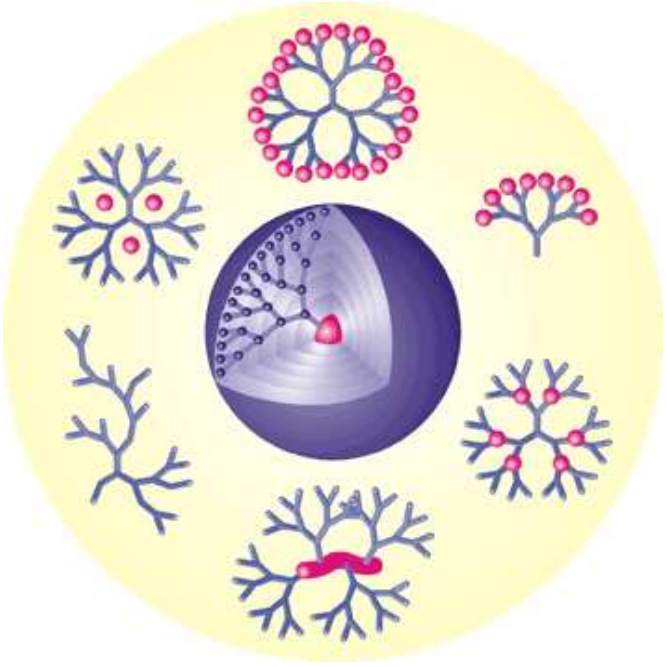
Synthesis of Dendronized Poly(fluorene)s with Peripheral Carbazole Groups

LI Yi

Outline

Introduction



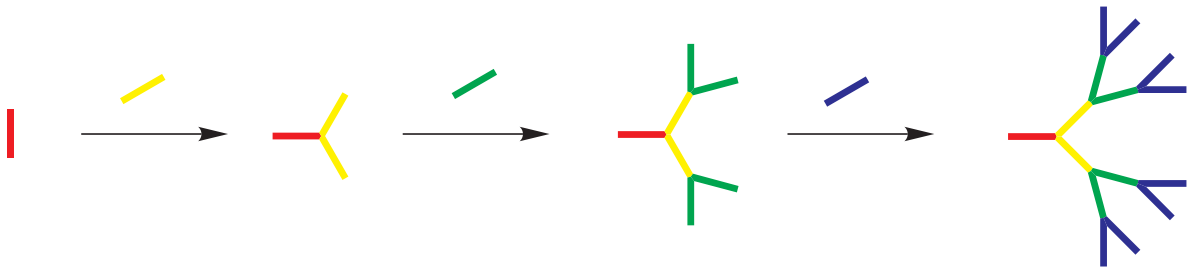
dendrimer = **dendros** + **meros**[1]

↓ *tree*

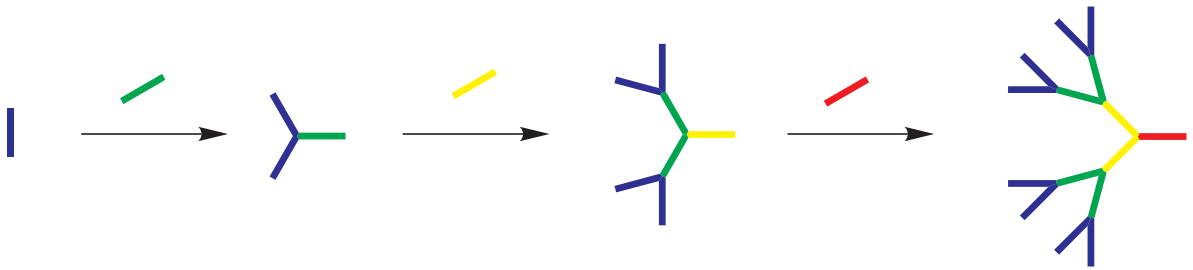
↓ *part*

Growth Strategies (I)

- Divergent[2]

