yield: 8.6 mg (22.8%). NMR spectroscopic data of **2a** prepared this way are identical to those of **2a** prepared by self-assembly reactions.

Directed-Assembly of 2b: To a 100 mL two-necked round bottom flask containing Pt(4,4'-di-tert-butyl-2,2'-dipyridyl)(**L**$_2$-H)$_2$ (69 mg, 0.05 mmol), CuI (10 mg, 0.05 mmol) and Pt(4,4'-di-tert-butyl-2,2'-dipyridyl)Cl_2 (53.4 mg, 0.05mmol) was added 30 mL of CH_2Cl_2 and followed by 0.5 mL of $NHEt_2$. The mixture was stirred at rt for 20 min. The mixture was passed through a short column to get rid of CuI. The solvent was removed under reduced pressure to afford the crude product, which was purified by column chromatography using dichloromethane:acetone (100:1 v/v). Yield: 16 mg (16.7%). NMR spectroscopic data of **2b** prepared this way are identical to those of **2b** prepared by self-assembly reactions.

3. Detailed description of photophysical studies.

Solid-state films of **2a** and **3a** were spin-casted from their dichloromethane solutions.

UV-vis absorption and PL spectra of thin films of **2a** and **3a** were shown in Figure S8. The excitation wavelength used to take the PL spectra is 367 nm. It is evident that the PL spectra of the solid-state films red-shifted and broadened a great deal with respect to the PL spectra of their solutions. Furthermore, the short-wavelength emissions that are apparent in the PL spectra of the solutions totally disappeared, indicating that the energy transfer from intraligand excited states to ^{3}MLCT become more efficient via intermolecular interactions.

Light-emitting diodes (LEDs) with structure ITO/PEDOT:PSS/EL layer/CsF/Al,[2] where PEDOT:PSS denotes poly(ethylene dioxythiophene) doped with poly(styrene sulfonate), were first made with **2a** and **3a** as the EL layer. The EL spectra resemble the PL spectra of the solid-state films, as shown in Figure S9. However, the device performance is rather poor, with highest brightness of less than 20 cd/m^2. We believe that poor device performance is a result of concentration quenching of the triplet emissions of 2a and 3a.[3]

To decrease triplet quenching caused by intermolecular interactions while keeping the carrier-transport ability, **2a** or **3a** was doped into poly(*N*-vinylcarbazole) (PVK),[4] a well-known hole-transport polymer via solution blending. The PL spectra of spin-coated films of the blends at different weight ratio are shown in Figure S10. The excitation wavelength is 336 nm, close to the absorption peak of PVK. The emissions from the **2a** and **3a** guests have experienced significant blue-shifts toward their corresponding solution triplet emissions, indicating that intermolecular interactions of **2a** and **3a** have been greatly reduced in their PVK blend films. It is also evident from Figure S10 that the energy transfer from PVK to **3a** is much more efficient than that to **2a**, presumably via efficient energy transfer from intraligand singlet excited states of PVK to intraligand singlet excited states of **3a** owing to the presence of uncoordinated alkynylnaphthyl moieties in **3a**. In **2a**, all the alkynylnaphthyl moieties are coordinated to Pt(II) centers, which causes red-shift of intraligand $\pi \rightarrow \pi^*$ transitions and thus results in less efficient energy transfer from PVK.

Compared with the PL spectra of the blends, the EL spectra of **2a** and **3a** exhibited mostly the long-wavelength emission, as shown in Figure S11. This implies that direct charge-trapping,[5] but not other processes such as inter/intra-molecular energy transfer, dominates in the EL process of the PVK blends of **2a** and **3a**. Consistent with this, the brightness and efficiency of LEDs based on the blends have increased greatly, as shown in

Table 2 of the manuscript. For the blend with 5% **2a**, the maximum brightness can reach 5470 cd/m^2 with maximum luminous efficiency of 0.93 cd/A.

References

1. Lee, S.J.; Hu, A.; Lin, W. *J. Am. Chem. Soc*. **2002**, *124*, 12948-12949.
2. (a) Jabbour, G.E.; Kippelen, B.; Armstrong, N.R.; Peyghambarian, N. *Appl. Phys. Lett*. **1998**, *73*, 1185. (b) Piromreun, P.; Oh, H.; Shen, Y.; Malliaras, G.G.; Scott, J.C.; Brock, P.J. *Appl. Phys. Lett*. **2000**, *77*, 2403.
3. (a) Connick, W.B.; Geiger, D.; Eisenberg, R. *Inorg. Chem*. 1**999**, *38*, 3264. (b) Kalinowski, J.; Stampor, W.; Mezyk, J.; Cocchi, M.; Virgili, D.; Fattori, V.; Di Marco, P. *Phys. Rev. B* **2002**, *66*, 235321.
4. Yang, M.-J.; Tsutsui, T. *Jpn. J. Appl. Phys*. **2000**, *39*, 828.
5. (a) Lamansky, S.; Djurovich, P.; Murphy, D.; Abdel-Razzaq, F.; Lee, H.E.; Adachi, C.; Burrows, P.E.; Forrest, S.R.; Thompson, M.E. *J. Am. Chem. Soc*. **2001**, *123*, 4304. (b) Gong, X.; Ostrowski, J.C.; Moses, D.; Bazan, G.C.; Heeger, A.J. *Adv. Funct. Mater*. **2003**, *13*, 439.

