Novel OLEDs from Emissive Photopatterned Polymer Brushes

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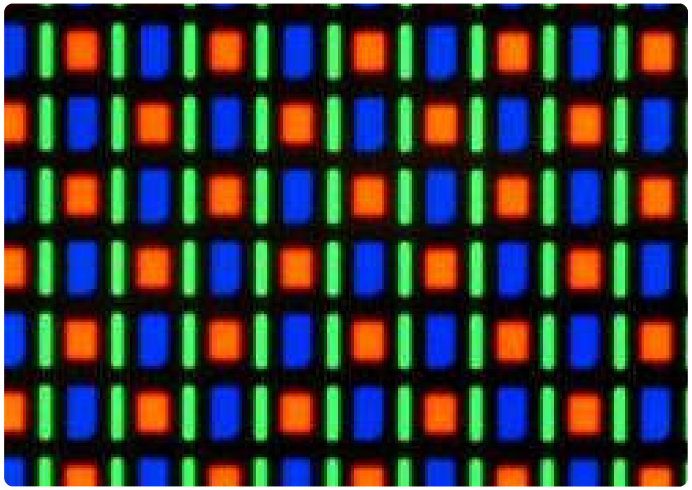
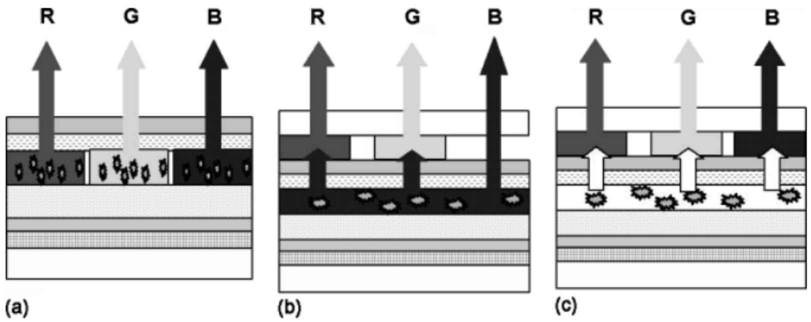
WIPF GROUP CURRENT LITERATURE

JULY 22ND, 2017

OLED Pixel Displays



- A pixel is typically made of three *subunit* pixels, one of red, blue, and green
- Various colors are generated by 'turning on' individual subunits in an area

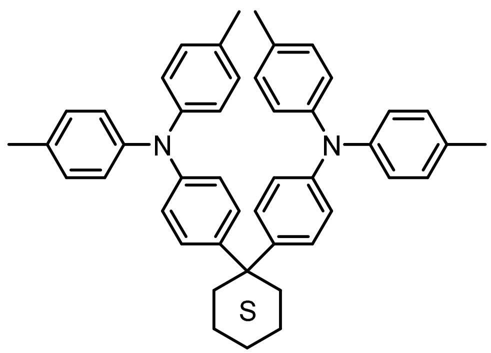


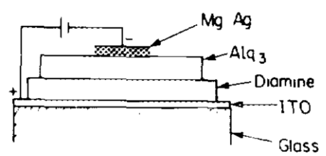
- OLED displays are typically patterned in one of the above three methods

PenTile RGBG matrix technology explained. https://www.oled-info.com/pentile

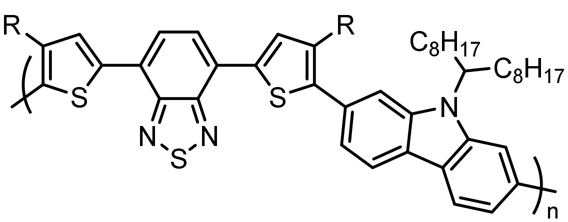
Geffroy, B.; le Roy, P.; Prat, C., *Polymer International* **2006**, *55* (6), 572-582.

Typical OLED Displays





- First efficient/low voltage OLED diode
- Emission at 550 nm, green light

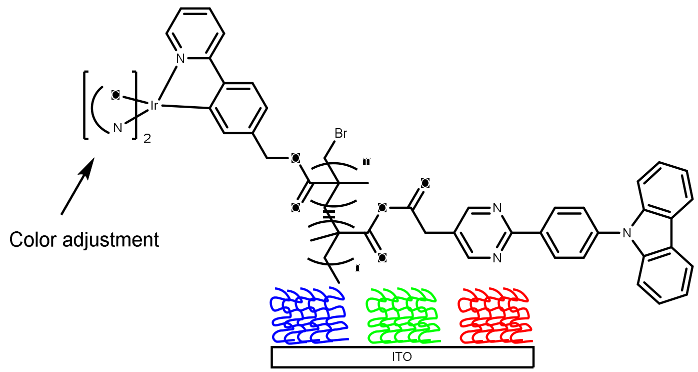


- Developed into red-emissive diodes
- Originally suffered from solubility problems

- OLED production suffers from
  - Cost of production
  - Limited patterning ability
  - Fabrication complexity
  - Use of undesirable reagents

1. Tang, C. W.; VanSlyke, S. A., *Appl. Phys. Lett.* **1987**, *51* (12), 913-915.
2. Lombeck, F.; Di, D.; Yang, L.; Meraldi, L.; Athanasopoulos, S.; Credgington, D.; Sommer, M.; Friend, R. H. *Macromolecules* **2016**, *49* (24), 9382-9387.
3. Page, Z. A.; Narupai, B.; Pester, C. W.; Bou Zerdan, R.; Sokolov, A.; Laitar, D. S.; Mukhopadhyay, S.; Sprague, S.; McGrath, A. J.; Kramer, J. W.; Trefonas, P.; Hawker, C. J. *ACS Central Science* **2017**, *3* (6), 654-661.

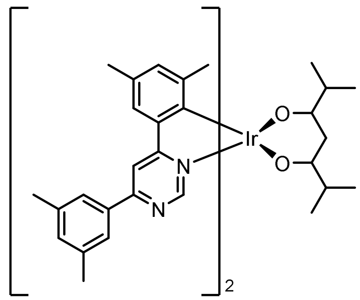
Novel Emissive Polymer Brushes



- Co-polymer brushes bound to indium tin oxide
- Color adjustment based on pyridine/quinoline ligands
- Ir(III) plays multiple roles

Page, Z. A.; Narupai, B.; Pester, C. W.; Bou Zerdan, R.; Sokolov, A.; Laitar, D. S.; Mukhopadhyay, S.; Sprague, S.; McGrath, A. J.; Kramer, J. W.; Trefonas, P.; Hawker, C. J. *ACS Central Science* **2017,** *3* (6), 654-661.

