

Copper Photoredox Catalysts For Polymerization Upon Near UV or Visible Light: Structure/Reactivity/Efficiency Relationships and Use in LED Projector 3D Printing Resins.

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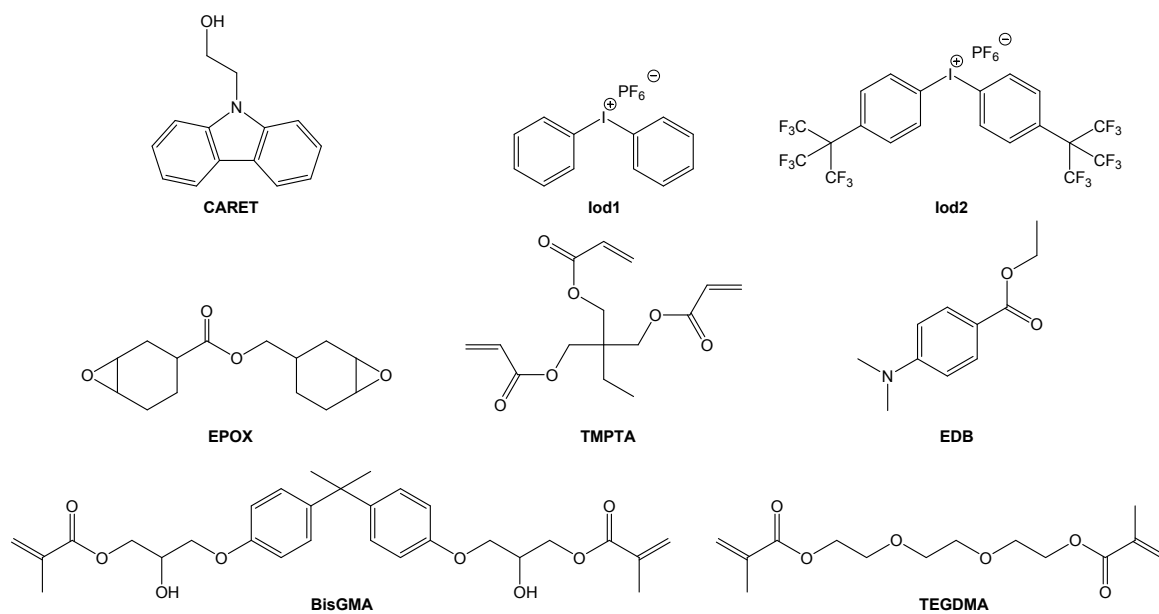
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Experimental part:

1/ Chemical compounds:

Diphenyliodonium hexafluorophosphate (Iod1), 9H-Carbazole-9-Ethanol (CARET), phenyl-*N-tert*-butylnitron (PBN) and ethyl 4-(dimethylamino) benzoate (EDB), were all obtained from Sigma Aldrich (Scheme S1). Bis-(4-*tert*-butylphenyl)-Iodonium hexafluorophosphate (Iod2) was obtained from Lambson (Speedcure 938). Trimethylolpropane triacrylate (TMPTA) and (3,4-epoxycyclohexane)methyl 3,4-epoxycyclohexylcarboxylate (EPOX; Uvacure 1500) were obtained from Allnex and used as benchmark monomers for radical and cationic photopolymerization. Bisphenol A-glycidyl methacrylate (BisGMA) and triethyleneglycol dimethacrylate (TEGDMA) were obtained from Aldrich and used with the highest purity available. 2-hydroxypyridine, pyrazole, 3-methyl-1H-pyrazole, 2-Iodopyridine, Phenyl-1H-pyrazole, 3-trifluoromethyl-1H-pyrazole, 3-nitro-1H-pyrazole, $[\text{Cu}(\text{CH}_3\text{CN})_4]\text{BF}_4$, $[\text{Cu}(\text{CH}_3\text{CN})_4]\text{PF}_6$, bis[2-(diphenylphosphino)phenyl]ether (POP) were purchased from commercial sources (Aldrich or TCI) and used without further purification. NMR spectra were recorded on a Bruker AC-300 or AC-400 spectrometer. X-ray diffraction experiments (Table S1) and CHN elemental analysis were performed at Spectropole, Aix-Marseille University. Crystal structures were

deposited on CCDC under the following deposition numbers: 1505694, 1505783, 1505784 and 1505785. 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.



