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Macromolecular Ruthenium catalyst for applications in flow photochemical reactions and *in-situ* recovery through size-exclusion nanofiltration





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Introduction

website: http://www.maos.net

Flow Set-Up

Dendrimer catalyst



- Nevertheless, the high price of this catalyst based on Ruthenium metal requires its recovery and recycling to reach a complete sustainable process.
- *In-situ* catalyst recycling facilitates the product purification and diminishes the cost of the whole synthetic process. Therefore for chemical processes that could be applied in the industrial sector, it is essential to find a procedure to reuse the catalyst.
- A 2nd generation Polyamidoamine (PAMAM) dendrimer is chosen as platform to anchor [Ru(bpy)3]²⁺ units. Dendrimer are hyperbranched macromolecules with low polydispersity, comprising a multifunctional core, several branching points and outer surface moieties.



[a] F.R. Bou-Hamdan, P.H. Seeberger Chem. Sci. 2012, 3, 1612-1616. [b] J.M.R. Narayanam, J.W. Tucker, C.R.J. Stephenson J. Am. Chem. Soc. 2009, *131*, 8756-8757.

[c] K. Gilmore, P.H. Seeberger Chem. Rec. 2014, 14, 410-418.

Catalyst Synthesis, Purification and Characterization



Product, reagents

• Vapourtec EasyMedChem coupled to Zaiput system.

- LED lamp at 450 nm as light source
- Peristaltic pump P_{max}: 10 bar
- Recycling studies currently under work.





Photochemical Reactions

[Ru] 0.65% mol Ru, CBr₄ R₁ Br 35-50 °C, 2-3 bar, 0.25 mL/min \mathbf{R}_2

 R_2

Substrate	[Substrate], mol/L	Cat.	Solvent	% Conv.
1-nonanol	0.2	Ru(bipy) ₃ Cl ₂	Acetone/DMF 1/2	99.8
1-nonanol	0.2	$Ru(bipy)_2(Me_2bipy)(PF_6)_2$	Acetone/DMF 1/2	99.0
1-nonanol*	0.2	G2-PAMAM(Ru) ₁₆	Acetone/DMF 1/6	99.6
Phenetyl alcohol	0.2	$Ru(bipy)_2(Me_2bipy)(PF_6)_2$	Acetone/DMF 12/1	94.4
Phenetyl alcohol	0.2	$G2-PAMAM(Ru)_{16}$	Acetone/DMF 2/1	> 99.9
Benzyl alcohol	0.2	$Ru(bipy)_2(Me_2bipy)(PF_6)_2$	Acetone/DMF 12/1	97.0
Benzydrol	0.2	$Ru(bipy)_2(Me_2bipy)(PF_6)_2$	Acetone/DMF 12/1	> 99.0
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Zaiput liquid-liquid separation system equipped with a Solsep membrane (NF080105).

UV-visible spectra of the G2-PAMAM Ru dendrimer and monomer.

Technique	Average Ru atoms/dendrimer
UV-Visible Spectroscopy	15.4
ICP-MS	14.7

The theoretical number of Ru atoms per dendrimer is 16. Both

*Reaction was performed with 0.35% mol of Ru.



Ph



Substrate	[Substrate], mol/L	Cat.	Solvent	% Conv.
Chalcone epoxide	0.2	$Ru(bipy)_2(Me_2bipy)(PF_6)_2$	ACN	98.5
Chalcone epoxide*	0.2	G2-PAMAM(Ru) ₁₆	ACN	>99.0
1-azide-4- chlorobenzene	0.1	$Ru(bipy)_2(Me_2bipy)(PF_6)_2$	ACN	>99.0
1-azide-4- chlorobenzene*	0.1	G2-PAMAM(Ru) ₁₆	ACN	>99.0

*Reaction were performed with 0.6% mol of Ru.

Recycling experiments through nanofiltration

- > Appel reaction crude mixture can be recycled although size exclusionmembranes are not stable under DMF and 50% of the catalyst is lost.
- > Reduction experiments currently showed a drop in the catalytic activity in the 2nd cycle due to catalyst decomposition. Further studies in this topic are presently performed in our laboratories.

techniques are in agreement and show the average of a statistical

dendrimer population.



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