Supporting Information

Tripodal Heptadentate Schiff Base as an Active Ligand for Atom Transfer Radical Polymerization

Xiaoling Xu,[ab] Chunyang Bao,[ab] Mei Hong,[ab] Die Li,[ab] Qiang Zhang*[ab]

[a] Key Laboratory of New Membrane Materials, Ministry of Industry and Information Technology, School of Environmental and Biological Engineering, Nanjing University of Science and Technology, Nanjing 210094, P. R. China.

[b] Institute of Polymer Ecomaterials, School of Environmental and Biological Engineering, Nanjing University of Science and Technology, Nanjing 210094, P. R. China.

*Email: zhangqiang@njust.edu.cn

Experimental Section

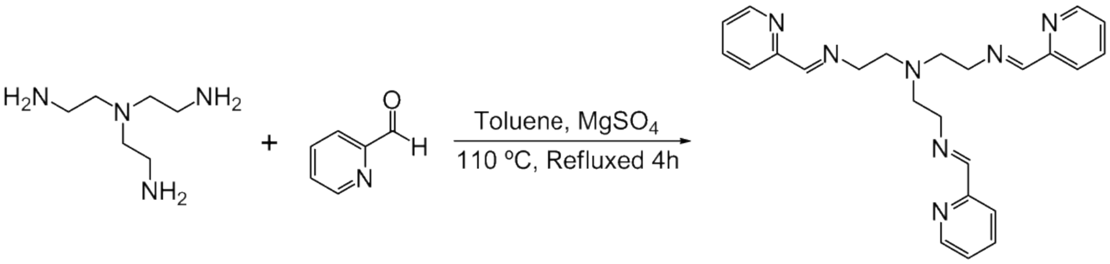
Materials

N-ethyl-2-pyridylmethanimine (PyEthyl) was synthesized according to literature procedures and stored at 2-8 °C.[1] *N*-isopropylacrylamide (NIPAM, 97%, Aladdin) was recrystallized from hexane before use to remove the inhibitor. Copper(I) bromide (CuBr, 98%, Aladdin) was washed sequentially with acetic acid and ethanol, and dried under vacuum before use. Copper wire (diameter = 0.25 mm) was pre-treated by washing in hydrochloric acid for 15 min and rinsed thoroughly with water, dried under nitrogen before use. Ethyl α-bromoisobutyrate (EBiB, 98%, TCI), 2-pyridinecarboxaldehyde (98.73%, bidepharm), tris(2-aminoethyl)amine (96%, Aladdin), ethylamine (70% in water, damas-beta), methylacrylate (MA, >99%, Aladdin), methyl methacrylate (MMA, >99.5%, Aladdin), styrene (St, Macklin), acrylonitrile (AN, >99.0%, TCI), *N, N*-dimethylbenzamide (DMF, 99%, Aladdin), dimethyl sulfoxide (DMSO, 99%, Aladdin) were used as received. All other reagents and solvents were obtained from Aladdin (China) and used without further purification unless otherwise stated.

Analytical techniques

^{1}H NMR spectra were recorded at 25 °C with a Bruker AV 500 M spectrometer using deuterated solvents obtained from Aladdin. The number-average molecular weight (M_n) and molecular weight distribution (M_w/M_n) were determined by Waters 1515 size exclusion chromatography (SEC) in N,N-dimethylformamide (DMF) at 40 °C with a flow rate of 1.00 mL min^{-1}, which was equipped with 2414 refractive index (RI) and 2489 UV detectors, a 20 μm guard column (4.6 mm × 30 mm, 100 - 10K) followed by three Waters Styragel columns (HR1, HR3, and HR4) and an autosampler. Narrow linear polystyrene standards in the range of 540 to 7.4×10^5 g mol^{-1} were used to calibrate the system. All samples were passed through 0.45 μm PTFE filter before analysis. Fourier transform infrared (FTIR) spectra were recorded on a Nicolet iS5 FTIR spectrometer using an iD7 diamond attenuated total reflectance optical base. Electrospray ionization mass spectrometry (ESI-MS) measurements were performed in positive mode through using a Bruker Esquire 3000 Plus instrument. Coordination complexes were *in-situ* generated in methanol by mixing $CuBr_2$ with Py_3Tren in different molar ratios and filtered before injection into the spectrometer. Cyclic voltammetry was performed using a CH-Instruments 760 E potentiostat.