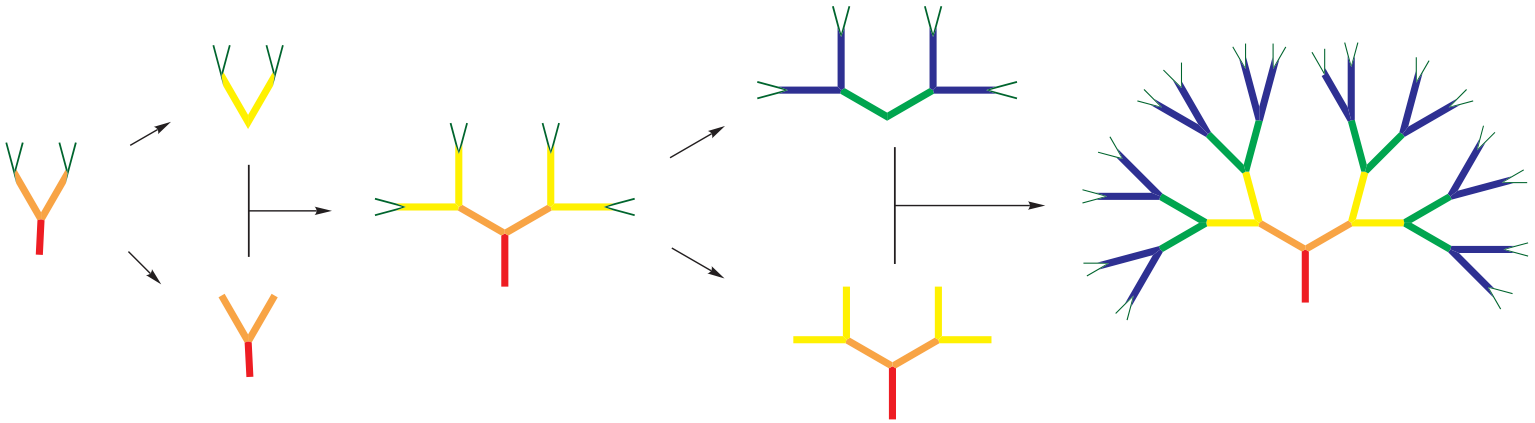


- Convergent[3]



Growth Strategies (II)

- Double exponential[4]



- Hyperbranched *etc.*

Palladium Catalyzed Cross-coupling: Reactions

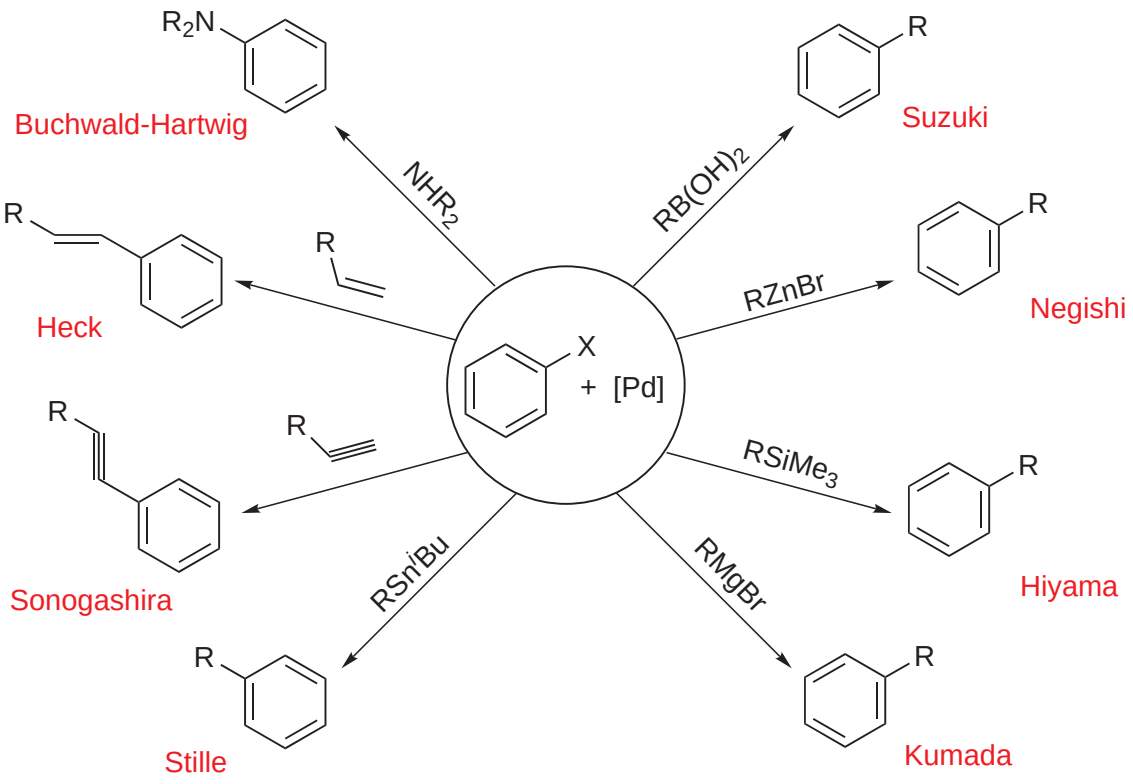


Figure: Palladium Catalyzed Cross-coupling Reactions[5]