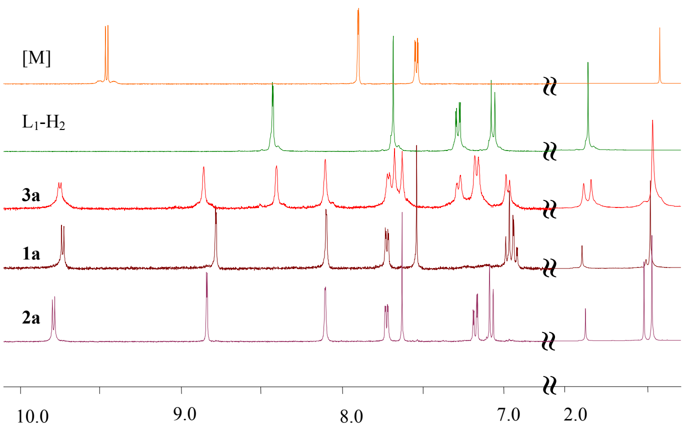


Figure S1. ^{1}H NMR Spectra of Pt(4,4'-dtbPy)Cl_2 ([M]), **L**$_1$-H_2, and **1a-3a** in CD_2Cl_2

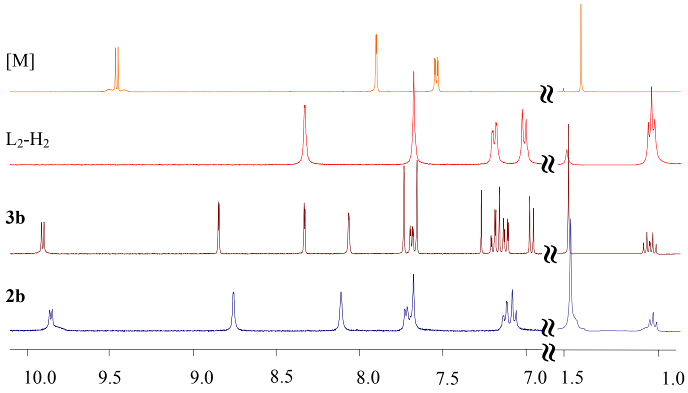


Figure S2. ^{1}H NMR Spectra of Pt(4,4'-dtbPy)Cl_2 ([M]), **L**$_2$-H_2, and **2b-3b** in CD_2Cl_2

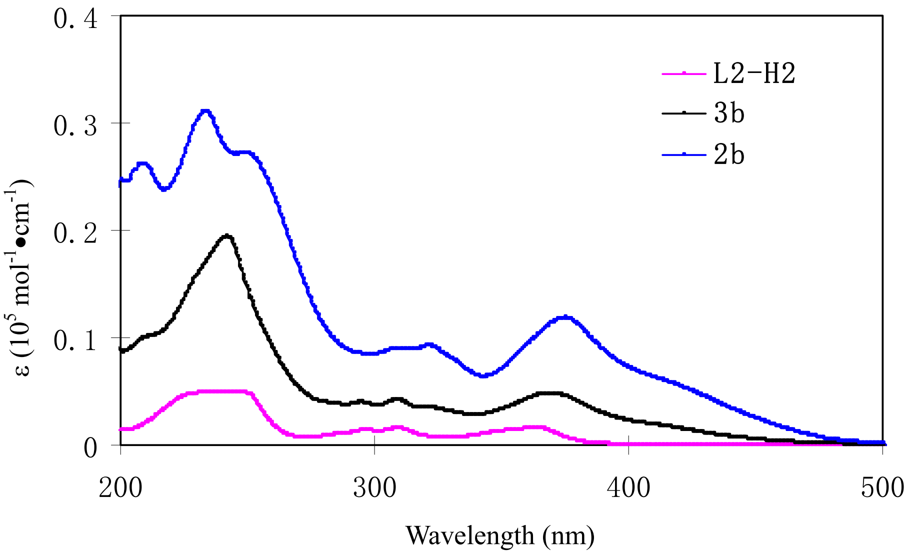


Fig S3. UV-vis spectra of **L**$_2$-H_2, **2b**, and **3b** in CH_2Cl_2.

