## **Supplementary Information**

# New copper (I) complex based initiating systems in redox polymerization and comparison with amine/benzoyl peroxide reference

P. Garra<sup>1</sup>, A. Kermagoret<sup>2</sup>, A. Al Mousawi<sup>1</sup>, F. Dumur<sup>2</sup>, D. Gigmes<sup>2</sup>, F. Morlet-Savary<sup>1</sup>, C. Dietlin<sup>1</sup>, J.P. Fouassier<sup>1</sup>, J. Lalevée<sup>1</sup>

<sup>1</sup>Institut de Science des Matériaux de Mulhouse IS2M, UMR CNRS 7361, UHA; 15, rue Jean Starcky, 68057 Mulhouse Cedex, France

<sup>2</sup>Aix Marseille Univ, CNRS, Institut de Chimie Radicalaire ICR, F-13397 Marseille, France

Compounds 4-nitro-aniline, 1,4-diaminobenzene, pyridinecarboxaldehyde,  $[Cu(CH_3CN)_4]BF_4$ ,  $[Cu(CH_3CN)_4]PF_6$  and bis[2-(diphenylphosphino)phenyl]ether (POP) were purchased from commercial sources (Aldrich, Acros or TCI) and used without further purification. NMR spectra were recorded on a Bruker AC-400 spectrometer. CHN elemental analysis, mass spectrometry and X-ray diffraction experiments were performed at Spectropole, Aix-Marseille University. high resolution mass spectrometer (electrospray ESI-MS) were recorded on a SYNAPT G2 HDMS (Waters) spectrometer equipped with atmospheric pressure ionization source (API). Samples were analyzed in ESI-MS positive mode: electrospray tension: 2.8 kV; exit tension: 20 V; nitrogen: 100 L/h.

#### Synthesis of ligand 4-Nitro-N-(2-pyridinylmethylene)benzenamine<sup>1</sup>

To a solution of 4-nitro-aniline (4.60 g, 33.3 mmol) in 100 mL of toluene, was added 2-Pyridinecarboxaldehyde (5.00 g, 46.7 mmol). The mixture was stirred at reflux for 2 days. Toluene was removed under reduced pressure and the solid was washed three times with diethyether. 4-Nitro-N-(2-pyridinylmethylene)benzenamine was recrystallized using ethyl acetate. Yield: 3.70 g (49%)

<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>)  $\delta$  8.76 (d, *J* = 4.6 Hz, 1H), 8.56 (s, 1H), 8.30 (d, *J* = 8.9 Hz, 2H), 8.20 (d, *J* = 7.9 Hz, 1H), 7.86 (ddd, *J* = 7.0 Hz, *J* = 4.9 Hz, *J* = 1.5 Hz, 1H), 7.50 – 7.39 (ddd, *J* = 4.9 Hz, *J* = 7.0 Hz, *J* = 1.5 Hz, 1H), 7.31 (d, *J* = 8.9 Hz, 2H). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>)  $\delta$  163.3 (s, CH), 156.9 (s, C), 153.7 (s, C), 150.0 (s, CH), 145.9

(s, C), 136.8 (s, CH), 125.9 (s, CH), 125.2 (s, CH), 122.4 (s, CH), 121.4 (s, CH).

#### Synthesis of ligand N-(2-pyridylmethylene)benzene-1,4-diamine<sup>2</sup>

To a solution of 1,4-diaminobenzene (2.62 g, 24.2 mmol) in 30 mL of ethanol, was slowly added a solution of pyridinecarboxaldehyde (2.60 g, 24.2 mmol) in 15 mL of ethanol (around 3 mL every 30 min). After addition, the mixture was stirred at room temperature for 2 h. The yellow precipitate was filtered and washed three times 10 mL of ethanol. *N-(2-pyridylmethylene)benzene-1,4-diamine* was recrystallized using 70 mL of toluene. Yield: 2.80 g (59%)

<sup>1</sup>H NMR (300 MHz, DMSO) δ 8.65 (d, *J* = 4.6 Hz, 1H), 8.58 (s, 1H), 8.09 (d, *J* = 7.9 Hz, 1H), 7.89 (td, *J* = 7.7, 1.4 Hz, 1H), 7.50 – 7.38 (m, 1H), 7.22 (d, *J* = 8.6 Hz, 2H), 6.62 (d, *J* = 8.6 Hz, 2H), 5.39 (s, 2H). <sup>13</sup>C NMR (75 MHz, DMSO) δ 155.5 (s), 154.2 (s), 149.9 (s), 149.3 (s), 138.8 (s), 137.2 (s),

125.0 (s), 123.5 (s), 120. 8 (s), 114.6 (s).