Palladium Catalyzed Cross-coupling: Mechanism

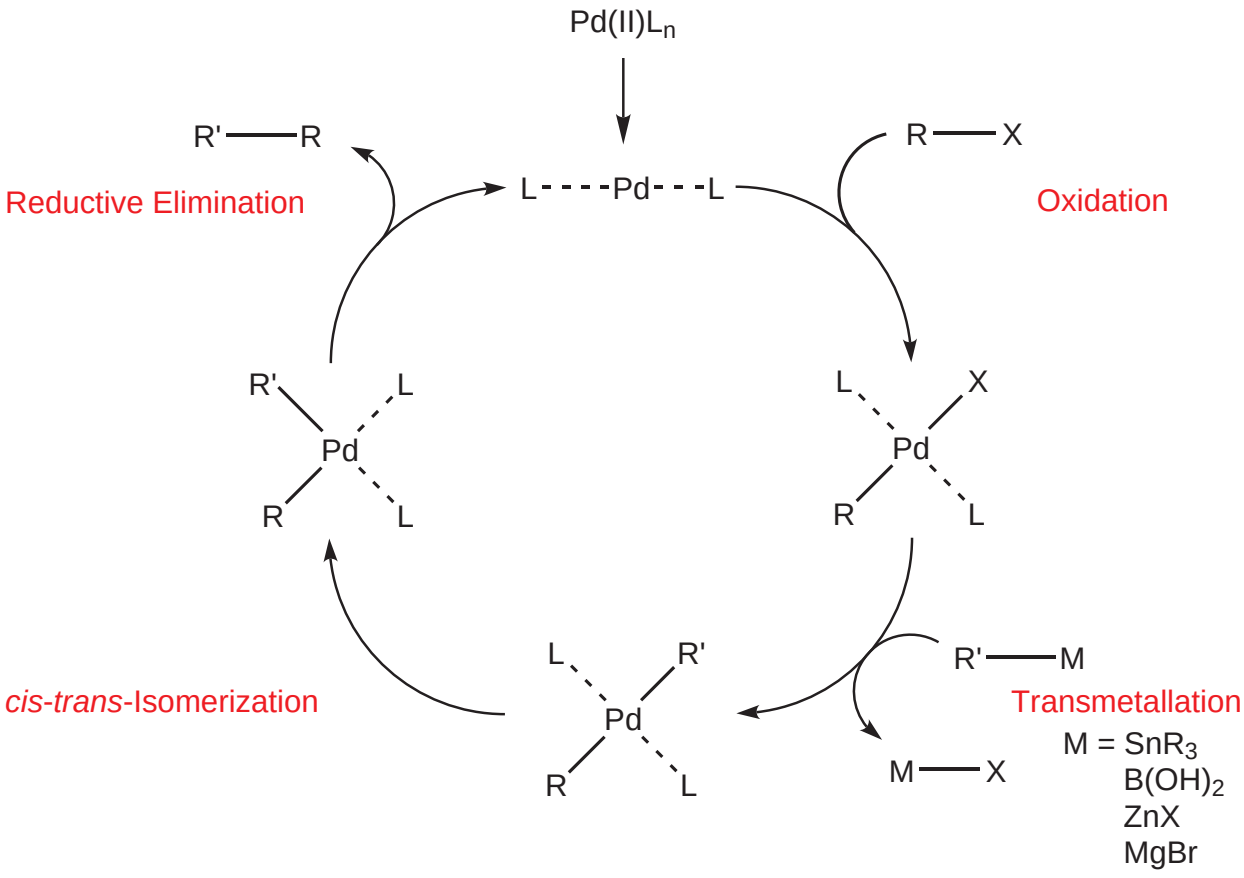


Figure: Palladium Catalyzed Cross-coupling Mechanism

Palladium Catalyzed Suzuki Cross-coupling (I)