Scheme S1. Other used chemical compounds.

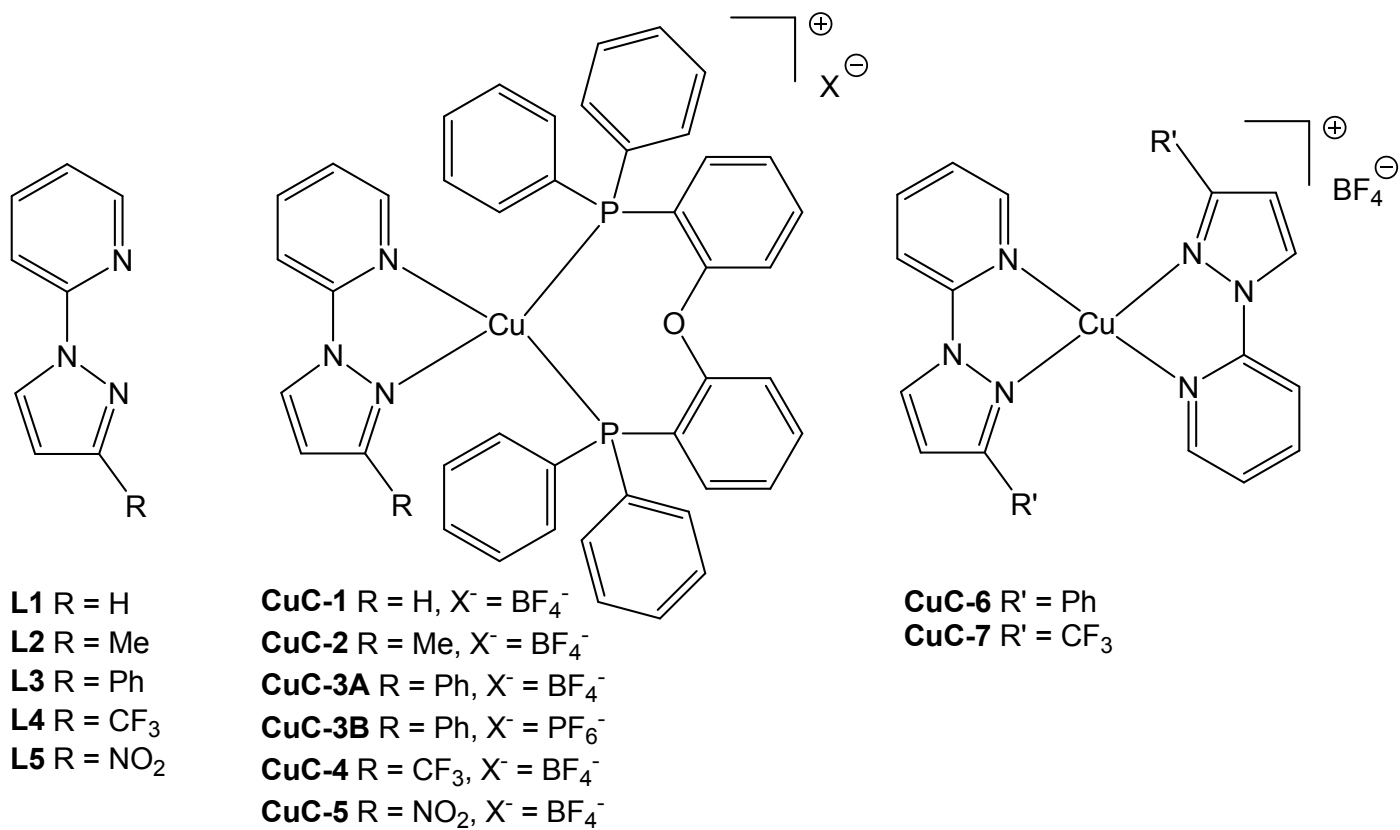
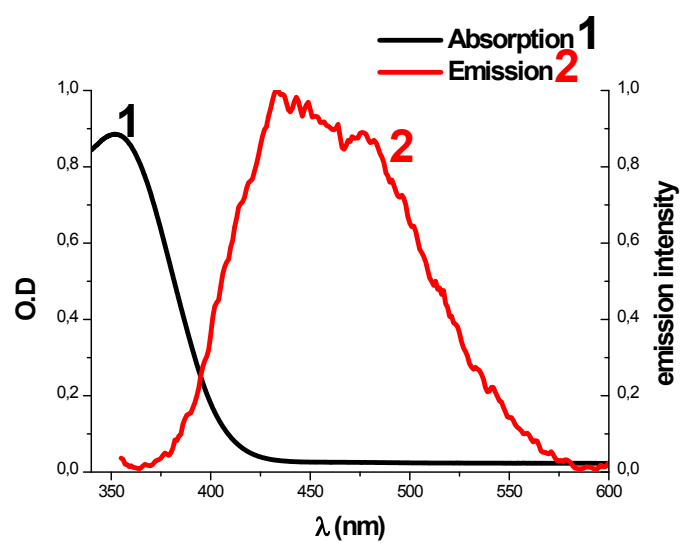