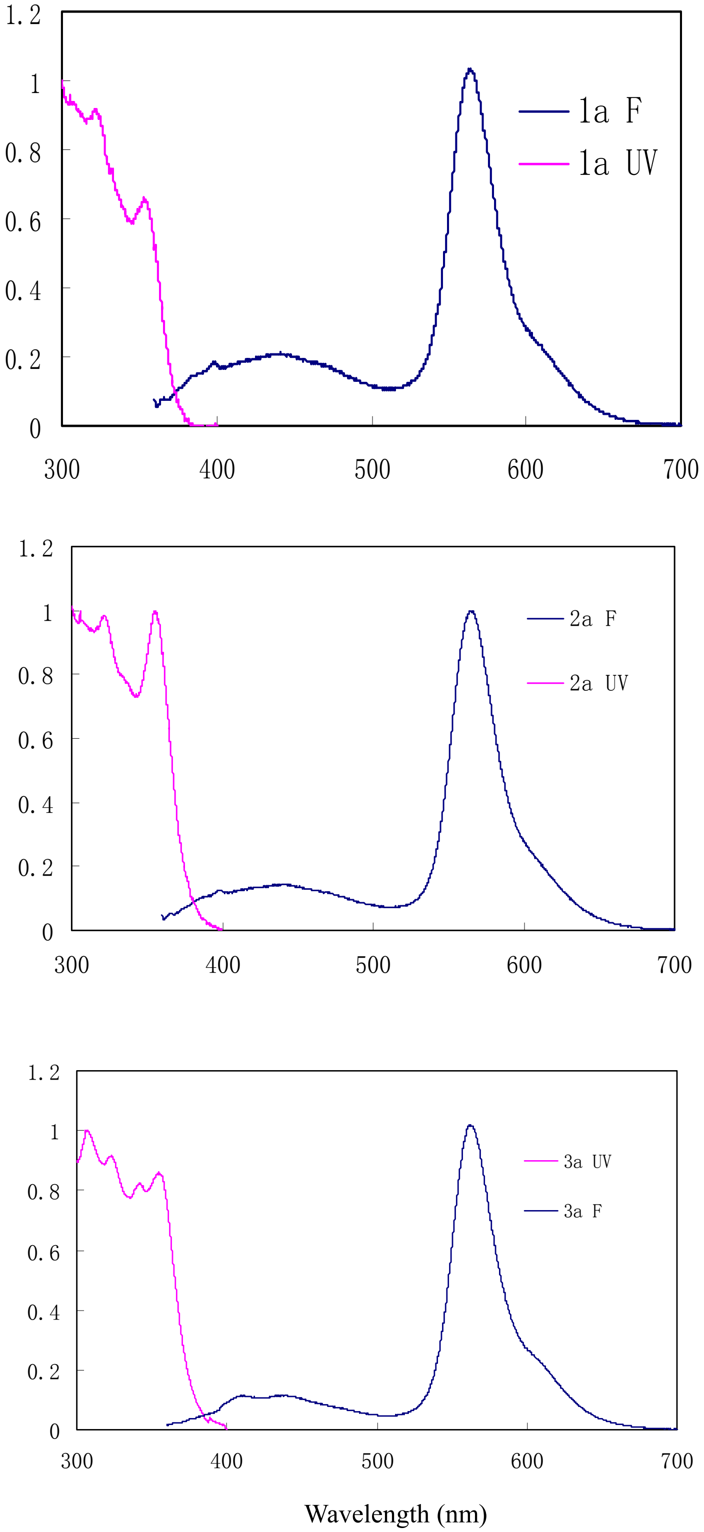


Figure S4. Normalized excitation and PL spectra of **1a-3a** in CH_2Cl_2.