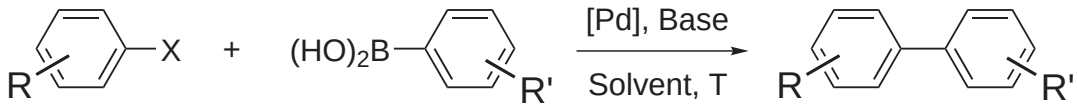
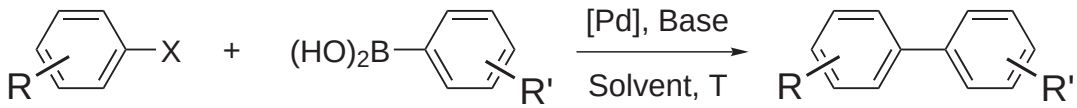


Table: Reaction Conditions[6]

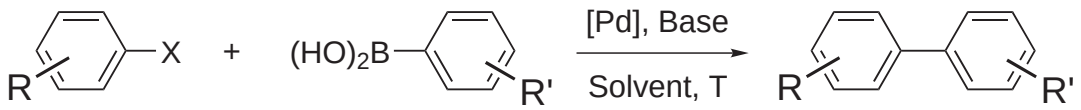
X	Catalysts	Bases / solvents	Temp. / ℃	References
I, Br	$Pd(PPh_3)_4$	$NaHCO_3$, Na_2CO_3 / DME / H_2O	reflux	*JOC*, **1997**, *62*, 7900-7901.
				JOC, **2000**, *65*, 3042-3046.
I, Br, OTf	$Pd(PPh_3)_4$	$K_3PO_4 \bullet nH_2O$ / dioxane or DMF	80	*OL*, **2000**, *2*, 1843-1845.
				Synlett, **1992**, 207-210.
				JOC, **1993**, *58*, 2201-2208.
I, Br	$Pd(PPh_3)_4$	CsF / DMF	reflux	*JOC*, **1994**, *59*, 6095-6097.
				JOC, **1997**, *62*, 8535-8539.
I, Br	$Pd(PPh_3)_4$	Na_2CO_3 / MeOH-H_2	reflux	*JACS*, **2000**, *122*, 52-57.
				JOC, **1996**, *61*, 1375-1384.

Palladium Catalyzed Suzuki Cross-coupling (II)

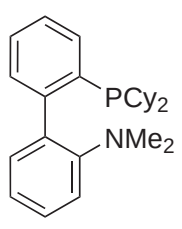


X	Catalysts	Bases / Solvents	Temp. / ℃	References
I, Br, OTf	$Pd(PPh_3)_4$	Na_2CO_3 or K_3PO_4 / toluene-H_2O	80-100	*JACS*, **1997**, *119*, 7281-7290.
				JACS, **2000**, *122*, 6935-6949.
				JOC, **1998**, *63*, 5675-5679.
				Synlett, **1999**, 966-968.
I, Br, OTf	$Pd(PPh_3)_4$	$Ba(OH)_2$ / DME / H_2O	reflux	*Synlett*, **1992**, 207-210.
				JOC, **1997**, *62*, 4943-4948.
Br	$Pd(OAc)_2$	K_2CO_3 / $^t Bu_4NBr$ / H_2	70	*JOC*, **1994**, *59*, 5034-5037.
				OL, **1999**, *1*, 965-967.
I	$Pd(OAc)_2$	K_2CO_3 or Cs_2CO_3 / acetone-H_2O	reflux	*JOC*, **1997**, *62*, 7170-7173.
				JOC, **2000**, *65*, 2837-2842.

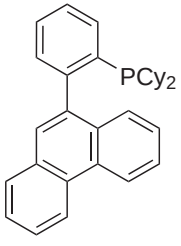
Palladium Catalyzed Suzuki Cross-coupling (III)



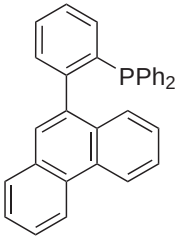
X	Catalysts	Bases / Solvents	Temp. / ℃	References
Br	$Pd_2(dba)_3$ / A	K_3PO_4, toluene	100	*JACS*, **2002**, *124*, 1162-1163.
Br	$Pd_2(dba)_3$ / B or C	K_3PO_4, toluene	100	*JACS*, **2002**, *124*, 1162-1163.
Cl	$Pd_2(dba)_3$ / $^tBu_3P$	Cs_2CO_3 / dioxane	rt	*ACIEE*, **1998**, *24*, 3387-3388.
				JACS, **2000**, *122*, 4020-4028.
	$Pd_2(dba)_3$ / $^tBu_3PHBF_4$	KF, THF	rt	*OL*, **2001**, *3*, 4295-4298.