Figure S1. Investigated pyridine-pyrazole ligands **L1-L5** and copper complexes **CuC1-CuC-**
7.

Figure S2. **CuC-4** absorption vs. emission spectrum in DCM.



2/ Preparation of ligands and copper complexes (Figure S1):

The diimine ligands 1-(2-pyridyl)pyrazole (**L1**) and 3-methyl-1-(2-pyridyl)pyrazole (**L2**) were synthesized according to a literature procedure by reacting 2-hydroxypyridine and pyrazole or 3-methyl-1H-pyrazole, respectively.^[1]

Synthesis of ligand 3-phenyl-1-(2-pyridyl)pyrazole L3

The ligand 3-phenyl-1-(2-pyridyl)pyrazole **L3** was prepared according to a similar literature procedure.^[2] A solution of 2.89 g of 2-Iodopyridine (14.10 mmol) in 10 mL of degassed CH₃CN was added into a Schlenk containing 1.35 g of 3-Phenyl-1H-pyrazole (9.36 mmol), 0.10 g of CuBr (0.70 mmol) 5.0 g of Cs₂CO₃ (25.9 mmol) and 40 mL of degassed CH₃CN under argon. The mixture was stirred at reflux for 24 h. Then the solution was filtered and all volatiles were removed under reduced pressure. The ligand was isolated as a white power by flash chromatography using a mixture of EtOAc, heptane and NEt₃ (5/94/1% to 20/79/1%). Yield: 1.25 g, 60%.

¹H NMR (300 MHz, CDCl₃) δ 8.61 (d, *J* = 2.6 Hz, 1H), 8.42 (d, *J* = 4.9 Hz, 1H), 8.12 (d, *J* = 8.3 Hz, 1H), 7.95 (d, *J* = 7.3 Hz, 2H), 7.81 (ddd, *J* = 8.3, 7.5, 1.8 Hz, 1H), 7.46 (m, 2H), 7.38 (dt, *J* = 4.8, 1.9 Hz, 1H), 7.16 (ddd, *J* = 7.3, 4.9, 1.0 Hz, 1H), 6.79 (d, *J* = 2.6 Hz, 1H). ¹³C NMR (75 MHz, CDCl₃) δ 153.77 (s, N=C-pyrazole), 151.64 (s, N=C-pyridine), 148.00 (s, N=C-CH-CH-pyridine), 138.59 (s, N=C-CH-CH-pyridine), 133.02 (s, C-phenyl), 128.68 (s, CH-CH-CH-phenyl), 128.27 and 128.25 (overlapped singlets, CH-pyrazole and CH-phenyl), 125.98 (s, C-CH-CH-phenyl), 121.19 (s, N-CH-CH-pyridine), 112.48 (s, N-CH-pyridine), 105.30 (s, CH-pyrazole).

Synthesis of ligand 3-trifluoromethyl-1-(2-pyridyl)pyrazole L4.

ligand 3-trifluoromethyl-1-(2-pyridyl)pyrazole **L4** was synthesized following the same procedure than **L3** by reacting 2-iodopyridine (1.90 g, 9.30 mmol), 3-trifluoromethyl-1H-pyrazole (1.00 g, 7.30 mmol), CuI (0.20 g, 1.40 mmol) and Cs₂CO₃ (3.0 g, 15.6 mmol) in 30 mL of dry and degassed CH₃CN under argon at reflux for 16 h. The ligand was isolated as a white power by sublimation under vacuum (10⁻⁵ Bar) at 60 °C. Yield: 0.820 g, 52%. NMR data were in good agreement with the literature.^[2]

Synthesis of ligand 3-nitro-1-(2-pyridyl)pyrazole L5.