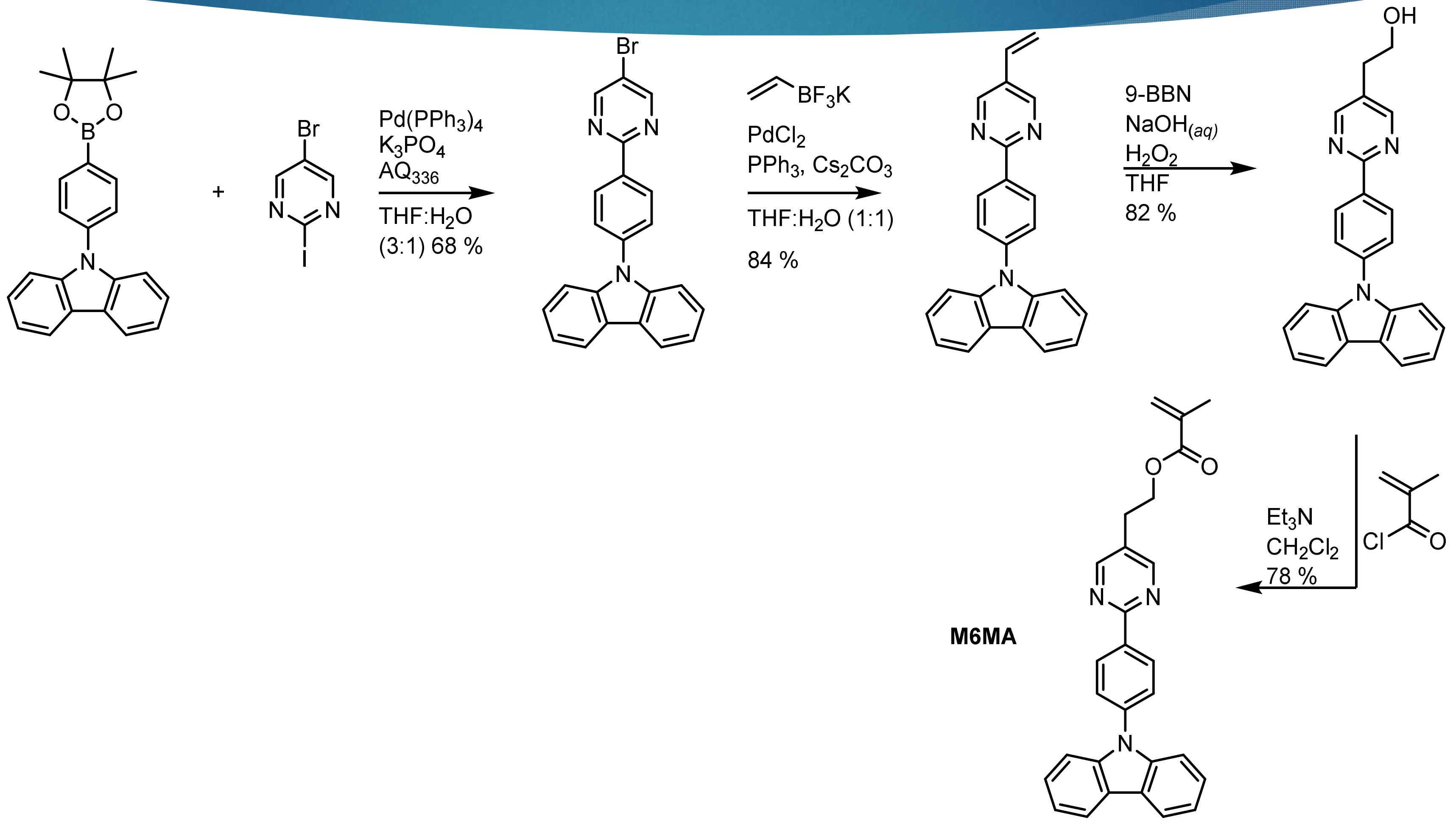
Ir(III) Complexes



- Ir(III) complexes used as dopants in OLED devices
  - High photoluminescence quantum yield
  - Stable
  - Spectral tunability
- Covalent Ir attachment improves device longevity

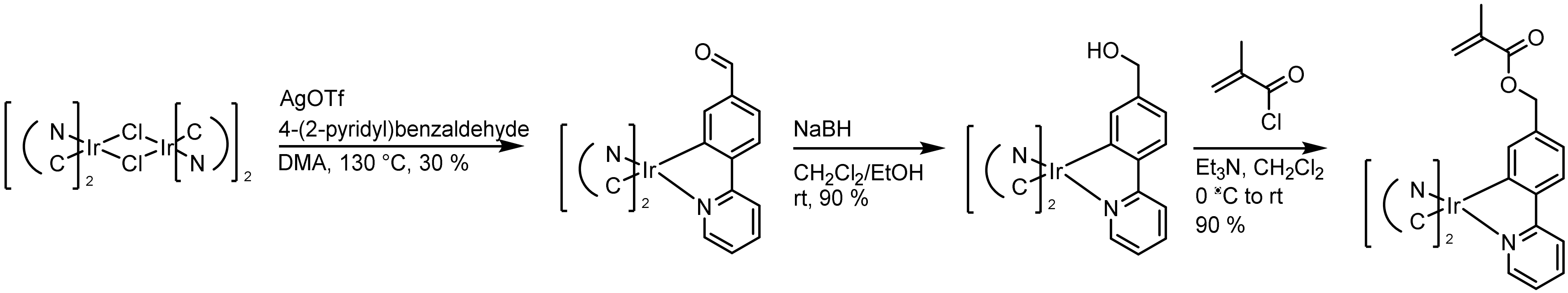
1. Deng, Y.-L.; Cui, L.-S.; Liu, Y.; Wang, Z.-K.; Jiang, Z.-Q.; Liao, L.-S. *Journal of Materials Chemistry C* **2016,** *4* (6), 1250-1256.
2. Page, Z. A.; Narupai, B.; Pester, C. W.; Bou Zerdan, R.; Sokolov, A.; Laitar, D. S.; Mukhopadhyay, S.; Sprague, S.; McGrath, A. J.; Kramer, J. W.; Trefonas, P.; Hawker, C. J. *ACS Central Science* **2017,** 3 (6), 654-661.

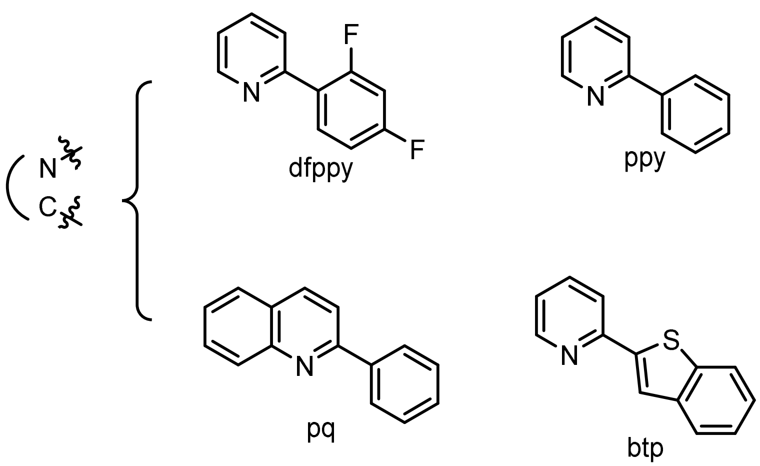
Host Monomer Synthesis



Page, Z. A.; Chiu, C.-Y.; Narupai, B.; Laitar, D. S.; Mukhopadhyay, S.; Sokolov, A.; Hudson, Z. M.; Bou Zerdan, R.; McGrath, A. J.; Kramer, J. W.; Barton, B. E.; Hawker, C. J., *ACS Photonics* **2017**, *4* (3), 631-641.