A

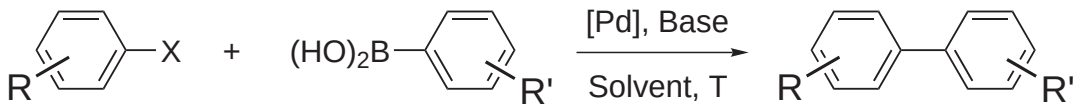


B

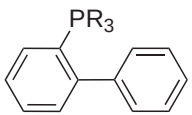


C

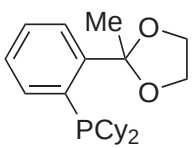
Palladium Catalyzed Suzuki Cross-coupling (IV)



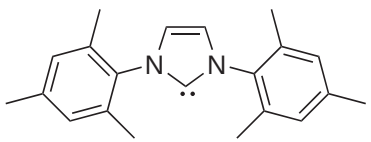
X	Catalysts	Bases / Solvents	Temp. / ℃	References
Cl	$Pd_2(dba)_3$ / D	K_3PO_4, toluene	80-100	*Om*, **1993**, *12*, 1665-1667.
				JACS, **1998**, *118*, 9722-9723.
				JACS, **1999**, *119*, 9550-9557.
	$Pd_2(dba)_3$ / E	KF, THF	rt	*JACS*, **1999**, *119*, 9550-9557.
	$Pd_2(dba)_3$ / F	CsF or K_3PO_4, toluene or dioxane	100	*JOC*, **1999**, *64*, 6797-6803.
	$Pd_2(dba)_3$ / G	Cs_2CO_3, dioxane	80	*JOC*, **1999**, *64*, 3804-3805.
	$Pd_2(dba)_3$ / H	K_3PO_4, toluene	100	*CC*, **2001**, 2408-2409.