ligand 3-nitro-1-(2-pyridyl)pyrazole **L5** was synthesized following the same procedure than **L3** by reacting 2-iodopyridine (1.35 g, 6.56 mmol), 3-nitro-1H-pyrazole (0.60 g, 5.30 mmol), CuI (0.20 g, 1.40 mmol) and Cs₂CO₃ (3.0 g, 15.6 mmol) in 25 mL of dry and degassed CH₃CN under argon at reflux for 16 h. The ligand was isolated as a white power by recrystallization in ethanol. Yield: 0.42 g, 42%. ¹H NMR (300 MHz, CDCl₃) δ 8.68 (d, *J* = 2.7 Hz, 1H, *CH*-pyrazole), 8.49 (d, *J* = 4.7 Hz, 1H, *N-CH*-pyridine), 8.11 (d, *J* = 8.3 Hz, 1H, *C-CH*-pyridine), 7.92 (ddd, *J* = 8.1, 7.7, 1.7 Hz, 1H, *C-CH-CH*-pyridine), 7.36 (ddd, 1H, *J* = 5.2, 4.9 Hz, 0.7 Hz, *N-CH-CH*-pyridine), 7.09 (d, *J* = 2.7 Hz, 1H, *CH*-pyrazole). ¹³C NMR (75 MHz, CDCl₃) δ 206.80 (s, C-NO₂), 150.11 (s, *C*-pyridine), 148.30 (s, *N-CH*-pyridine), 139.28 (s, *C-CH-CH*-pyridine), 129.48 (s, *CH*-pyrazole), 123.49 (s, *N-CH-CH*-pyridine), 113.06 (s, *C-CH*-pyridine), 104.07 (s, *CH*-pyrazole).

Synthesis of copper complexes CuC-1, CuC-2 and CuC-4.

Copper complexes **CuC-1**, **CuC-2** and **CuC-4** are reported in the literature and were prepared following the same procedure:^[1] a mixture of [Cu(CH₃CN)₄]BF₄ (1 equiv.) and bis[2-(dipenylphosphino)phenyl]ether (POP, 1 equiv.) in degassed CH₂Cl₂ (10 mL) was stirred at room temperature for 1 h and then a CH₂Cl₂ solution of the corresponding diimine ligand (1 equiv.) was added under an argon atmosphere. The reaction mixture was stirred for another 2 h. The complex was precipitated by addition diethyl ether (40 mL), filtrated, washed two times with diethyl ether and dried under reduced pressure. The NMR spectra are in good agreement with the literature^[1] and the purity of the copper complexes is verified by CHN elemental analysis:

[Cu(L1)(POP)]BF₄ (**CuC-1**). Anal. Calcd for C₄₄H₃₅BCuF₄N₃OP₂: C, 63.36; H, 4.23; N, 5.04; found: C, 63.06; H, 4.41; N, 4.94.

[Cu(L2)(POP)]BF₄ (**CuC-2**). Anal. Calcd for C₄₅H₃₇BCuF₄N₃OP₂: C, 63.73; H, 4.40; N, 4.95; found: C, 63.42; H, 4.52; N, 4.96.

C₄₅H₃₇BCuF₄N₃OP₂ [Cu(L4)(POP)]BF₄ (**CuC-4**). Anal. Calcd for C₄₅H₃₄BCuF₇N₃OP₂: C, 59.92; H, 3.80; N, 4.66, found: C, 59.22; H, 3.68; N, 4.42.

Synthesis of copper complexes [Cu(L3)(POP)]BF₄ CuC-3A

a mixture of 200 mg of [Cu(CH₃CN)₄]BF₄ (0.64 mmol) and 343 mg of bis[2-(dipenylphosphino)phenyl]ether (POP, 0.64 mmol) in degassed CH₂Cl₂ (10 mL) was stirred at

room temperature for 1 h and then a CH₂Cl₂ solution of ligand **L3** (141 mg, 0.64 mmol) was added under an argon atmosphere. The reaction mixture was stirred for another 2 h at room temperature. The complex was precipitated by addition of diethyl ether (50 mL), filtrated, washed two times with diethyl ether and dried under reduced pressure. Yield: 0.445 g, 77%.

Single crystals of complex **CuC-3A** suitable for X-ray diffraction measurements were obtained by diffusion of diethyl ether into the CH₂Cl₂ solutions of the products.