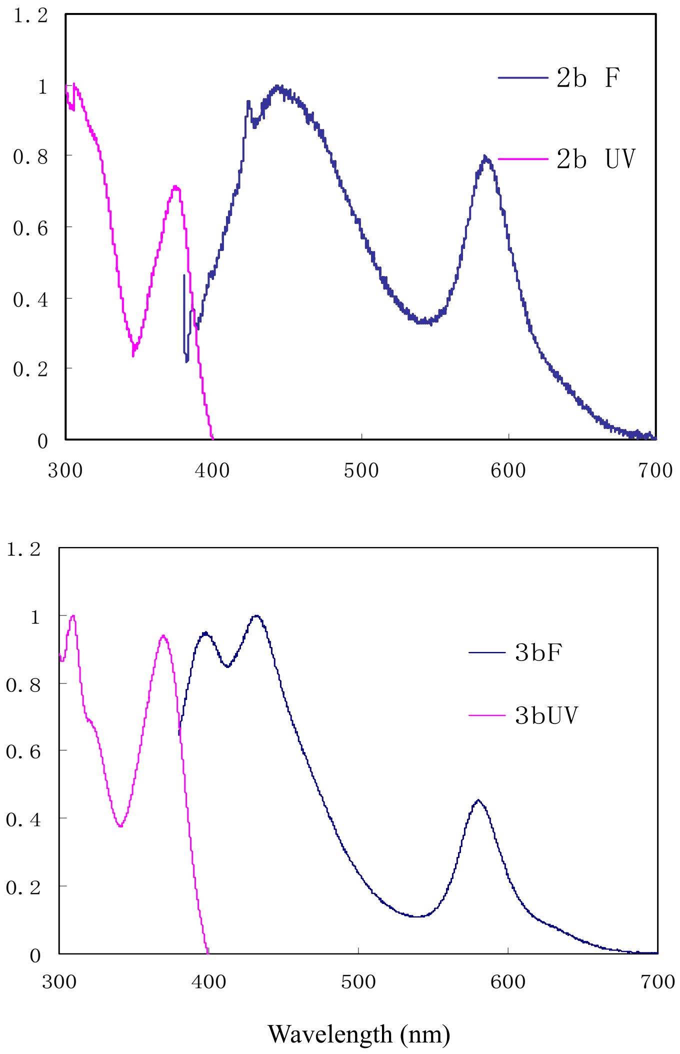


Figure S5. Normalized excitation and PL spectra of **2b** and **3b** in sCH$_2$Cl$_2$.