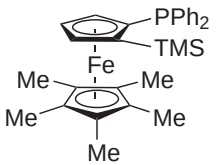
D: R=Cy
E: R=*t*-Bu



F

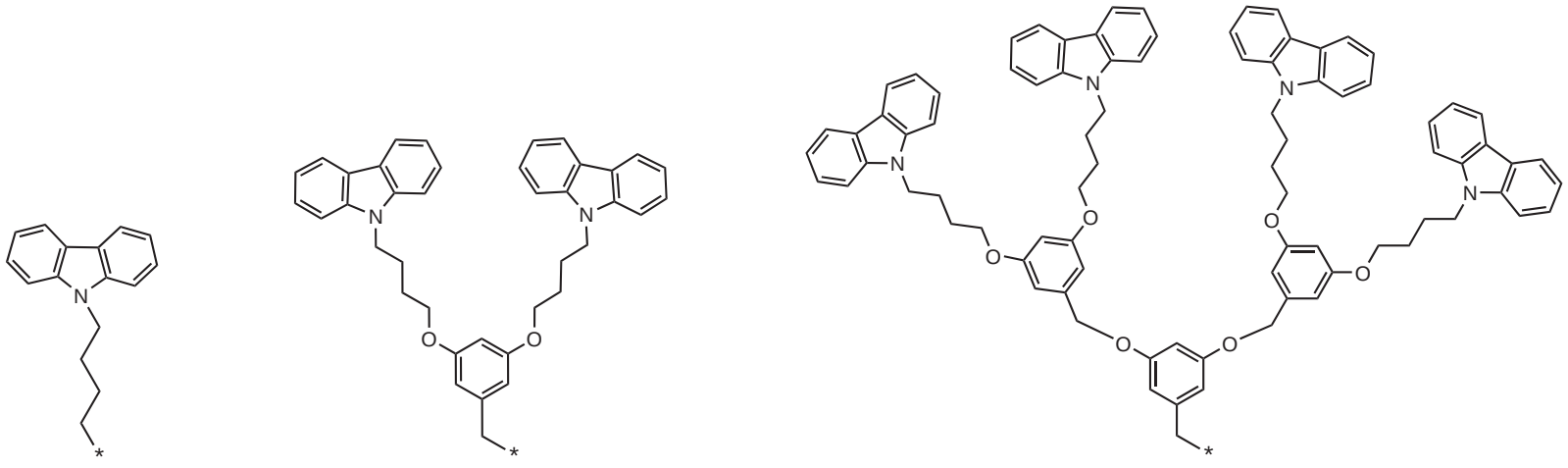


G

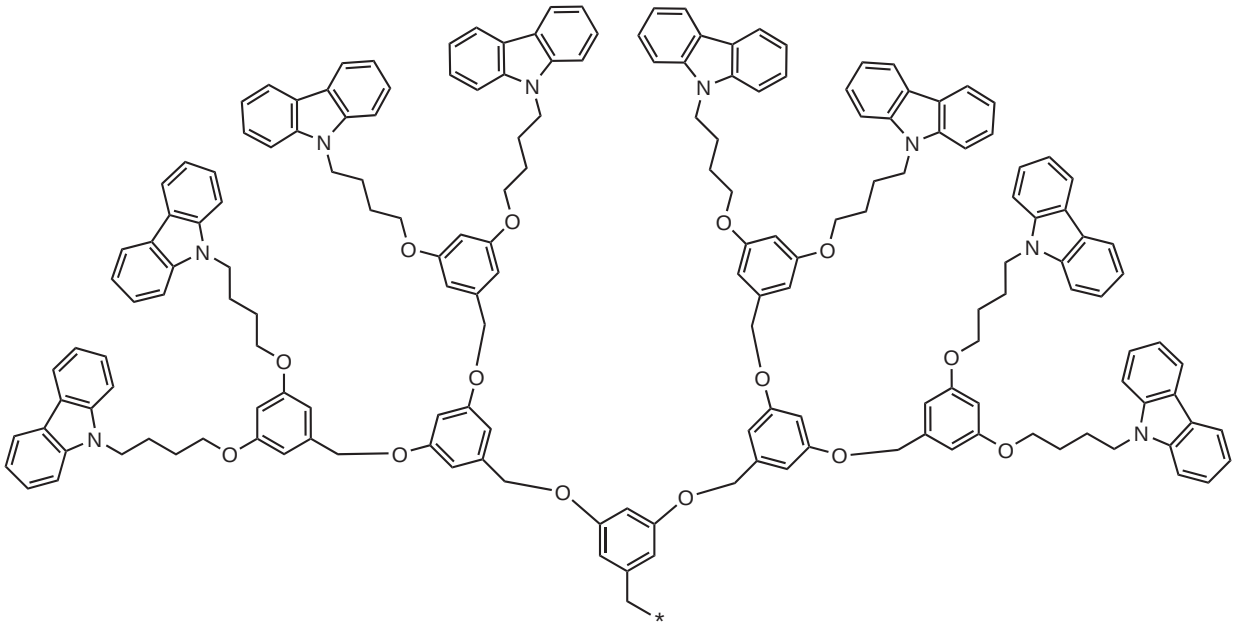


H

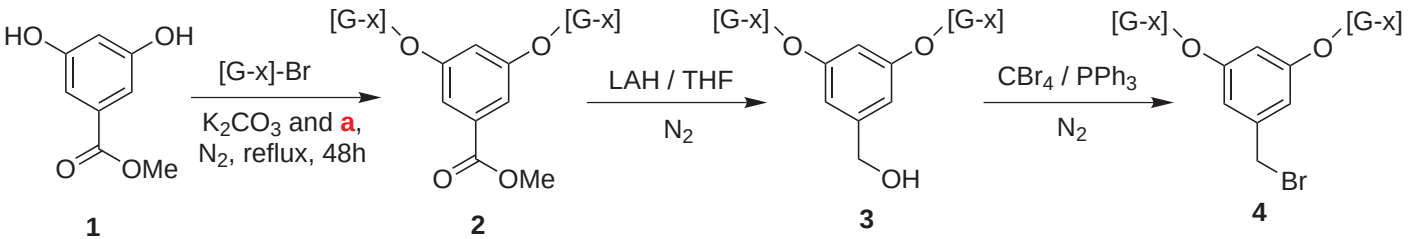
Dendrons (I)



Dendrons (II)