Ir(III) Co-monomer Synthesis

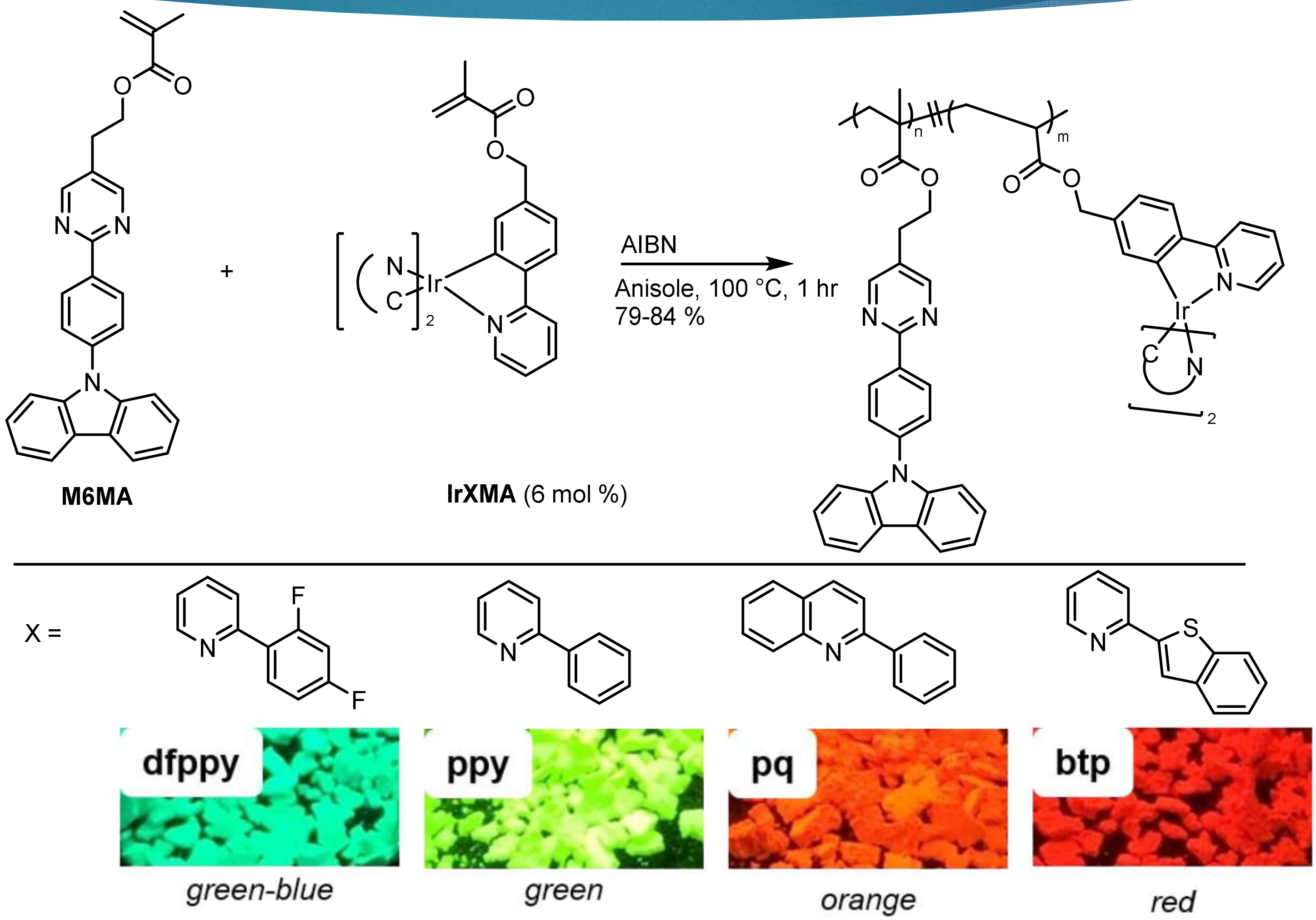




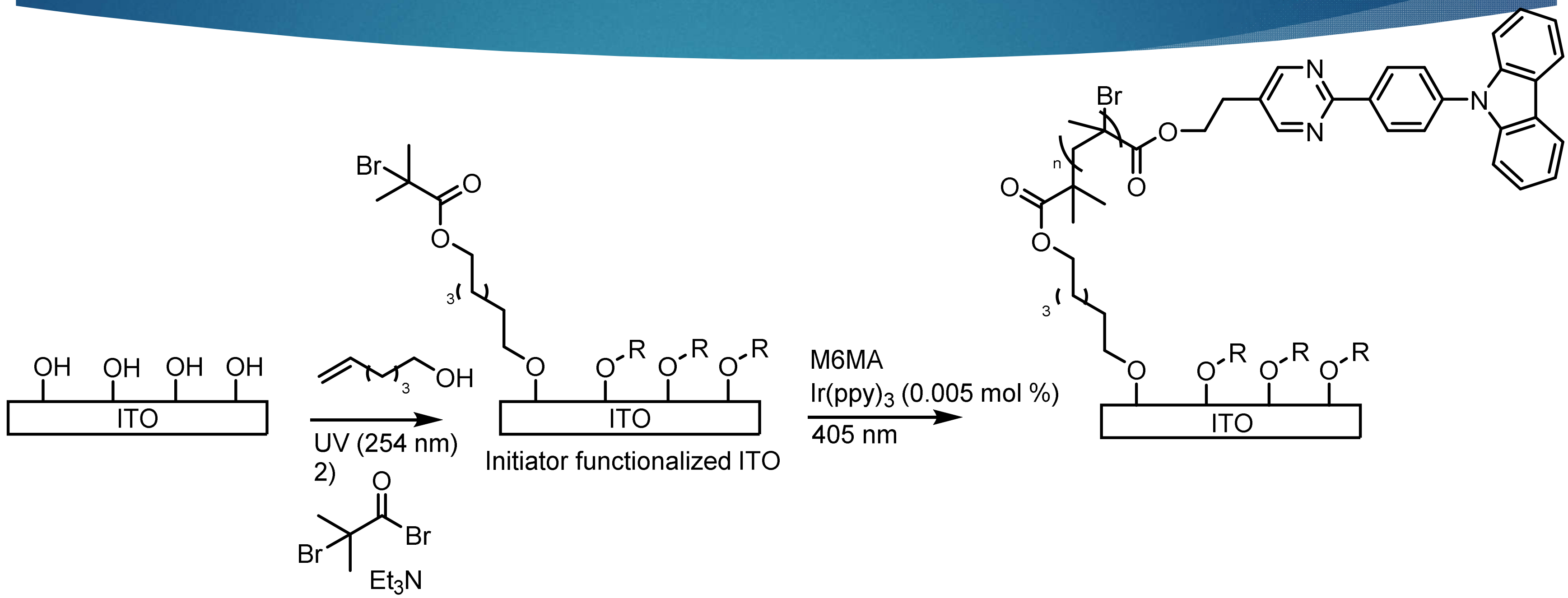
- Different triplet (T_1) energy dictates emission colors

Page, Z. A.; Narupai, B.; Pester, C. W.; Bou Zerdan, R.; Sokolov, A.; Laitar, D. S.; Mukhopadhyay, S.; Sprague, S.; McGrath, A. J.; Kramer, J. W.; Trefonas, P.; Hawker, C. J. *ACS Central Science* **2017,** 3 (6), 654-661.