### Synthesis of copper complex CuC-f, Cu-e, CuC-c and CuC-g.

### Copper complex *CuC-f*

To a suspension of  $[Cu(CH_3CN)_4]BF_4$  (410 mg, 1.1 mmol) in 30 mL of degassed CH<sub>2</sub>Cl<sub>2</sub>, was added N-(2-pyridylmethylene)benzene-1,4-diamine (500 mg, 2.5 mmol) under argon. The solution turned red immediately and was stirred at room temperature for 2 h under argon. Then 200 mL of diethylether was added under argon and placed at 6 °C overnight. The precipitate was filtered, washed three times with diethylether and isolated as a dark solid. Yield: 614 mg (67%)

**CuC-f**. Anal. Calcd for C<sub>24</sub>H<sub>22</sub>CuF<sub>4</sub>N<sub>6</sub>P: C, 47.81; H, 3.68; N, 13.94; found: C,47.23; H,3.58; N,13.33.

HRMS (ESI) calcd for [C<sub>24</sub>H<sub>22</sub>N<sub>6</sub>Cu]+: 457.1196; found 457.1193

<sup>1</sup>H NMR (400 MHz, Acetone)  $\delta$  9.30 (s, 1H), 8.66 (d, J = 4.5 Hz, 1H), 8.24 (t, J = 7.7 Hz, 1H), 8.14 (d, J = 7.7 Hz, 1H), 7.80 – 7.69 (m, 1H), 7.46 (d, J = 8.7 Hz, 2H), 6.63 (d, J = 8.7 Hz, 2H), 5.23 (s, 2H).

Copper complex CuC-e

To a suspension of  $[Cu(CH_3CN)_4]BF_4$  (345 mg, 1.1 mmol) in 10 mL of degassed  $CH_2Cl_2$ , was added a solution of 4-Nitro-N-(2-pyridinylmethylene)benzenamine (500 mg, 2.2 mmol) in degassed  $CH_2Cl_2$  (10 mL). The solution turned red immediately and was stirred at room temperature for 2 h under argon. Then the solution was concentrated to 10 mL under reduced pressure and 90 mL of diethylether was added under argon and placed at -20 °C for 3 h. The precipitate was filtered, washed three times with diethylether and isolated as a dark red solid. Yield: 660 mg (78%)

**CuC-e**. Anal. Calcd for C<sub>24</sub>H<sub>18</sub>BCuF<sub>4</sub>N<sub>6</sub>O<sub>4</sub>: C, 47.66; H, 3.00; N, 13.90; found: C, 47.30; H ,3.01; N, 14.37.

HRMS (ESI) calcd for [C<sub>24</sub>H<sub>18</sub>N<sub>6</sub>O<sub>4</sub>Cu]+: 517.0680; found 517.0677

<sup>1</sup>H NMR (400 MHz, CD<sub>2</sub>Cl<sub>2</sub>) δ 9.08 (br s, 1H),8.57 (br s, 1H), 8.13 (br s,4H), 7.71 (br s, 1H), 7.43 (br s, 2H).

#### Copper complex *CuC-c*

To a suspension of  $[Cu(CH_3CN)_4]BF_4$  (499 mg, 1.6 mmol) and POP ligand (855 mg, 1.6 mmol) in 25 mL of degassed CH<sub>2</sub>Cl<sub>2</sub> under argon, was added a solution of N-(2-pyridylmethylene)benzene-1,4-diamine (313 mg, 1.6 mmol) in degassed CH<sub>2</sub>Cl<sub>2</sub> (5 mL). The solution turned red immediately and was stirred at room temperature for 1 h under argon. Then the solution was concentrated to 10 mL under reduced pressure and 100 mL of diethylether was added under argon and placed at 6 °C for 3 h. The orange precipitate was filtered, washed three times with ethyl acetate (30 mL) and isolated as an orange solid. Yield: 1.29 g (78%). Single crystals of CuC-c were obtained by slow diffusion of diethyl ether into a CH<sub>2</sub>Cl<sub>2</sub> solution of the complex at -20 °C.

<sup>1</sup>H NMR (300 MHz, Acetone)  $\delta$  8.87 (s, 1H), 8.36 (d, J = 5.0 Hz, 1H), 8.02 – 7.88 (overlapped signals of a triplet (J = 7.0 Hz) and a doublet (J = 1.2 Hz), 2H), 7.40 – 7.04 (m, 20H), 6.99 (t, J = 6.9 Hz, 11H), 6.73 (ddd, J = 7.8, 5.0, 1.6 Hz, 2H), 6.34 (d, J = 8.8 Hz, 2H), 5.01 (s, 2H).