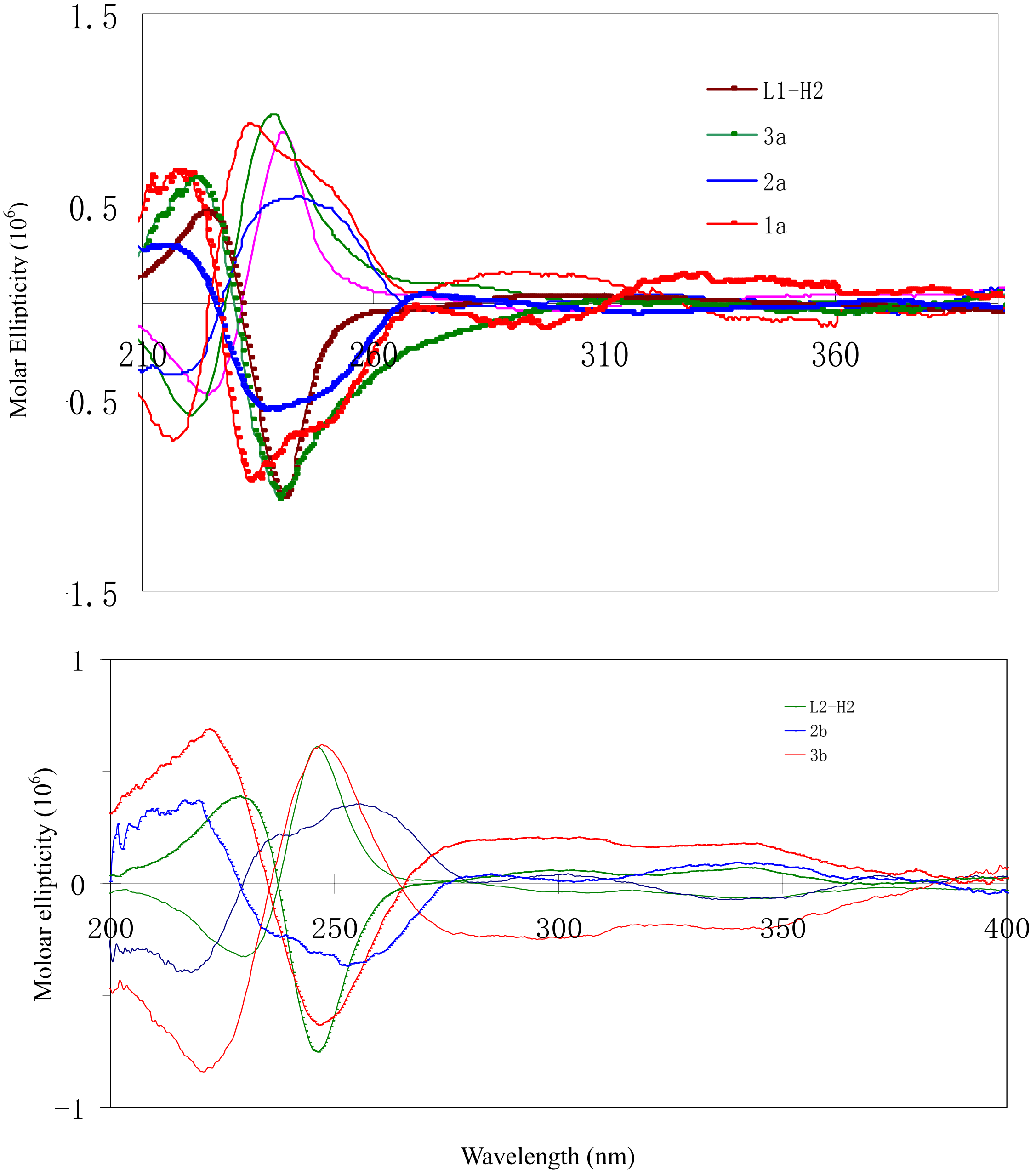
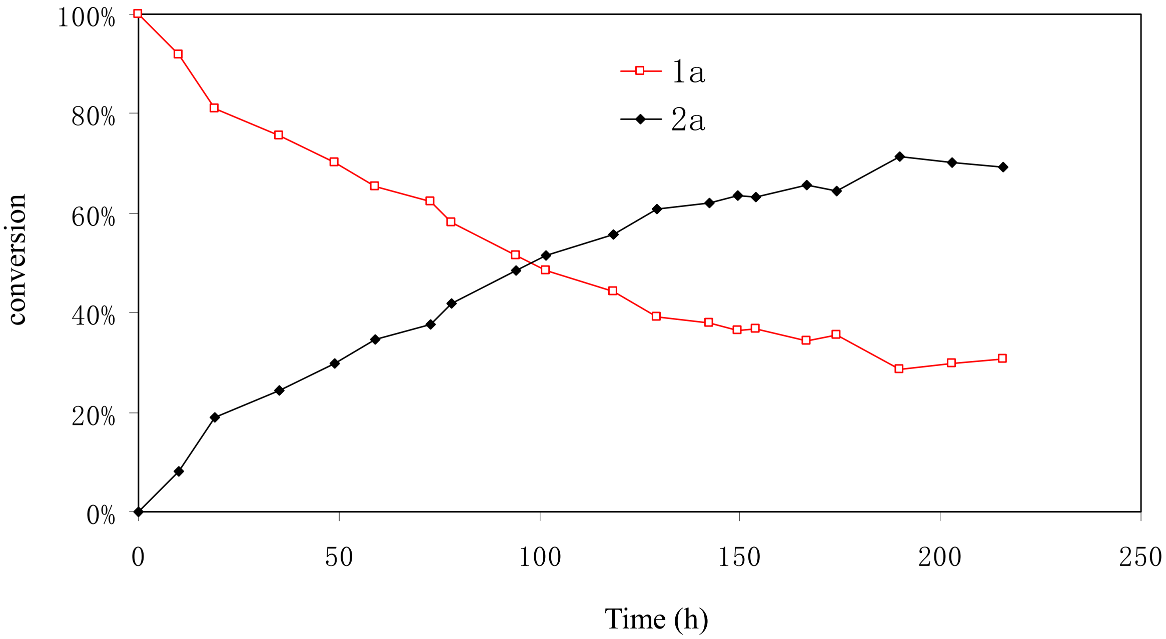


Fig S6. Top, CD spectra of **L**$_1$-H$_2$ and **1a-3a** in CH$_2$Cl$_2$. Bottom, CD spectra of **L**$_2$-H$_2$, **2b**, and **3b** in CH$_2$Cl$_2$.