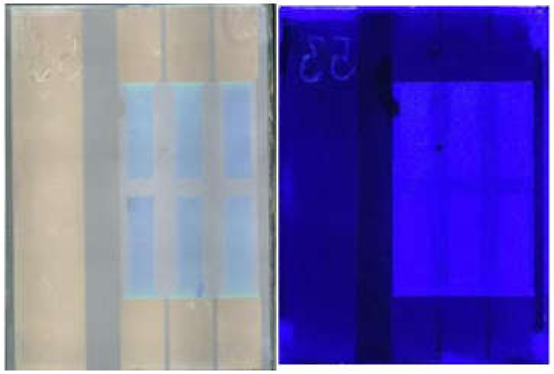
Monomer Compatability Tests



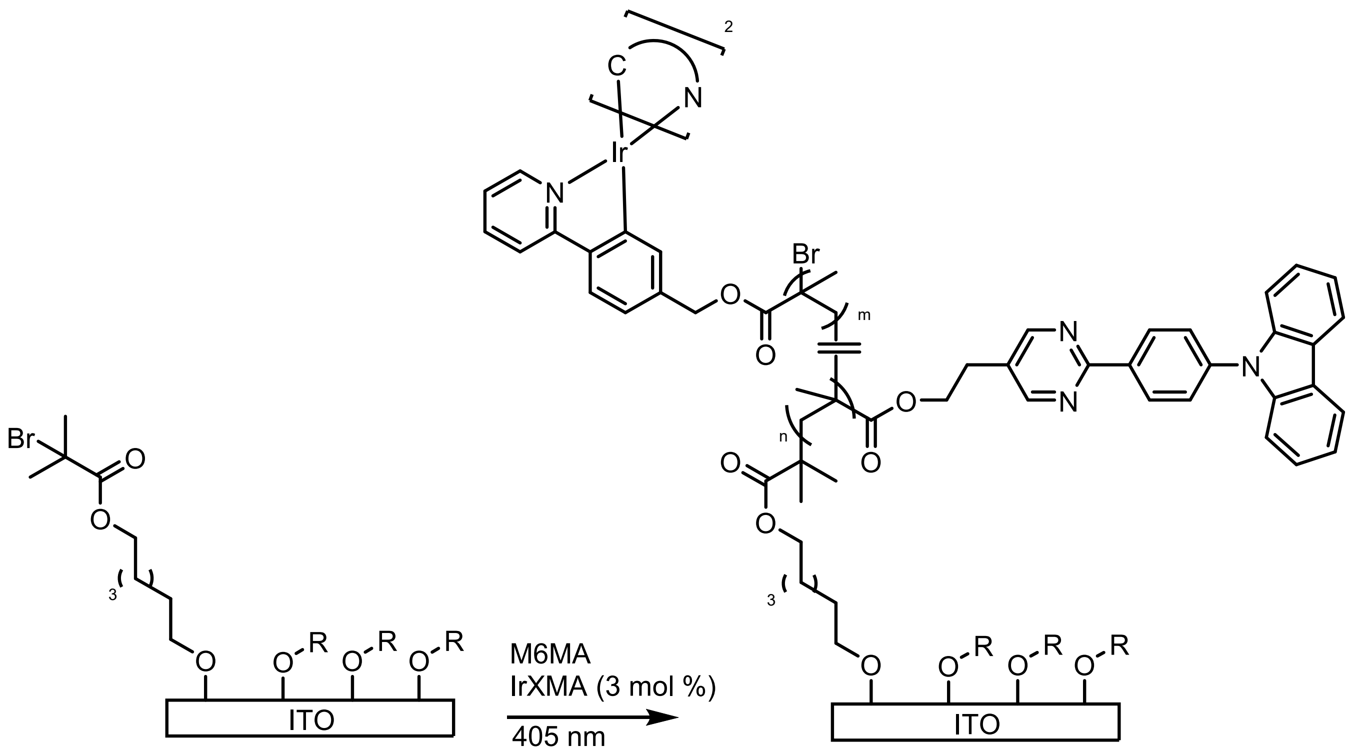
Homopolymer Grafting



- UV activated addition of 5-hexenol followed by acetylation with BIBB
- Provides polyermization initiation sites covalently attached to the surface
- $Ir(ppy)_3$ as just photocatalyst, not color-dopant



General Co-Polymer Grafting

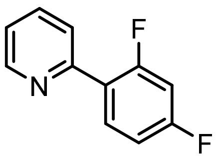


- Larger quantities of IrXMA (compared to $Ir(ppy)_3$) reduced the amount of light required for brush growth