[Cu(L3)(POP)]BF₄ (**CuC-3A**). ¹H NMR (400 MHz, Acetone) δ 8.96 (d, *J* = 2.8 Hz, 1H), 8.16 (m, 2H), 8.04 (d, *J* = 5.1 Hz, 1H), 7.74 (d, *J* = 7.4 Hz, 2H), 7.48 (t, *J* = 7.5 Hz, 1H), 7.45 – 7.30 (m, 8H), 7.25 (t, *J* = 7.4 Hz, 4H), 7.22 – 7.06 (m, 14H), 7.01 (d, *J* = 5.1 Hz, 4H), 6.88 (dt, *J* = 6.2, 3.6 Hz, 2H). ³¹P NMR (162 MHz, Acetone) δ -11.5 (s).

Anal. Calcd for C₅₀H₃₉BCuF₄N₃OP₂: C, 65.98; H, 4.32; N, 4.62; found: C, 65.27; H, 4.34; N, 4.41.

HRMS (ESI) calcd for [C₅₀H₃₉CuN₃OP₂]⁺: 822.1864; found 822.1859

Synthesis of copper complexes [Cu(L5)(POP)]BF₄ CuC-5

A mixture of 331 mg of [Cu(CH₃CN)₄]BF₄ (1.05 mmol) and 566 mg of bis[2-(diphenylphosphino)phenyl]ether (POP, 1.05 mmol) in degassed CH₂Cl₂ (20 mL) was stirred at room temperature for 1 h and then a CH₂Cl₂ solution of ligand **L3** (200 mg, 1.05 mmol) was added under an argon atmosphere. The reaction mixture was stirred for another 2 h at room temperature. The red solution was concentrated to 20 mL under reduced pressure. The complex was precipitated by addition diethyl ether (80 mL), filtrated, washed two times with diethyl ether and dried under reduced pressure. Yield: 0.805 g, 87%.

Single crystals of complex **CuC-5** suitable for X-ray diffraction measurements were obtained by diffusion of heptane into the CH₂Cl₂ solutions of the products.

[Cu(L5)(POP)]BF₄ (**CuC-5**). ¹H NMR (300 MHz, Acetone) δ 9.12 (d, *J* = 2.8 Hz, 1H), 8.40 (d, *J* = 8.2 Hz, 1H), 8.25 (t, *J* = 7.9 Hz, 1H), 8.02 (d, *J* = 4.3 Hz, 1H), 7.76 – 6.89 (m, overlapped broad signals, 30H). ³¹P NMR (162 MHz, Acetone) δ -11.2 (s).

Anal. Calcd for C₅₀H₃₉BCuF₄N₃OP₂: C, 59.98; H, 4.12; N, 6.36; found: C, ; H, 3.74; N, 6.34.

HRMS (ESI) calcd for [C₅₀H₃₉CuN₃OP₂]⁺: 791.1397; found 791.1403

Synthesis of copper complex [Cu(L3)₂]BF₄ CuC-6

Copper complex **CuC-6** was prepared by reacting ligand **L3** (1.42 mmol, 315 mg) and $[\text{Cu}(\text{CH}_3\text{CN})_4]\text{BF}_4$ (0.71 mmol, 220 mg) in degassed CH_2Cl_2 (30 mL) at room temperature for 2 h under argon atmosphere. The solution was concentrated to 10 mL under reduced pressure and the complex was then precipitated by addition of diethyl ether (100 mL), filtrated, washed two times with diethyl ether and dried under reduced pressure. Single crystals of complex **CuC-6** suitable for X-ray diffraction measurements were obtained by diffusion of diethyl ether into the CH_2Cl_2 solutions of the products.

$[\text{Cu}(\text{L3})_2]\text{BF}_4$ (**CuC-6**). ^1H NMR (400 MHz, Acetone) δ 9.07 (s, 2H), 8.61 (s, 2H), 8.34 (s, 4H), 7.87 (d, $J = 6.9$ Hz, 4H), 7.59 (s, 2H), 7.35 (s, 2H), 7.27 (t, $J = 7.2$ Hz, 2H), 7.18 (t, $J = 7.3$ Hz, 4H).

Anal. Calcd for

$\text{C}_{28}\text{H}_{22}\text{BCuF}_4\text{N}_6$: C, 56.72; H, 3.74; N, 14.18; found: C, 56.61; H, 3.42; N, 13.86.