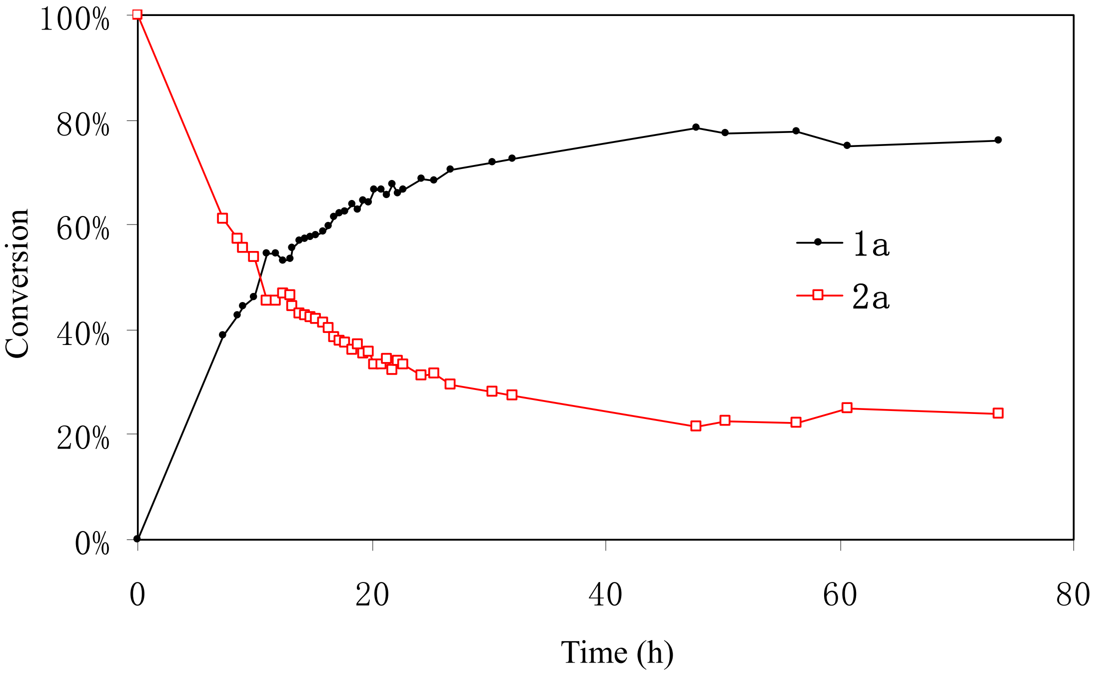
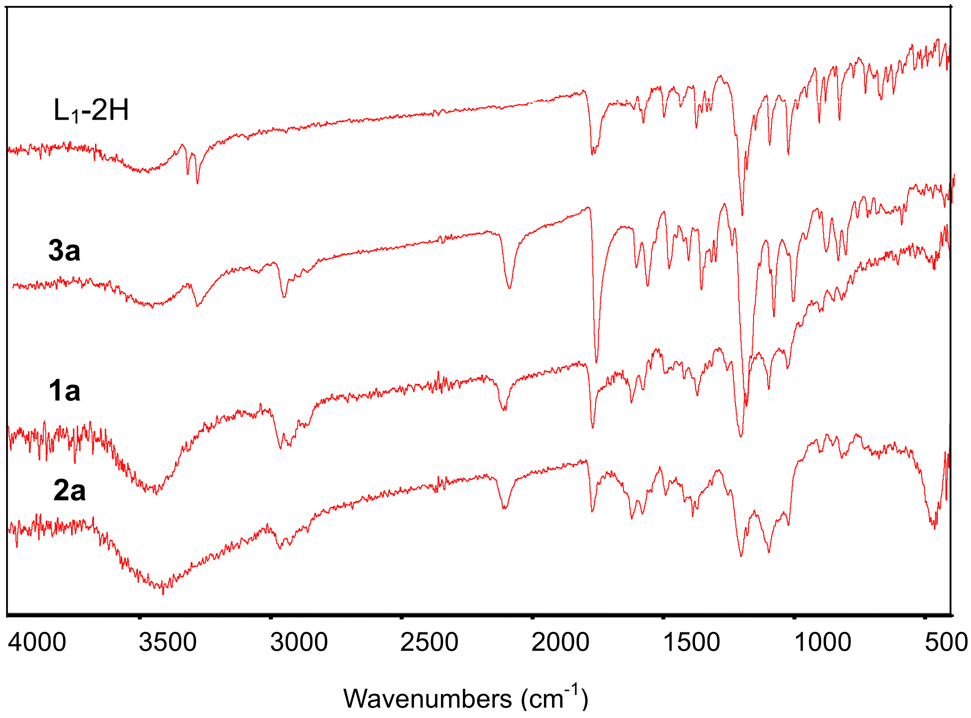


Figure S7. Time profile for the conversion of **1a** to **2a** in CD_2Cl_2 at rt. The initial concentrations of **1a** are 4.02 and 12.3 mM for the top and bottom figure, respectively.