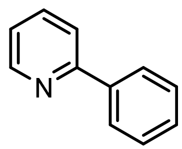
General Co-Polymer Grafting

Polymer Photoluminescence

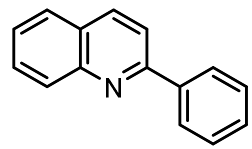
dfppy



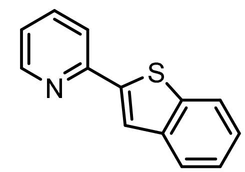
ppy

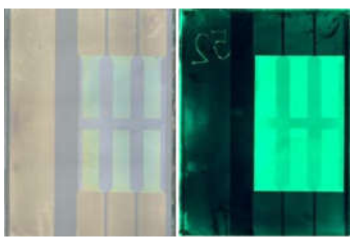


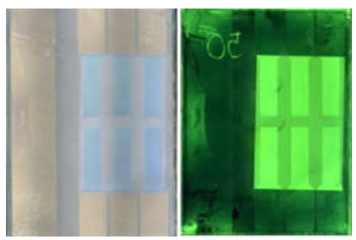
pq

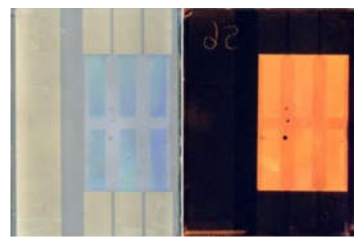


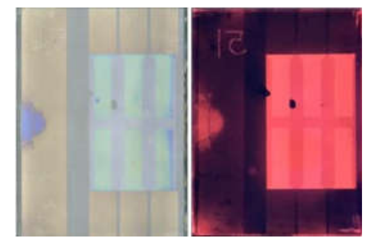
btp

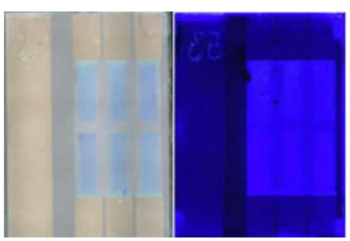


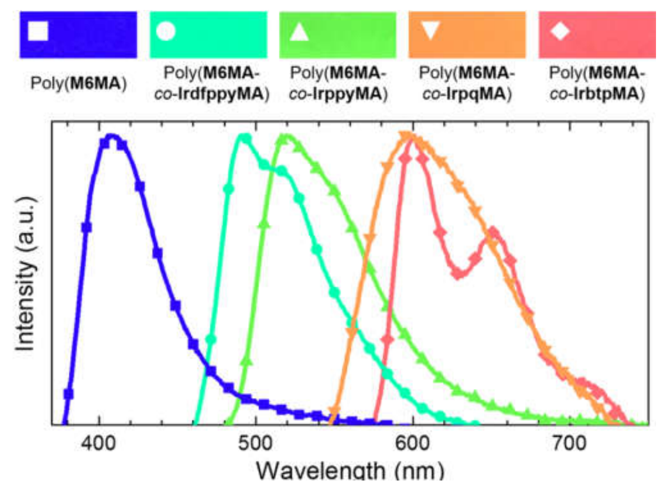








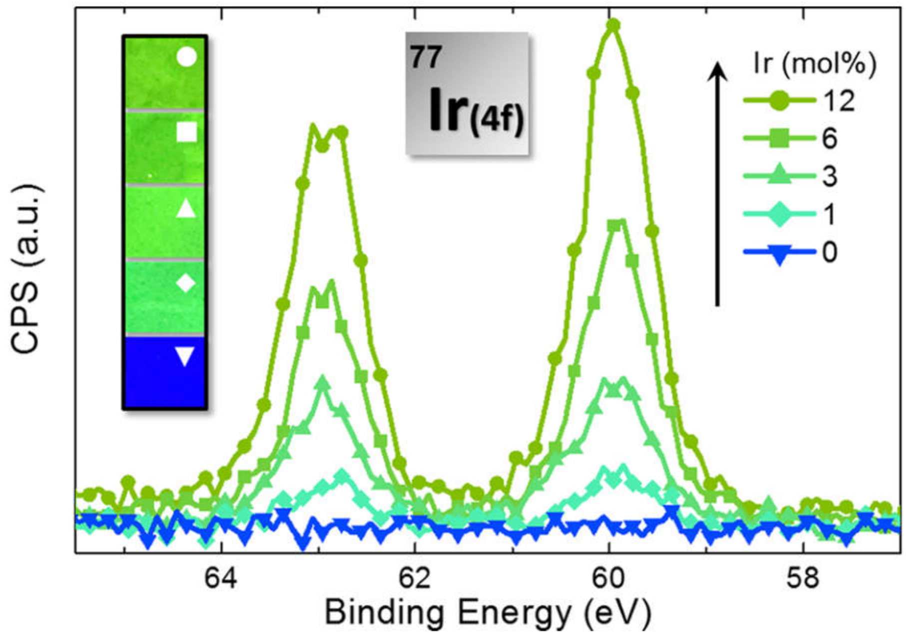




- Little to no residual blue fluorescence
  - Efficient energy transfer to Ir(III) dopants

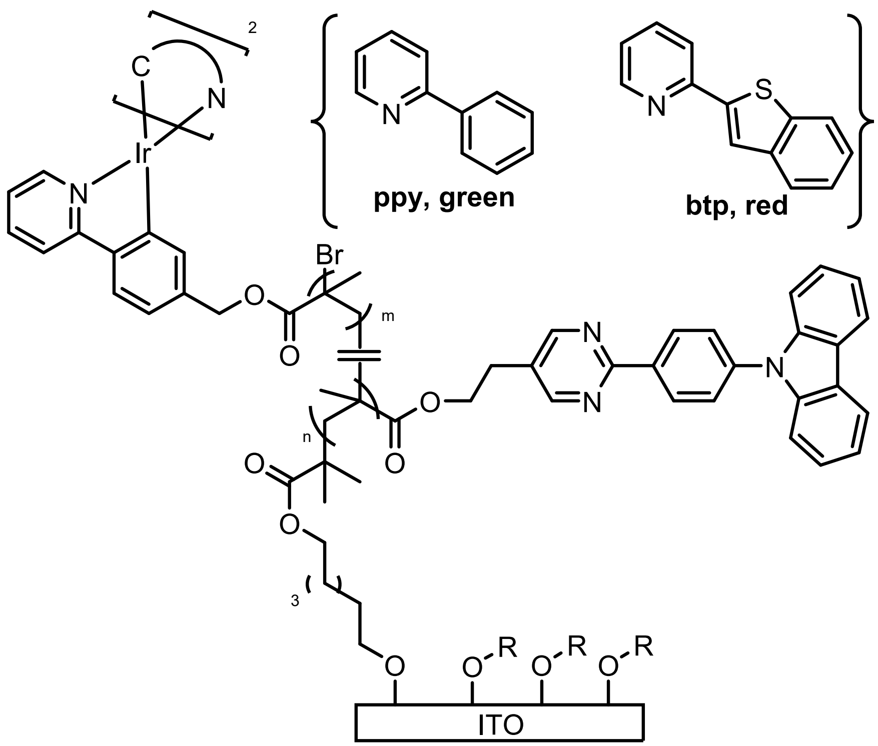
Varying Ir(III) Incorporation

- Higher loadings lead to emission broadening and bathochromic shift
- Indication that specific doping and tunable optical performances is available

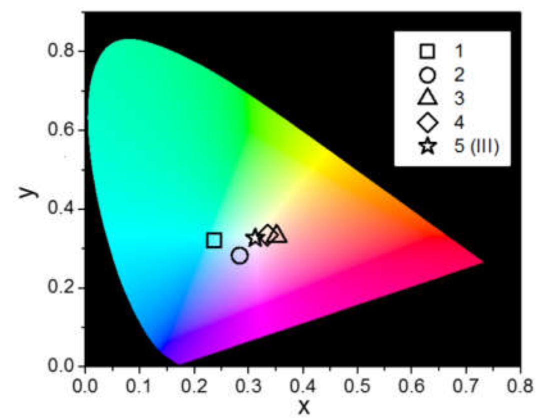


Generating a White Brush

- White emission in typical arrays is generated by lighting all three RGB subunits
- Ternary co-polymer brush generation with small doping quantities of green and red Ir(III) monomers



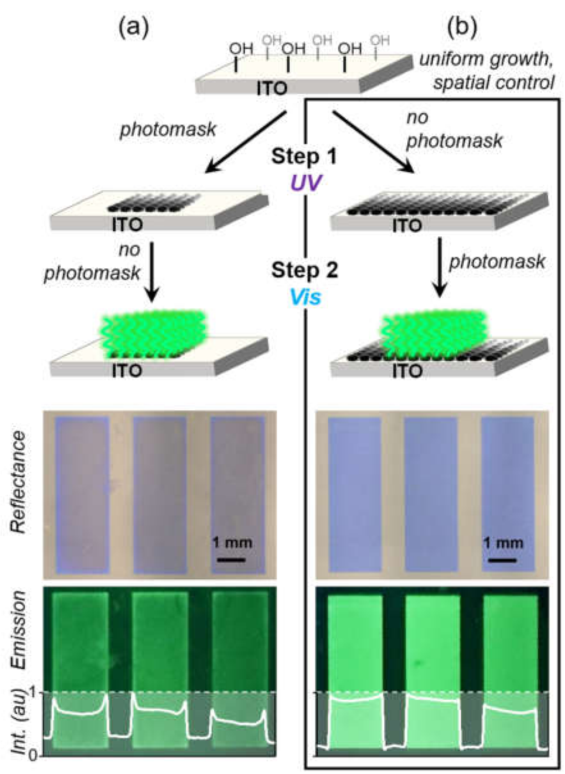
Sample	IrppyMA (mol %) (Green)	IrbtpMA (mol %) (Red)	CIE (x,y)
1	0.05	0.20	0.23, 0.32
2	0.23	0.15	0.28, 0.28
3	0.40	0.20	0.35, 0.33
4	0.32	0.20	0.33, 0.33
5	0.25	0.195	0.31, 0.33



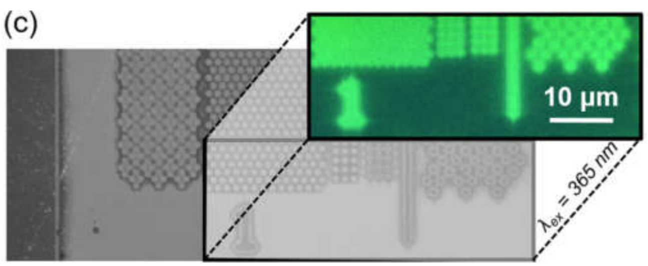
- Matches white-point following the 1931 Commission Internationale de L'Eclairage (CIE) guidelines

Further Tests – Spatial Control

- Pixel arrays have defined architectures
- Significant need for spatial control of the emissive brushes