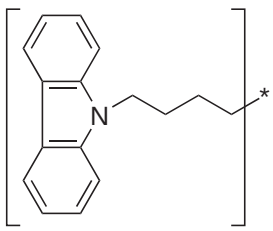


Monomers

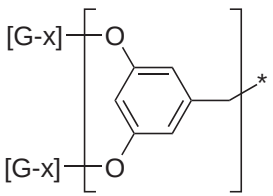


1 **2** **3** **4**

x = 0, **a** = *n*-Butanone
x = 1, 2, **a** = 18-Crown-6, Acetone

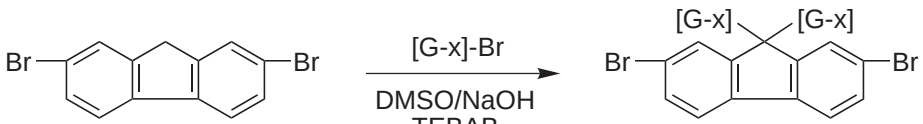


= [G-0]-*

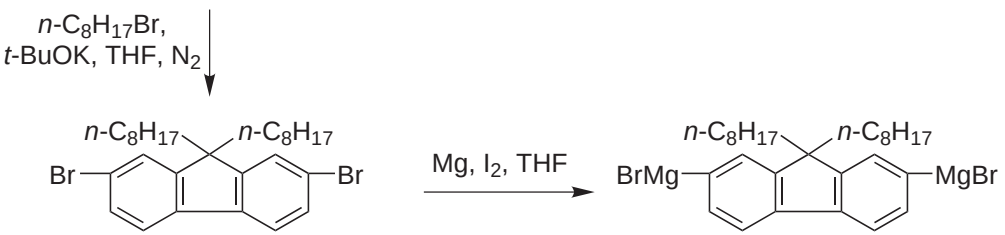


= [G-(x+1)]-*

(x = 0, 1, 2)

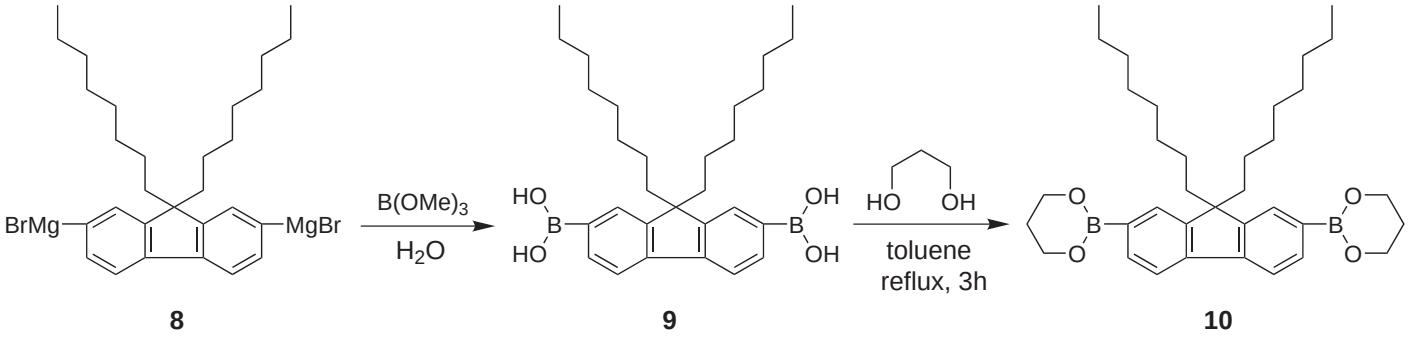


5 **6**

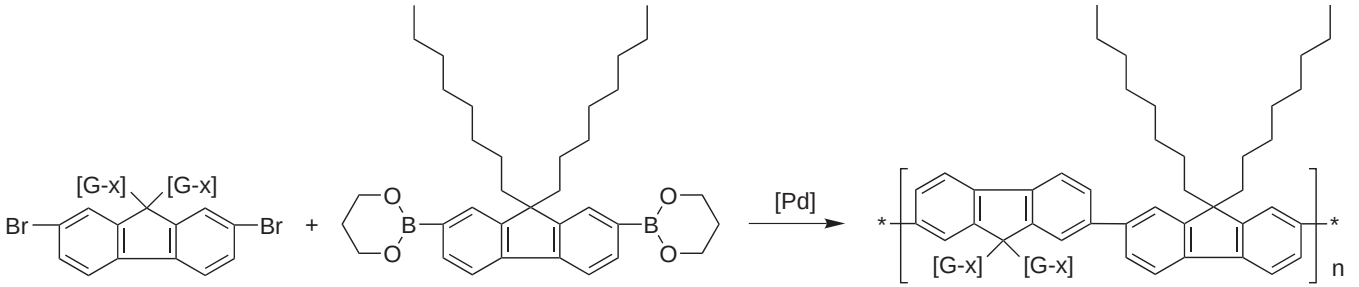


7 **8**

Suzuki Polycondensation (SPC)



