Supplementary Information

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

P. Garra¹, A. Kermagoret², A. Al Mousawi¹, F. Dumur², D. Gigmes², F. Morlet-Savary¹, C. Dietlin¹, J.P. Fouassier¹, J. Lalevée¹

¹Institut de Science des Matériaux de Mulhouse IS2M, UMR CNRS 7361, UHA; 15, rue Jean Starcky, 68057 Mulhouse Cedex, France
²Aix Marseille Univ, CNRS, Institut de Chimie Radicalaire ICR, F-13397 Marseille, France

Compounds 4-nitro-aniline, 1,4-diaminobenzene, pyridinecarboxaldehyde, [Cu(CH₃CN)₄]BF₄, [Cu(CH₃CN)₄]PF₆ 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 spectrometry (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)benzenamine¹

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%)

¹H NMR (300 MHz, CDCl₃) δ 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).

¹³C NMR (75 MHz, CDCl₃) δ 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 \(N-(2\text{-pyridylmethylene})\text{benzene-1,4-diamine}\) \(^2\)

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. \(N-(2\text{-pyridylmethylene})\text{benzene-1,4-diamine}\) was recrystallized using 70 mL of toluene. Yield: 2.80 g (59%)

\(^1\)H NMR (300 MHz, DMSO) \(\delta\) 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).

\(^{13}\)C NMR (75 MHz, DMSO) \(\delta\) 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 \(\text{CuC-f, Cu-e, CuC-c and CuC-g}\).

Copper complex \(\text{CuC-f}\)

To a suspension of \([\text{Cu(CH}_3\text{CN)}_4\text{]}\text{BF}_4\) (410 mg, 1.1 mmol) in 30 mL of degassed \(\text{CH}_2\text{Cl}_2\), was added \(N-(2\text{-pyridylmethylene})\text{benzene-1,4-diamine}\) (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%)

\(\text{CuC-f}\). Anal. Calcd for \(\text{C}_{24}\text{H}_{22}\text{CuF}_4\text{N}_6\text{P}\): C, 47.81; H, 3.68; N, 13.94; found: C,47.23; H,3.58; N,13.33.

HRMS (ESI) calcd for \([\text{C}_{24}\text{H}_{22}\text{N}_6\text{Cu}]^+\): 457.1196; found 457.1193

\(^1\)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 \(\text{CuC-e}\)
To a suspension of [Cu(CH$_3$CN)$_4$]BF$_4$ (345 mg, 1.1 mmol) in 10 mL of degassed CH$_2$Cl$_2$, was added a solution of 4-Nitro-N-(2-pyridinylmethylene)benzenamine (500 mg, 2.2 mmol) in degassed CH$_2$Cl$_2$ (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$_{24}$H$_{18}$BCuF$_4$N$_6$O$_4$: C, 47.66; H, 3.00; N, 13.90; found: C, 47.30; H, 3.01; N, 14.37.

HRMS (ESI) calcd for [C$_{24}$H$_{18}$N$_6$O$_4$Cu]+: 517.0680; found 517.0677

$^1$H NMR (400 MHz, CD$_2$Cl$_2$) 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$_3$CN)$_4$]BF$_4$ (499 mg, 1.6 mmol) and POP ligand (855 mg, 1.6 mmol) in 25 mL of degassed CH$_2$Cl$_2$ under argon, was added a solution of N-(2-pyridylmethylene)benzene-1,4-diamine (313 mg, 1.6 mmol) in degassed CH$_2$Cl$_2$ (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$_2$Cl$_2$ solution of the complex at -20 °C.

$^1$H NMR (300 MHz, Acetone) δ 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$_3$CN)$_4$]BF$_4$ (353 mg, 1.1 mmol) in 10 mL of degassed CH$_2$Cl$_2$ under argon, was added a solution of N-(2-pyridylmethylene)benzene-1,4-diamine (443 mg, 2.2 mmol) in degassed CH$_2$Cl$_2$ (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$_2$Cl$_2$ solution of the complex at -20 °C.

$^1$H NMR (300 MHz, Acetone) δ 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
Table 1. X-ray diffraction Data for CuC-c·C₄H₁₀O and CuC-g·CH₂Cl₂.

<table>
<thead>
<tr>
<th></th>
<th>CuC-c</th>
<th>CuC-g</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chemical formula</td>
<td>C₄₈H₃₉CuN₃OP₂·BF₄·C₄H₁₀O</td>
<td>C₂₄H₂₆CuN₆·BF₄·CH₂Cl₂</td>
</tr>
<tr>
<td>CCDC Number</td>
<td>1531314</td>
<td>1531313</td>
</tr>
<tr>
<td>Mr</td>
<td>960.23</td>
<td>629.75</td>
</tr>
<tr>
<td>Crystal system, space group</td>
<td>Monoclinic, P2₁/c</td>
<td>Monoclinic, P2₁/n</td>
</tr>
<tr>
<td>Temperature (K)</td>
<td>293</td>
<td>173</td>
</tr>
<tr>
<td>a, b, c (Å)</td>
<td>12.3268 (3), 21.2128 (5), 19.3122 (5)</td>
<td>11.15632 (15), 11.63305 (16), 22.4830 (3)</td>
</tr>
<tr>
<td>α, β, γ (°)</td>
<td>104.764 (3)</td>
<td>102.7581 (13)</td>
</tr>
<tr>
<td>V (Å³)</td>
<td>4883.1 (2)</td>
<td>2845.85 (7)</td>
</tr>
<tr>
<td>Z</td>
<td>4</td>
<td>4</td>
</tr>
<tr>
<td>Radiation type</td>
<td>Mo Kα</td>
<td>Cu Kα</td>
</tr>
<tr>
<td>µ (mm⁻¹)</td>
<td>0.57</td>
<td>3.27</td>
</tr>
<tr>
<td>Crystal size (mm)</td>
<td>0.2 × 0.18 × 0.12</td>
<td>0.2 × 0.2 × 0.05</td>
</tr>
</tbody>
</table>

Data collection

| Diffractometer       | SuperNova, Dual, Cu at zero, AtlasS2 diffractometer                  | SuperNova, Dual, Cu at zero, AtlasS2 diffractometer                  |
| Tₘᵢₙ, Tₚₒₜₓ       | 0.854, 1.000                                                          | 0.768, 1.000                                                         |
| No. of measured, independent and observed [I > 2σ(I)] reflections | 74466, 11275, 8488                                                   | 22167, 5244, 4715                                                   |
| Rₓₑₜ                | 0.037                                                                | 0.027                                                                |
| (sin θ/λ)max (Å⁻¹)  | 0.675                                                                | 0.605                                                                |

Refinement

| R[F² > 2σ(F²)], wR(F²), 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                                       |
| Δρₓₑₜ, Δρᵣₑₜ (e Å⁻³)     | 0.83, −0.75                                                         | 0.93, −0.54                                                          |