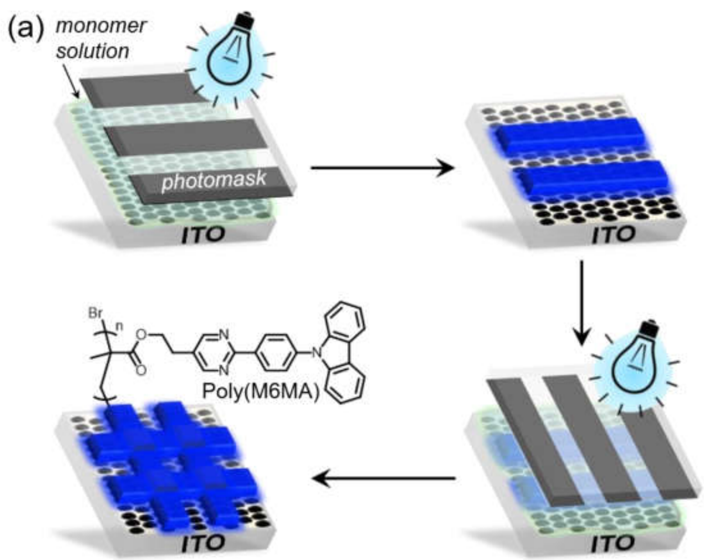
- Notable color difference between methods
  - Likely due to brush height
- Improved uniformity with applying photomask for polymerization (step 2)
  - This method was used for all further tests



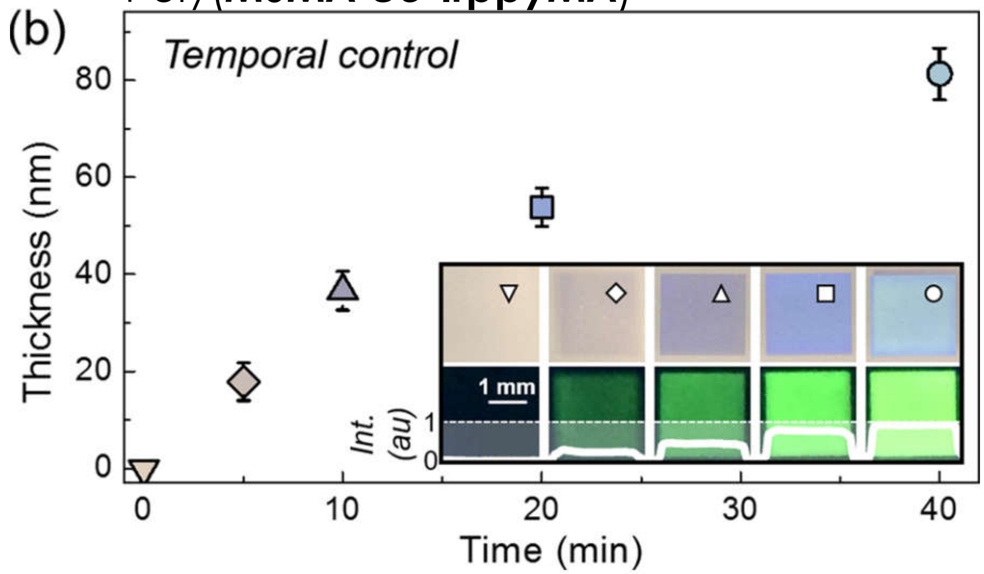
- Methodology delivered brush patterns with micron level resolution

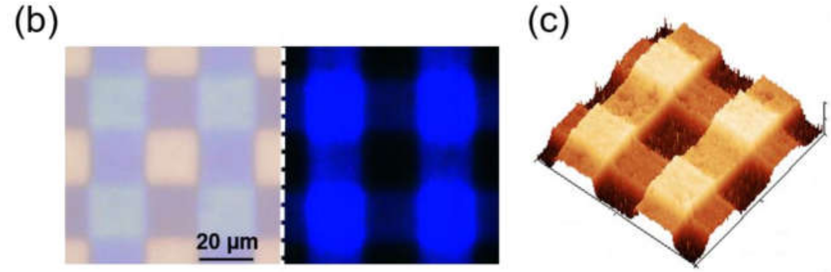
Further Tests – Temporal Control

- OLED stack layer thicknesses are critical to device performance
- Clear correlation between polymerization time and brush thickness

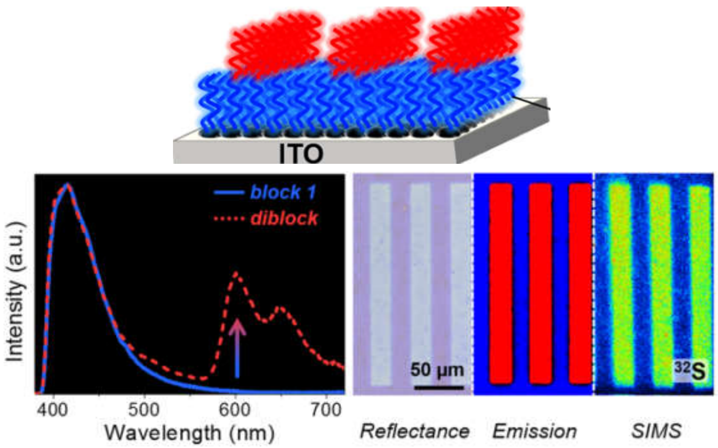


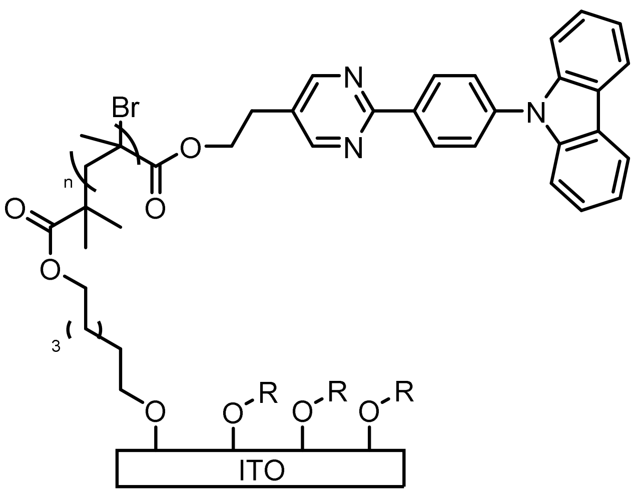
Poly(**M6MA**-*co*-**IrppyMA**)