Synthesis of tris[*N*-(2-pyridylmethyl)-2-iminoethyl]amine (Py_3Tren)



Scheme S1. Synthetic route of Py_3Tren ligand.

The ligand Py_3Tren was prepared according to a modification of previously reported methods.[2, 3] To a round bottom flask fitted with a magnetic stir bar, 2-

pyridinecarboxaldehyde (6.4 g, 60 mmol), tris(2-aminoethyl)amine (2.92 g, 20 mmol), toluene (40 ml) and anhydrous magnesium sulfate were charged. The mixture was then refluxed for 4 h. After cooling to room temperature, centrifuge was performed to obtain the filtrate. Toluene was then evaporated under reduced pressure and the residue was dried in vacuum to yield brown oil in quantitative yield. The ligand was used without further purification.

Cyclic Voltammetry (CV)

A standard three-electrode cell equipped with an Ag/AgCl reference electrode, a 3 mm glassy carbon disc working electrode, and a platinum counter electrode was established. The glassy carbon working electrode was polished with 1.0, 0.3, 0.05 μm alumina powder respectively, rinsed sequentially with ethanol, deionized water, and ethanol prior to each use. The platinum wire counter electrode was soaked in a dilute hydrochloric acid solution, followed by ultrasonic washing in deionized water, and finally washed with deionized water and ethanol before use. All experiments were carried out in a 0.1 M tetraethylammonium tetrafluoroborate (Et_4NBF_4) solution in DMSO or in MeCN solution of 0.1 M Et_4NBF_4 in the presence of 5 mM EBiB under a nitrogen atmosphere. A concentration of 1 mM copper complexes (1 equivalent $CuBr_2$ with 1 equivalent Py_3Tren or 2 equivalent PyEthyl, respectively) and scanning rate of 50 mV/s were used for CV measurements. The ferrocene / ferrocenium redox couple (Fc/Fc^+) was used for internal calibration.

General procedures for Normal ATRP

The normal ATRP was performed using the standard Schlenk technique under nitrogen protection. To a Schlenk tube (50 ml) with a magnetic stirring bar, CuBr (13.4 mg, 0.0935 mM) was charged and sealed with a rubber septum, then the Schlenk tube was recycled five times between a vacuum and a nitrogen atmosphere to remove oxygen from the system. EBiB (13.7 μL, 0.0935 mM), monomer such as MMA (1 ml, 9.35 mM), Py_3Tren (38.6 mg, 0.0935 mM) and DMF (2 ml) were charged into another Schlenk tube and the mixture was degassed by four freeze-pump-thaw cycles. The solution was then introduced into the first Schlenk tube, and the polymerization started when the Schlenk tube was immersed into an oil bath that was preheated to the desired temperature. The samples were withdrawn at suitable time periods throughout the reaction and diluted with $CDCl_3$ for the determination of conversion by ^1H NMR spectroscopy. Copper catalyst was removed by filtering through the column filled with basic alumina prior to SEC analysis.

General Procedure for ARGET ATRP of MMA

EBiB (65 μL, 0.44 mM), MMA (2.3 ml, 22 mM), Py_3Tren (1.82 mg, 0.0044 mM), $CuBr_2$ (0.98 mg, 0.0044 mM) and DMSO (5 ml) were charged in a 25 mL glass vial with a rubber seal and magnetic stir bar. The mixture was sonicated for 5 min to get a green clear solution, which was then bubbled with nitrogen for 20 min. Deoxygenated Finally, a solution of ascorbic acid in DMSO (0.1 mL, containing 0.8 mg ascorbic acid) was slowly injected into the vial *via* a micro-injection pump (5 μL / min) to activate the catalyst and start the polymerization under 30 °C. The samples were withdrawn and diluted with $CDCl_3$ for the determination of conversion by ^{1}H NMR spectroscopy and the molecular weight of the polymer was determined by SEC.