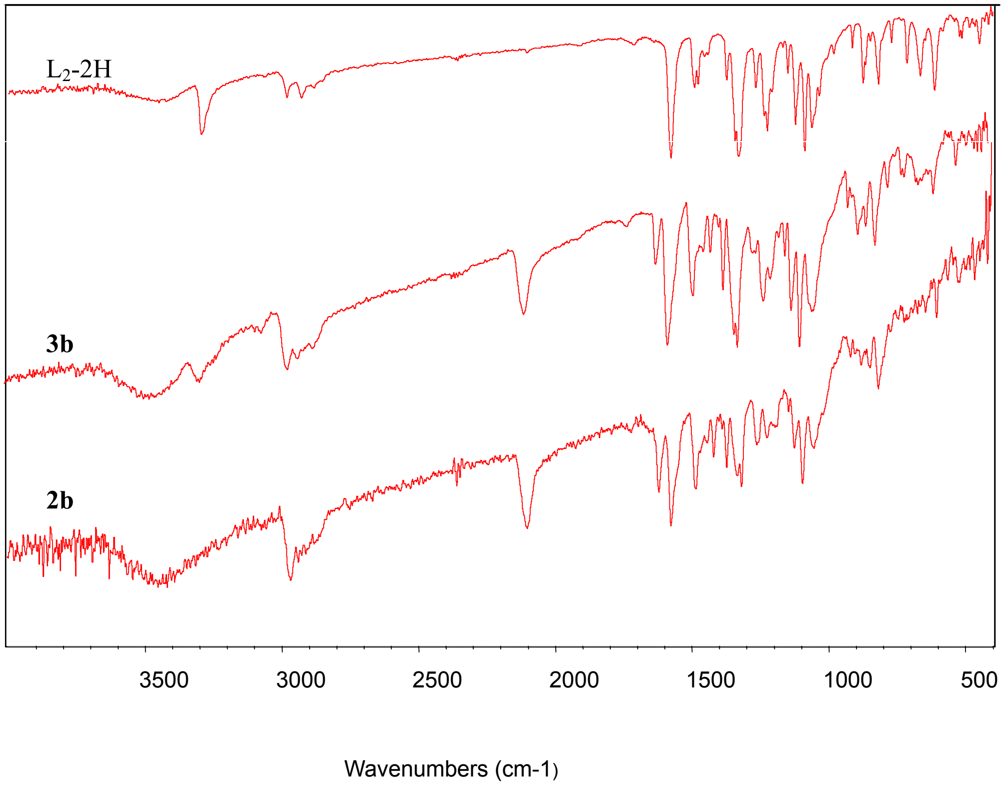
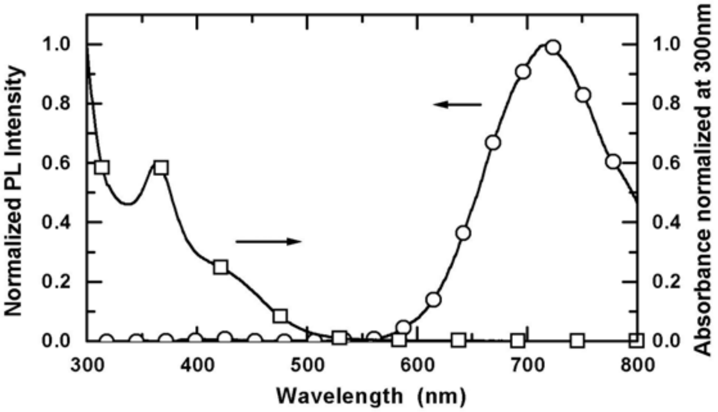


Figure S8. Top, IR spectra of L_1-H_2, and **1a-3a**. Bottom, IR spectra of L_2-H_2, and **2b-3b**



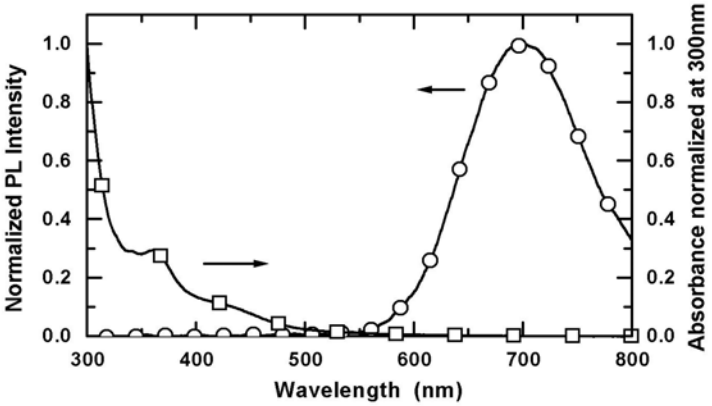


Fig S9. Top, UV-vis and PL spectra of spin-coated films of **2a**. Bottom, UV-vis and PL spectra of spin-coated films of **3a**. The PL spectra were taken with an excitation wavelength of 367 nm.