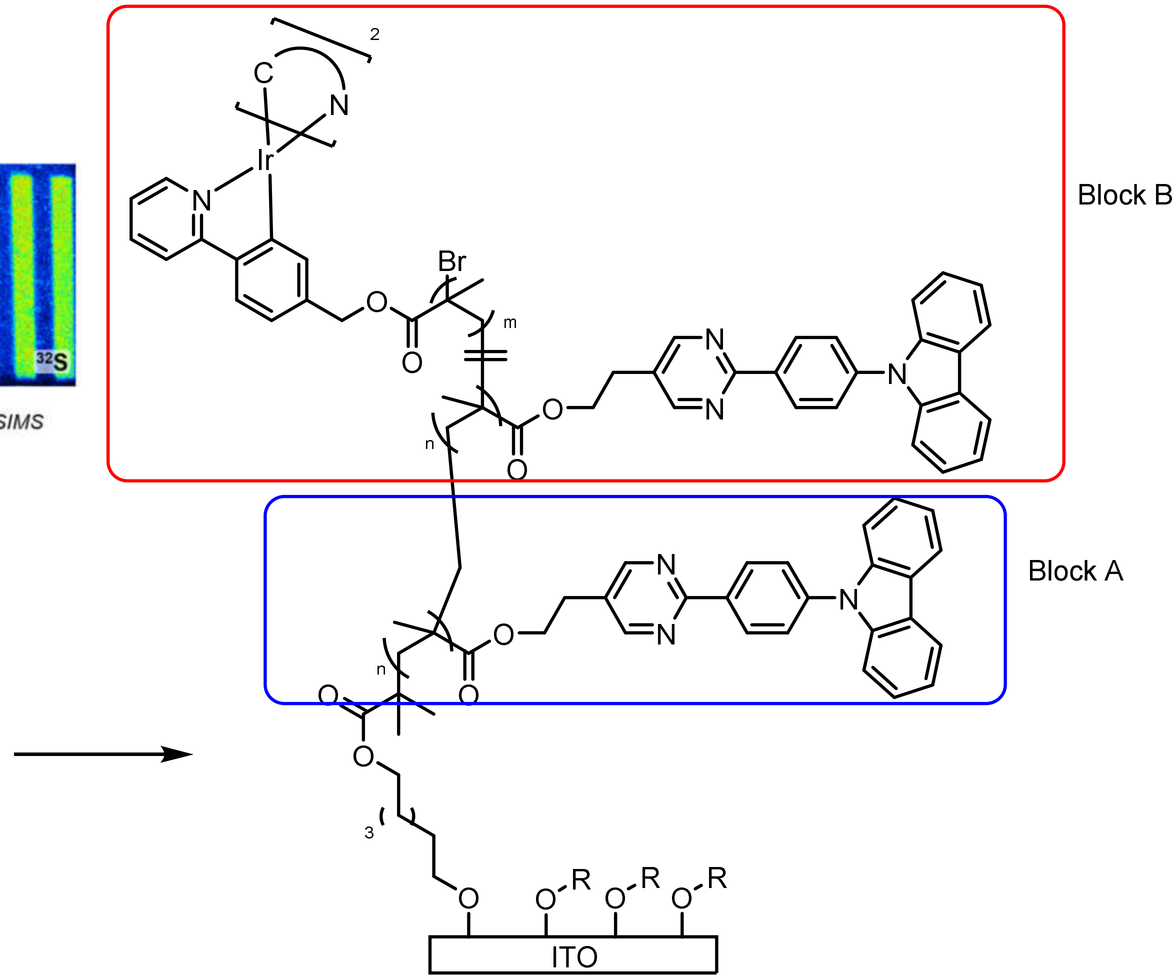




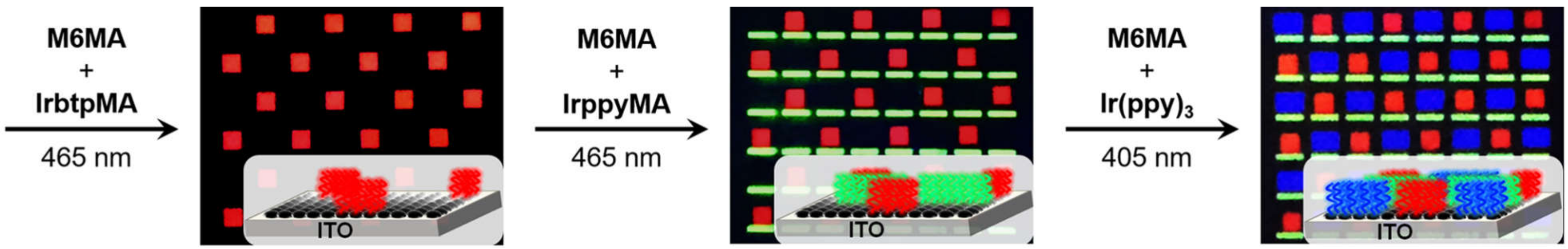
Further Tests – Multilayer Blocks

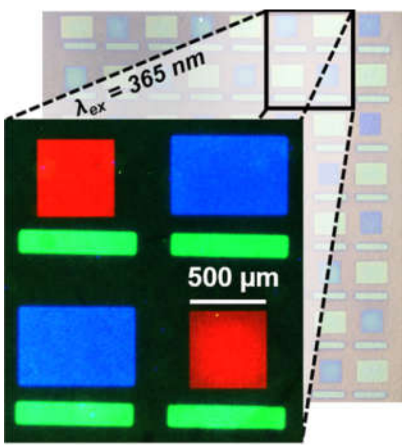


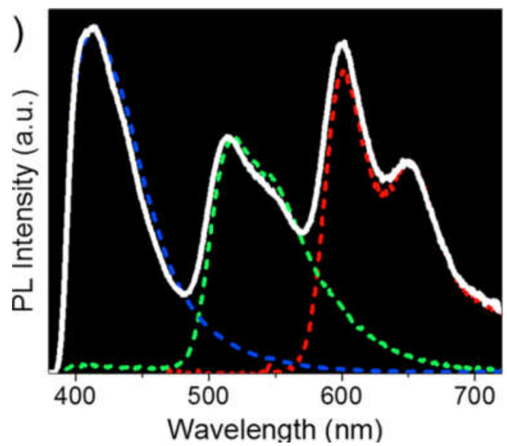


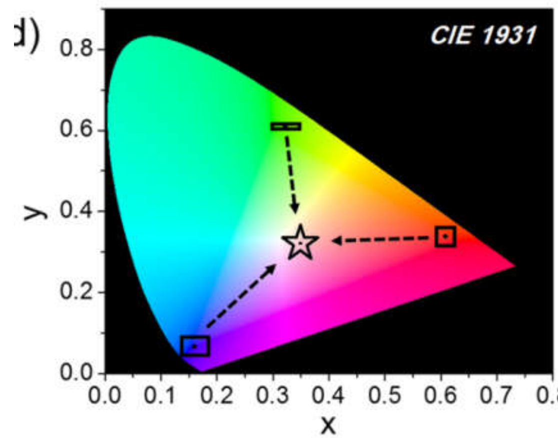


Device Applications – PenTile Array



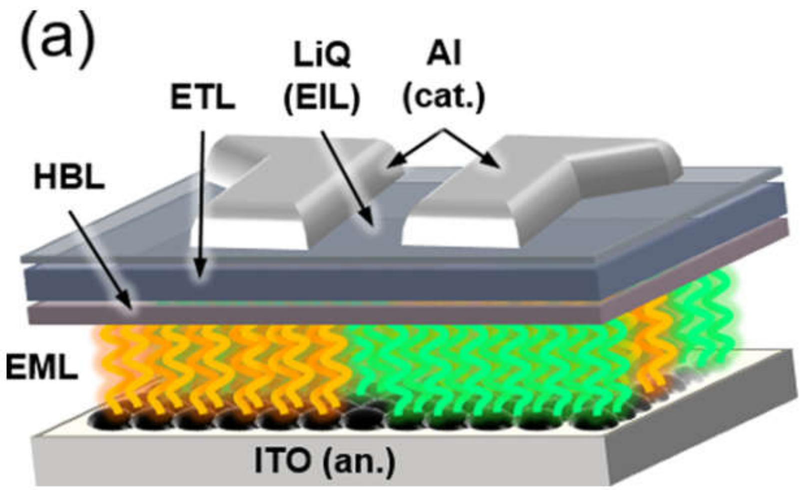


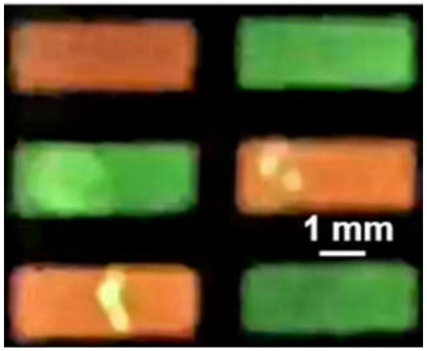




- Reflectance microscopy w/photoluminescence enlargement
- Photoluminescence profiles
- CIE coordinates w/sum white emission