Copper complex *CuC-g* 

To a suspension of  $[Cu(CH_3CN)_4]BF_4$  (353 mg, 1.1 mmol) in 10 mL of degassed CH<sub>2</sub>Cl<sub>2</sub> under argon, was added a solution of N-(2-pyridylmethylene)benzene-1,4-diamine (443 mg, 2.2 mmol) in degassed CH<sub>2</sub>Cl<sub>2</sub> (20 mL). The solution turned red immediately and was stirred at room temperature for 1 h under argon. Then the solution was concentrated to 10 mL under reduced pressure and diethylether was added under argon. The dark precipitate was filtered, washed with diethylether and isolated as a dark solid. Yield: 780 mg (98%). Single crystals of CuC-g were obtained by slow diffusion of diethyl ether into a CH<sub>2</sub>Cl<sub>2</sub> solution of the complex at -20 °C.

<sup>1</sup>H NMR (300 MHz, Acetone)  $\delta$  9.16 (s, 2H), 8.51 (d, J = 4.4 Hz, 2H), 8.09 (t, J = 7.6 Hz, 2H), 8.00 (d, J = 7.6 Hz, 2H), 7.66 – 7.55 (m, 2H), 7.31 (d, J = 8.6 Hz, 4H), 6.48 (d, J = 8.7 Hz, 4H), 5.09 (s, 4H).



Figure S1: Cyclic voltammograms in DCM under air, sweeping rate 0.1 V/S, potential vs SCE. A: 2 mM CuC-d. B: 5 mM CuC-g

	CuC-c	CuC-g
Chemical formula	$C_{48}H_{39}CuN_3OP_2 \cdot BF_4 \cdot C_4H_{10}O$	$C_{24}H_{22}CuN_6 \cdot BF_4 \cdot CH_2Cl_2$
CCDC Number	1531314	1531313
M <sub>r</sub>	960.23	629.75
Crystal system, space group	Monoclinic, $P2_1/c$	Monoclinic, $P2_1/n$
Temperature (K)	293	173
a, b, c (Å)	12.3268 (3), 21.2128 (5),	11.15632 (15), 11.63305 (16),
	19.3122 (5)	22.4830 (3)
α, β, γ (°)	104.764 (3)	102.7581 (13)
$V(Å^3)$	4883.1 (2)	2845.85 (7)
Z	4	4
Radiation type	Μο Κα	Cu <i>K</i> α
$\mu$ (mm-1)	0.57	3.27
Crystal size (mm)	$0.2 \times 0.18 \times 0.12$	0.2  imes 0.2  imes 0.05
Data collection		
Diffractometer	SuperNova, Dual, Cu at zero,	SuperNova, Dual, Cu at zero,
	AtlasS2	AtlasS2
	diffractometer	diffractometer
Absorption correction	Multi-scan	Multi-scan
	CrysAlis PRO, Agilent	CrysAlis PRO, Agilent
	Technologies, Version	Technologies, Version
	1.171.37.35 (release 13-08-2014	1.171.37.35 (release 13-08-2014
	CrysAlis171 .NET) (compiled	CrysAlis171 .NET) (compiled
	Aug 13 2014,18:06:01)	Aug 13 2014,18:06:01)
	Empirical absorption correction	Empirical absorption correction
	using spherical harmonics,	using spherical harmonics,
	implemented in SCALE3	implemented in SCALE3
	ABSPACK scaling algorithm.	ABSPACK scaling algorithm.
$T_{\min}, T_{\max}$	0.854, 1.000	0.768, 1.000
No. of measured, independent	74466, 11275, 8488	22167, 5244, 4715
and observed $[I > 2\sigma(I)]$		
reflections		
R <sub>int</sub>	0.037	0.027
$(\sin \theta / \lambda) \max (A-1)$	0.675	0.605
Refinement		
$R[F^2 > 2\sigma(F^2)], wR(F^2), S$	0.057, 0.165, 1.01	0.044, 0.125, 1.04
No. of reflections	11275	5244
No. of parameters	587	354
No. of restraints	4	-
H-atom treatment	H-atom parameters constrained	H-atom parameters constrained
$\Delta \rho_{\text{max}}, \Delta \rho_{\text{min}}$	0.83, -0.75	0.93, -0.54
$(e Å^{-3})$		

# Table 1. X-ray diffraction Data for CuC-c $\cdot C_4H_{10}O$ and CuC-g $\cdot CH_2Cl_2$ .

(1) Telitel, S.*et al. J. Polym. Sci. Part A* **2016**, *54*, 702.
(2) Marjani, K.*et al. J. Chem. Crystallogr.* **2011**, *41*, 1451.