General Procedure for SARA ATRP of MMA and MA

4 cm copper wire was wrapped on a magnet stirrer bar and immersed in concentrated hydrochloric acid in a 25 mL glass vial with a rubber stopper, kept stirring for 15 min, washed several times with distilled water, and then dried under nitrogen. EBiB (65 μL, 0.44 mM), monomer (22 mM), Py_3Tren (18.2 mg, 0.044 mM), $CuBr_2$ (9.8 mg, 0.044 mM) and DMSO (5 ml) were charged into a 25 mL glass vial with a rubber seal and the mixture was degassed by bubbling nitrogen for 20 min. Subsequently, the magnetic stirrer wrapped with the activated copper wire was added into the solution quickly under nitrogen protection to start the polymerization under 30 °C. Sample was taken and diluted with $CDCl_3$ for analysis of the conversion by ^{1}H NMR spectroscopy and the molecular weight of the polymer was determined by SEC.

General procedure for *in-situ* chain extension reactions

4 cm copper wire was wrapped on a magnet stirrer bar and immersed in concentrated hydrochloric acid in a 25 mL glass vial with a rubber stopper, kept stirring for 15 min, washed several times with distilled water, and then dried under nitrogen. EBiB (65 μL, 0.44 mM), MMA (22 mM), Py_3Tren (18.2 mg, 0.044 mM), $CuBr_2$ (9.8 mg, 0.044 mM) and DMSO (5 ml) were charged into a 25 mL glass vial with a rubber seal and the

mixture was degassed by bubbling nitrogen for 20 min. Subsequently, the magnetic stirrer wrapped with the activated copper wire was added into the solution quickly under nitrogen protection to start the polymerization under 30 °C. After 10 h a degassed solution of MMA (50 eq) and DMSO (1: 1 v/v) was added into the reaction mixture *via* degassed syringe. Samples were taken periodically and conversions were measured using ^{1}H NMR and SEC analysis.

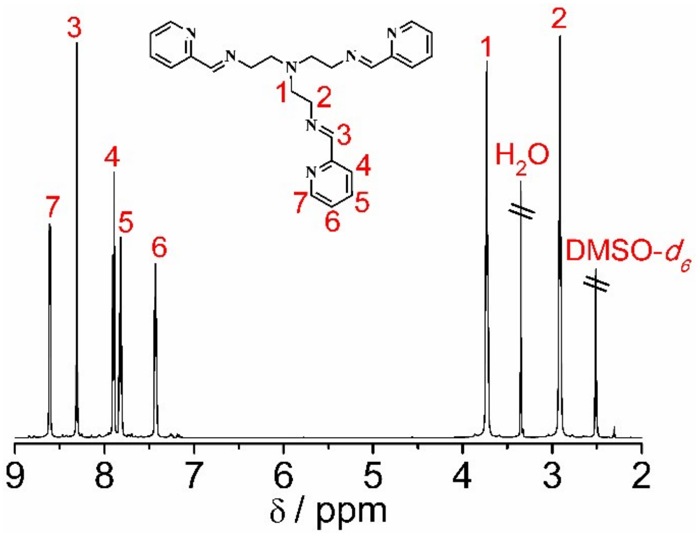


Figure S1. ^{1}H NMR spectrum of Py$_3$Tren in DMSO-d_6.