Device Applications – OLED Device





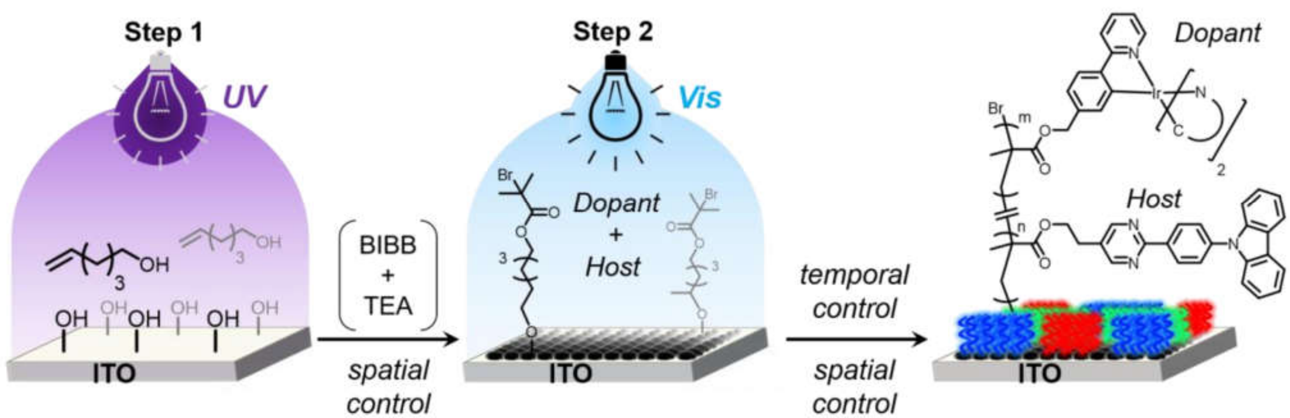
- Most efficient OLEDs are multi-layered
  - Hole Transport (HTL)
  - Electron Blocking (EBL)
  - **Emissive layer (EML)**
  - Hole blocking (HBL)
  - Electron transport (ETL)

- Multicolored OLED of poly(**M6MA**)-co-**IrpqMA** (orange) and poly (**M6MA**)-co-**IrppyMA** (green)
- Two distinct colors visible but device had poor lifetime at the necessary high driving voltage
  - Attributed to lack of hole injection layer

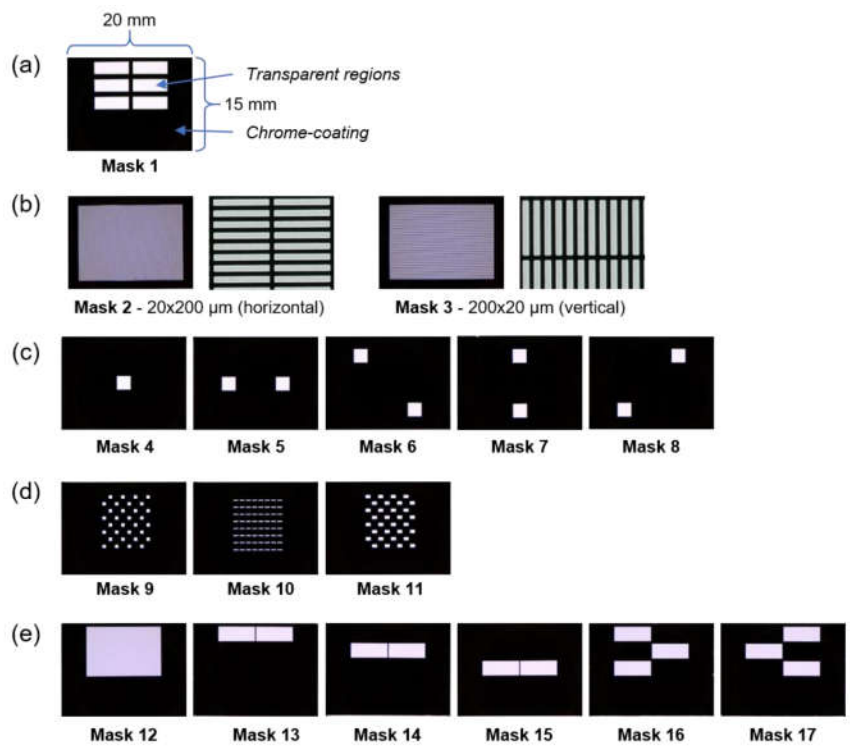
Conclusions

- A series of novel electronically active brush copolymers were generated with a doping Ir(III) component
- Significant amount of control over color, size, shape, and architecture
- Novel Ir pendant monomers acted as both a visible light polymerization photocatalyst as well as being incorporated into the molecule as a color adjuster

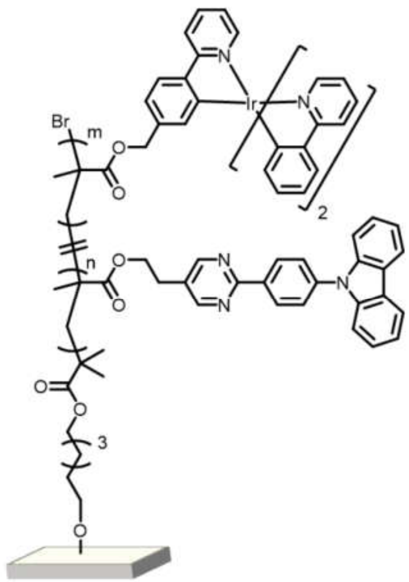
General synthetic scheme

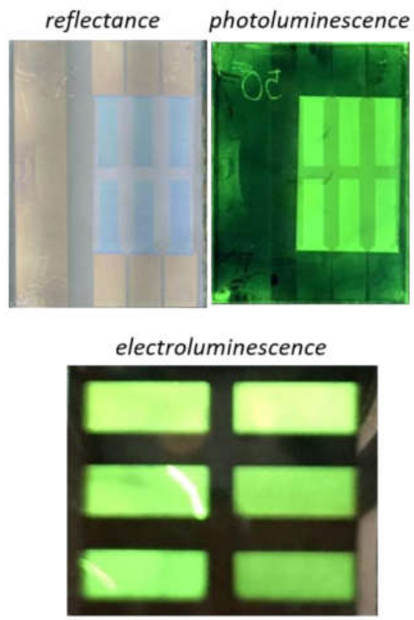


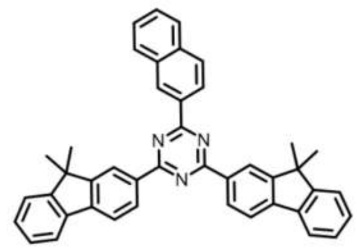
Photomask arrays



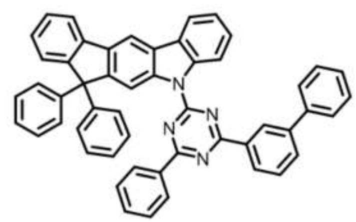
OLED device SI







2,4-bis(9,9-dimethyl-9H-fluoren-2-yl)-6-(naphthalen-2-yl)-1,3,5-triazine (ETL)



5-(4-([1,1'-biphenyl]-3-yl)-6-phenyl-1,3,5-triazin-2-yl)-7,7-diphenyl-5,7-dihydroindeno[2,1-b]carbazole (HBL)