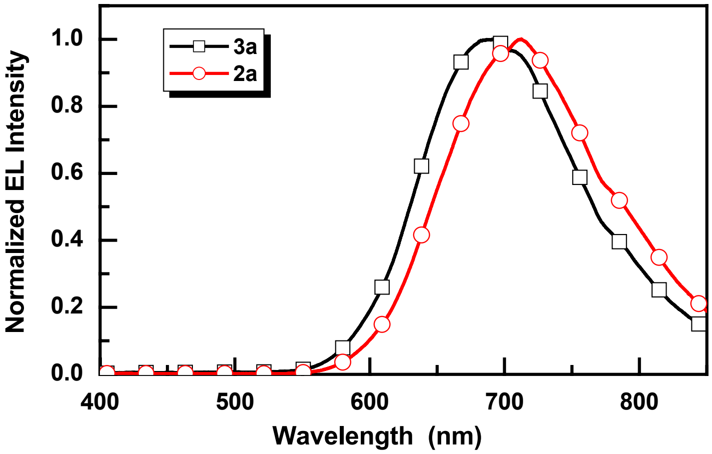
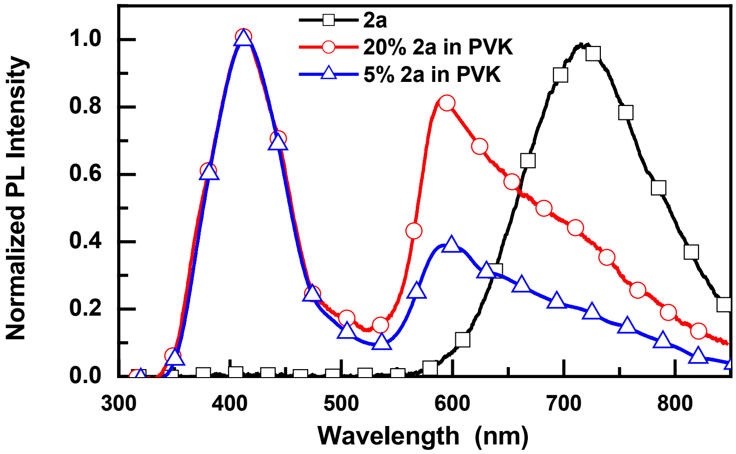


Fig S10. Normalized EL of **2a** and **3a**.



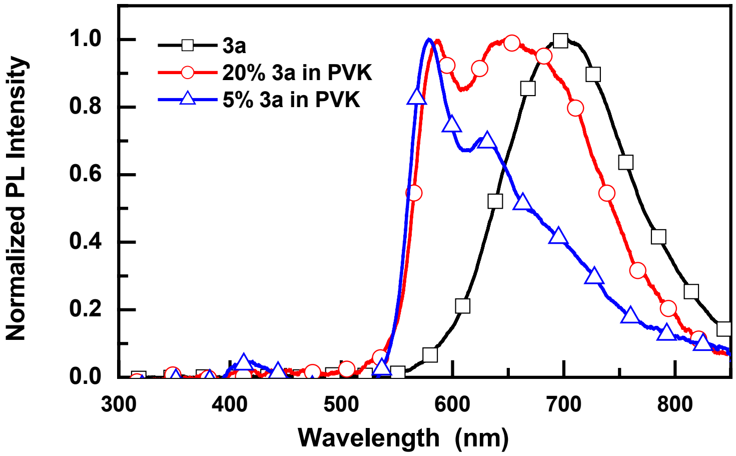


Fig S11. Normalized PL spectra of thin films, 20% blend in PVK, and 5% blend in PVK of **2a** (top) and **3a** (bottom).

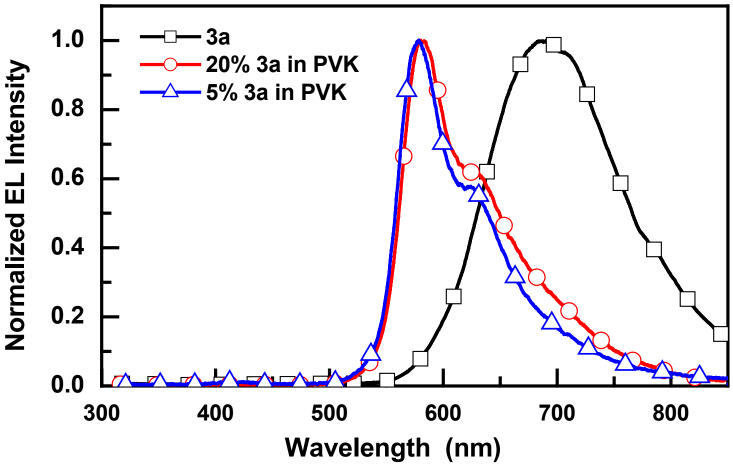


Fig S12. Normalized EL spectra of thin films, 20% blend in PVK, and 5% blend in PVK of **3a**.