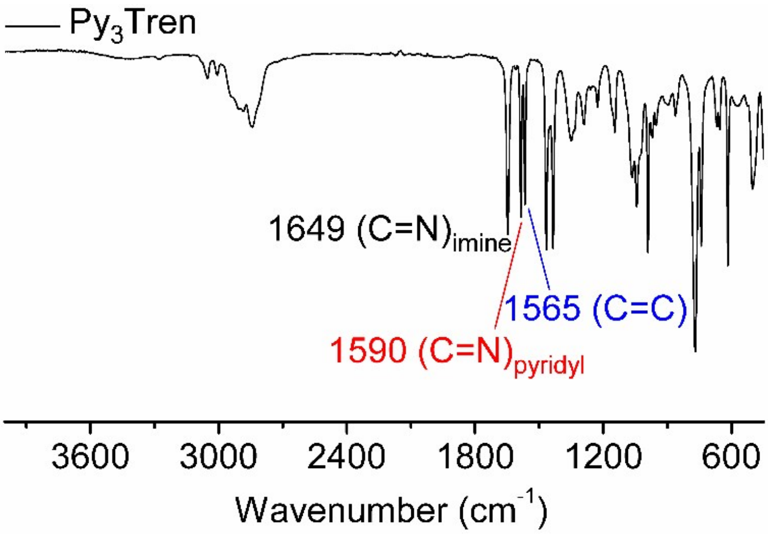


Figure S2. FTIR spectrum of Py$_3$Tren.

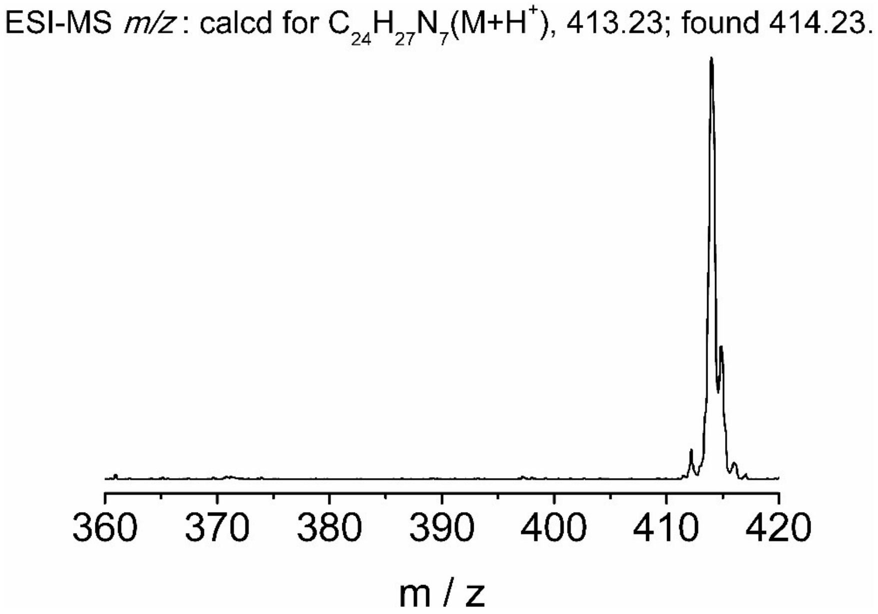


Figure S3. ESI-MS spectrum of Py$_3$Tren.

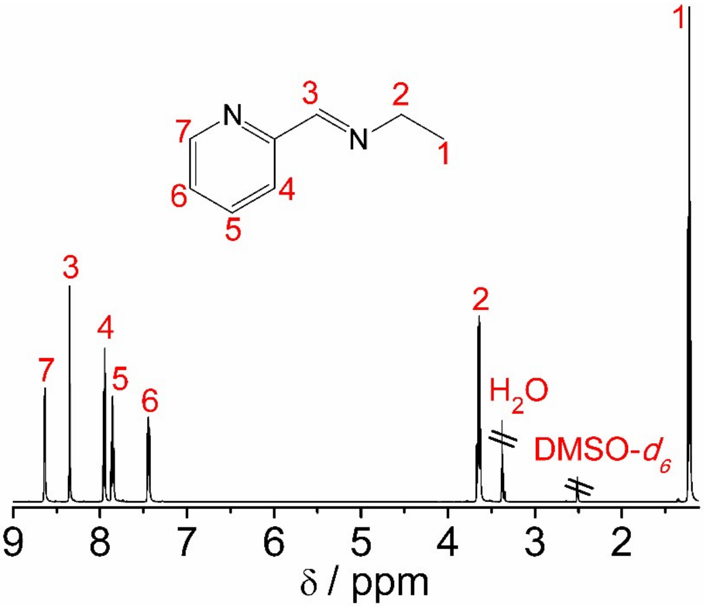


Figure S4. ^{1}H NMR spectrum of PyEthyl in DMSO-d_6.

