A recyclable supported Cu(I) catalyst for azide-alkyne click polymerization

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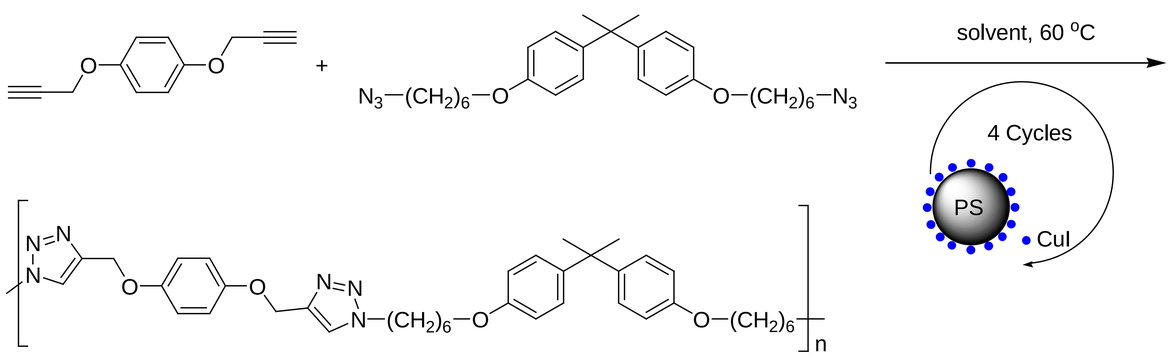
INTRODUCTION

Typical azide-alkyne click polymerization is catalyzed by Cu(I) complexes, which are difficult to completely removed after reaction and will detriment the optoelectronic properties of the polymers, or cause cytotoxicity in their biomedical application.[1,2] Herein, we describe an efficient supported Cu(I) catalyzed azide-alkyne click polymerization under mild condition, and polytriazoles with low copper content were produced.[3] Furthermore, this catalyst is reusable for 4 cycles.

RESULTS AND DISCUSSION

CuI@A-21 catalyzed click polymerization



Effect of the solvent on the polymerization

No.	solvent	yield (%)	M_w[a]	PDI[a]	S[b]	[Cu] (ppm)[c]
1	THF	86.1	55500	1.61	√	210
2	dioxane	79.3	47700	1.96	√	148
3	toluene	61.8	132000	1.90	Δ	126
4	DMF	96.0	73500	2.24	Δ	1717

The reaction was carried out at 60 °C for 12 h under the catalysis of CuI@A-21 with the protection of nitrogen at a monomer concentration of 0.1 M. [a] M_w and PDI of polymer were estimated by GPC in THF on the basis of a PS calibration. [b] Solubility, √ = completely soluble in THF, Δ = partially soluble in THF. [c] Copper content, estimated by atomic absorption spectroscopy.

Catalyst performance comparison

No.	catalyst	solvent	yield (%)	M_w	PDI	S	[Cu] (ppm)
1	CuI@A-21	THF	86.1	55500	1.61	√	210
2	CuI	DMF	79.0	43700	1.71	Δ	5282
3	$CuSO_4$/SA	THF	97.4	88400	1.83	Δ	2800
4	$Cu(PPh_3)_3Br$	THF	86.9	25700	2.04	√	3207

Effect of post-purification of the polytriazoles on the copper residues

No.	catalyst	yield (%)	M_w	PDI	S	[Cu] (ppm)
1	CuI@A-21	83.0	60500	2.14	√	25
2	$Cu(PPh_3)_3Br$	89.0	21200	1.93	Δ	235

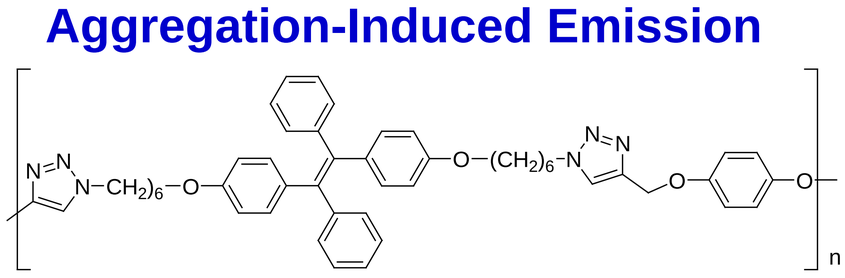
The reaction mixture was diluted with THF and then dropped into 5 % EDTA solution through a cotton filter.