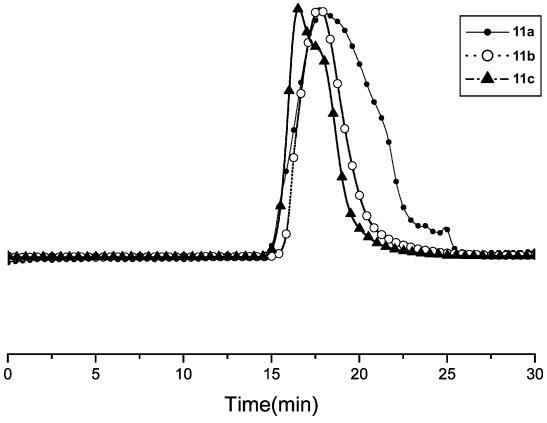
8 **9** **10**



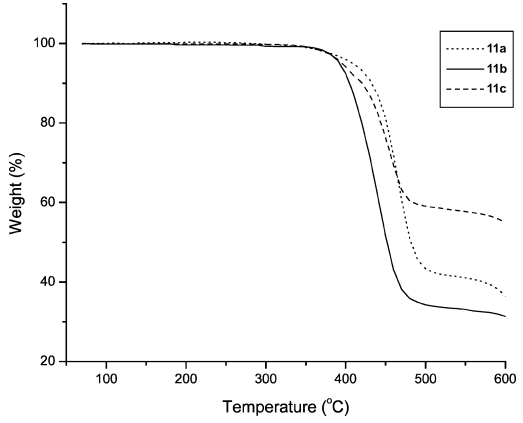
6 **10** **11**

11a: x=0
11b: x=1
11c: x=2

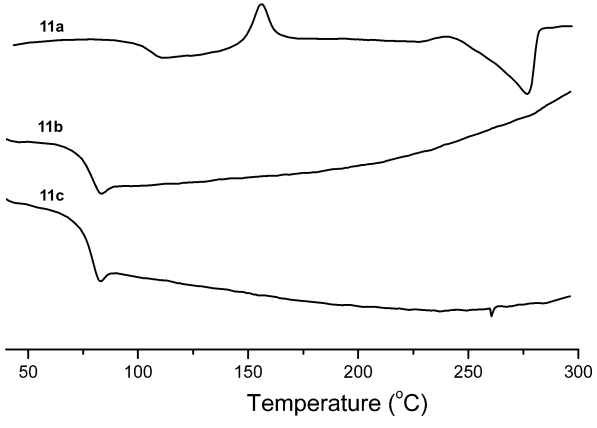
Characterization (I)



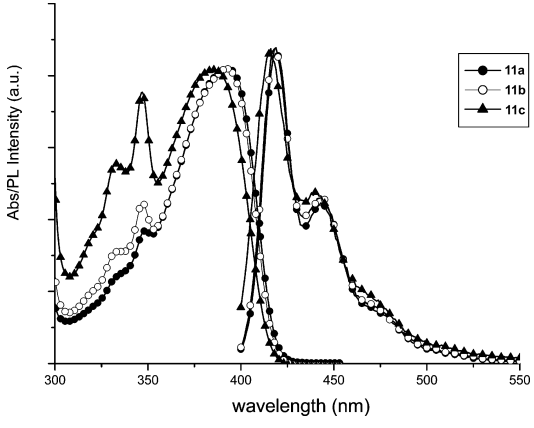
GPC[7]



TGA[7]



DSC[7]



UV-vis and PL[7]

Characterization (II)

Table: Molecular Weights, Thermal Properties, and the Flurenscene Quantum Yields of the Dendronized Polymers (in THF and as Films)[7]

Polymers	M_n	P_n	M_w	P_w	M_w / M_n	T_G	Φ_F	
							in solution	films
11a	46 700	47	104 000	104	2.21	103	0.93	0.29
11b	131 000	78	157 000	93	1.20	73	0.96	0.55
11c	143 000	47	171 000	60	1.19	73	0.86	0.64

References

[1] A. D. Schlüter, *Top. Curr. Chem.* **197**, 165-191. (1998)

[2] D. A. Tomalia, et al., *Polymer J.* **17**, 117-132. (1985)

[3] C. J. Hawker, et al., *JACS* **112**, 7638-7647. (1990)

[4] T. Kawaguchi, et al., *JACS* **117**, 2159-2165. (1995)

[5] N. Miyaura, *Top. Curr. Chem.* **219**, 1-9. (2002)

[6] A. B. Charette, *CHM6315, U. Montrèal* (2004)

[7] Y. Fu, et al., *Macromolecules* **37**, 6395-6400. (2004)

Thank you !