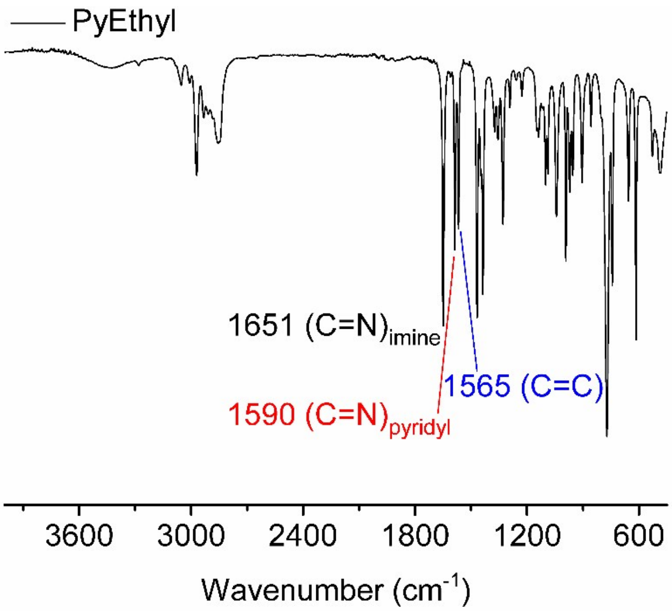
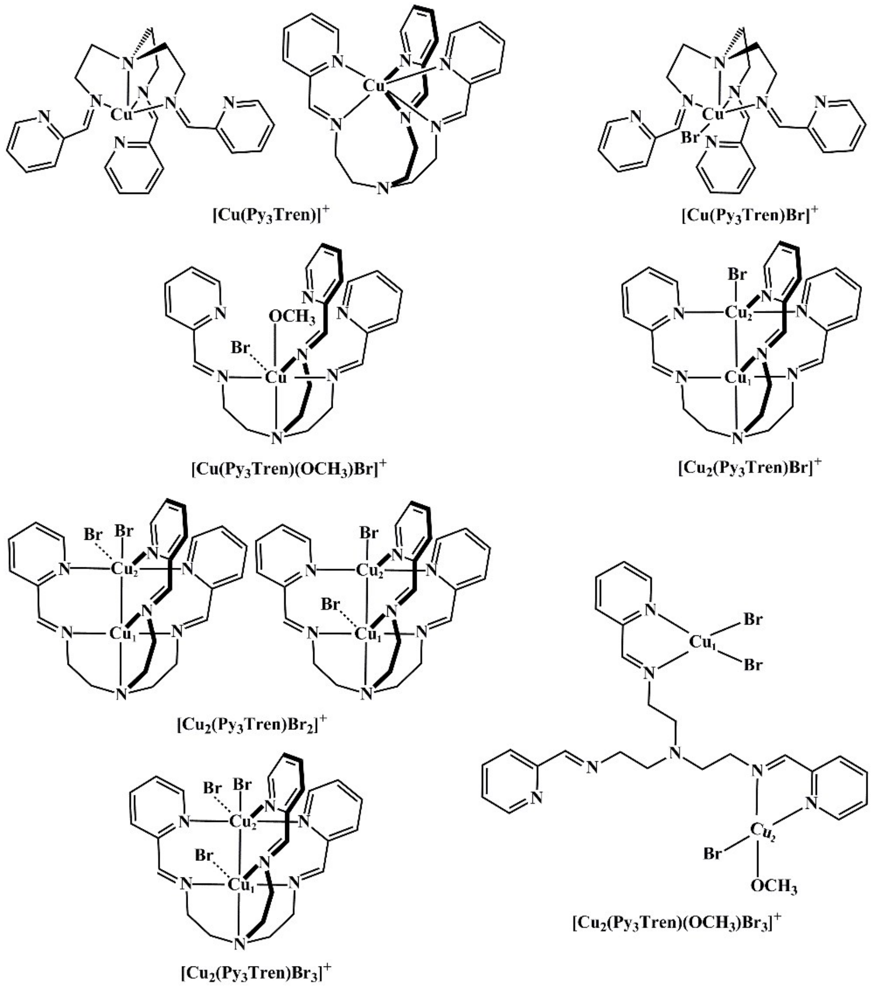


Figure S5. FTIR spectrum of PyEthyl.