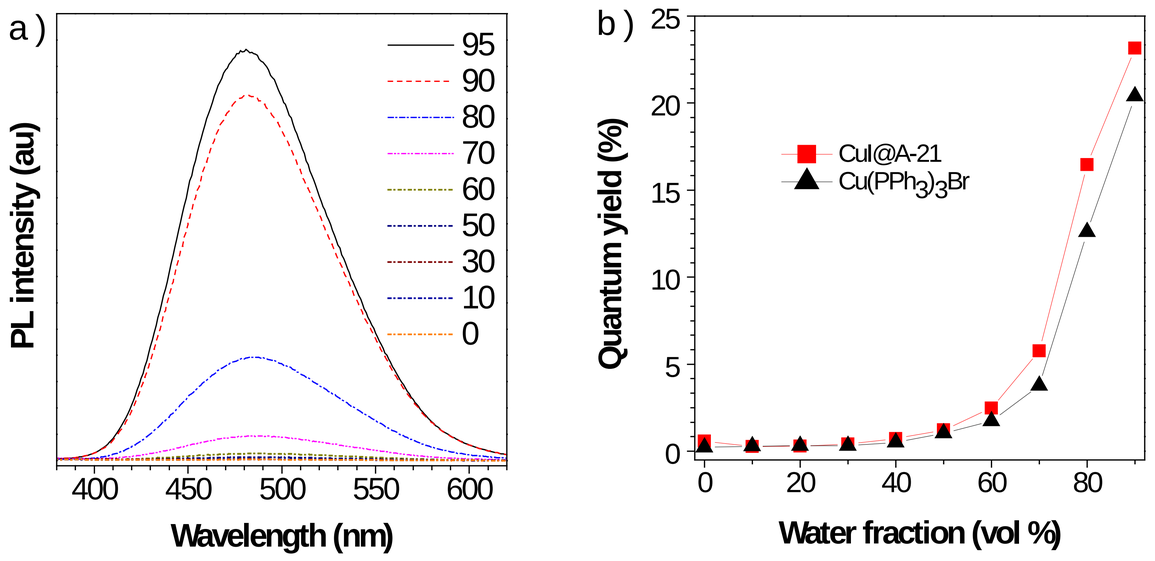
Recycling of the CuI@A-21

No.	Catalyst	yield (%)	M_w	PDI	[Cu] (ppm)
1	CuI@A-21[a]	67.1	80300	3.21	260
2	CuI@A-21[b]	96.1	94400	2.72	170
3	CuI@A-21[c]	92.8	91000	2.32	180
4	CuI@A-21[d]	84.5	22500	2.51	140

The CuI@A-21 catalyst was separated from THF solution after polymerization for 12 h, and run another cycle immediately. [a] 1st recycle. [b] 2nd recycle. [c] 3rd recycle. [d] 4th recycle.

Aggregation-Induced Emission





The fluorescence performance of the TPE-containing polytriazoles catalyzed by two types of Cu(I) catalysts. a) PL spectra of the polymers in THF/water mixtures with different water fractions. Polymer concentration: 10 μM; excitation wavelength: 326 nm. b) Variation in the quantum yields (Φ_F) with water fraction in the THF/water mixture. The Φ_F values were estimated using quinine sulfate in 0.1 N H_2SO_4 (Φ_F = 54.6%) as standard.

CONCLUSION

A new supported Cu(I)-catalyzed click polymerization was successfully developed, and the produced polytriazoles have better solubility and greatly decreased copper residue compared to those catalyzed by CuI, $CuSO_4$/SA and $Cu(PPh_3)_3Br$ etc. It is worth noting that the CuI@A-21 is reusable, and the polymer without decreasing yield and molecular weight could be obtained even in the 4th cycle, making this method more economic and widely applicable.

ACKNOWLEDGEMENT

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REFERENCE

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