$[Cu(Py_3Tren)]^+$

$[Cu(Py_3Tren)Br]^+$

$[Cu(Py_3Tren)(OCH_3)Br]^+$

$[Cu_2(Py_3Tren)Br]^+$

$[Cu_2(Py_3Tren)Br_2]^+$

$[Cu_2(Py_3Tren)(OCH_3)Br_3]^+$

$[Cu_2(Py_3Tren)Br_3]^+$

Figure S6. Proposed configurations of copper complexes with Py_3Tren ligand.

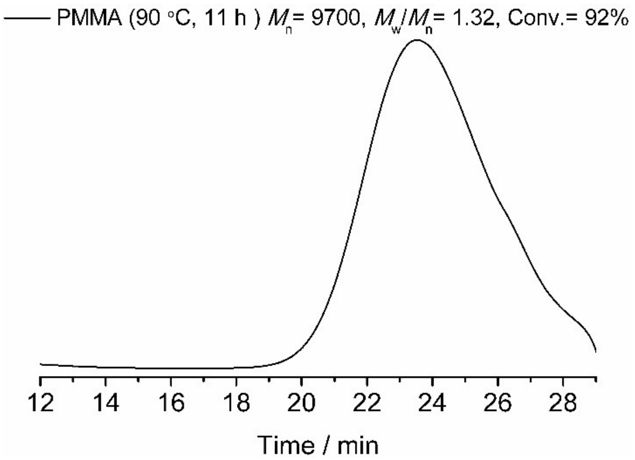


Figure S7. GPC evolution curve of PMMA.

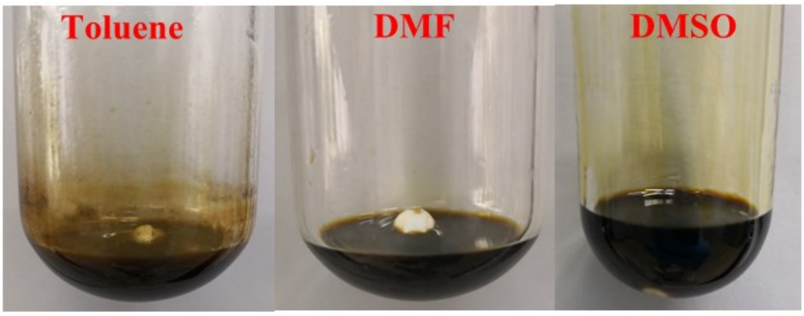


Figure S8. Images for the ATRP of MMA in different solvents at 90 ºC.

Table S1. Electrochemical Data for the different coordination complexes obtained by cyclic voltammetry.

Complex	$E_{p,a}$(V)	$E_{p,c}$(V)	ΔE (mV)	$E_{1/2}$(mV)
$CuBr_2/Py_3Tren$[a]	-0.038	-0.15	112	-94
$CuBr_2$/PyEthyl[a]	0.19	0.097	93	144
$CuBr_2/Py_3Tren$[b]	-0.11	-0.2	90	-155
$CuBr_2$/PyEthyl[b]	0.24	0.05	190	145

[a] Cyclic voltammograms of copper complexes in DMSO solution of 0.1 M Et_4NBF_4; [b] Cyclic voltammograms of copper complexes in the presence of ethyl α-bromoisobutyrate (EBiB, 5mM) in MeCN solution of 0.1 M Et_4NBF_4.

REFERENCES

1. D. M. Haddleton, M. C. Crossman, B. H. Dana, D. J. Duncalf, A. M. Heming, D. Kukulj and A. J. Shooter, *Macromolecules* 1999, **32**, 2110-2119.
2. S. Mandal, D. K. Seth and P. Gupta, *Polyhedron*, 2012, **31**, 167-175.
3. I. n. Morgenstern-Badarau, F. o. Lambert, J. P. Renault, M. l. Cesario, J.-D. Mare´chal and F. Maseras, *Inorganica Chimica Acta*, 2000, **297**, 338–350.