HRMS (ESI) calcd for $[\text{C}_{28}\text{H}_{22}\text{CuN}_6]^+$: 505.1202; found 505.1197

*Synthesis of copper complex $[\text{Cu}(\text{L4})_2]\text{BF}_4$ **CuC-7***

Copper complex **CuC-7** was prepared by reacting ligand **L4** (1.27 mmol, 270 mg) and $[\text{Cu}(\text{CH}_3\text{CN})_4]\text{BF}_4$ (0.63 mmol, 200 mg) in degassed CH_2Cl_2 (15 mL) at room temperature for 1 h under argon atmosphere. The solution was concentrated to 10 mL under reduced pressure and the complex was then precipitated by addition of heptane (100 mL), filtrated, washed two times with diethyl ether and dried under reduced pressure. Yield: 0.335 g, 92%.

Single crystals of complex **CuC-7** suitable for X-ray diffraction measurements were obtained by diffusion of heptane into the CH_2Cl_2 solutions of the products.

$[\text{Cu}(\text{L3})_2]\text{BF}_4$ (**CuC-7**). ^1H NMR (300 MHz, Acetone) δ 9.23 (s, 2H), 8.73 (s, 2H), 8.44 (d, $J = 7.1$ Hz, 4H), 7.77 (s, 2H), 7.35 (s, 2H).

Anal. Calcd for $\text{C}_{18}\text{H}_{12}\text{BCuF}_{10}\text{N}_6$: C, 37.49; H, 2.10; N, 14.57; found: C, 37.38; H, 1.94; N, 14.13.

HRMS (ESI) calcd for $[\text{C}_{18}\text{H}_{12}\text{CuF}_6\text{N}_6]^+$: 489.0318; found 489.0318

*Synthesis of copper complexes $[\text{Cu}(\text{L3})(\text{POP})]\text{PF}_6$ **CuC-3B***

A mixture of 337 mg of $[\text{Cu}(\text{CH}_3\text{CN})_4]\text{PF}_6$ (0.90 mmol) and 487 mg of bis[2-(diphenylphosphino)phenyl]ether (POP, 0.90 mmol) in degassed CH_2Cl_2 (15 mL) was stirred at room temperature for 1 h and then a CH_2Cl_2 solution of ligand **L3** (200 mg, 0.90 mmol) was added under an argon atmosphere. The reaction mixture was stirred for another 3 h at room temperature. All volatiles were removed reduced pressure and 10 mL of diethyl ether was added. The complex was precipitated by addition of pentane (80 mL), filtrated, dried under reduced pressure and isolate as a white solid. Yield: 0.865 g, 98%.

$[\text{Cu}(\text{L3})(\text{POP})]\text{PF}_6$ (**CuC-3B**). ^1H NMR (400 MHz, Acetone- D_6) δ 8.96 (d, $J = 2.8$ Hz, 1H), 8.16 (m, 2H), 8.04 (d, $J = 5.1$ Hz, 1H), 7.74 (d, $J = 7.4$ Hz, 2H), 7.48 (t, $J = 7.5$ Hz, 1H), 7.45 – 7.31 (m, 8H), 7.25 (t, $J = 7.4$ Hz, 4H), 7.22 – 7.05 (m, 15H), 7.01 (d, $J = 5.1$ Hz, 4H), 6.88 (dt, $J = 6.2, 3.6$ Hz, 2H). ^{31}P NMR (162 MHz, Acetone- D_6) δ -12 (very broad singlet), -144.25 (appearance of quintuplet, $J = 707.4$ Hz). ^{19}F NMR (376 MHz, Acetone- D_6) δ -72.6 (d, $J = 705.0$ Hz)

Anal. Calcd for $\text{C}_{50}\text{H}_{39}\text{CuF}_6\text{N}_3\text{OP}_3$: C, 62.02; H, 4.06; N, 4.34; found: C, 62.57; H, 4.00; N, 3.98.

3/ Irradiation sources:

The following Light Emitting Diodes (LEDs) were used as irradiation sources: i) LED@375 nm - incident light intensity at the sample surface: $I_0 \approx 40 \text{ mW cm}^{-2}$; ii) LED@405nm ($I_0 \approx 110 \text{ mW cm}^{-2}$).

4/ Cationic Photopolymerization (CP) and Free Radical Photopolymerization (FRP):

The two-component photoinitiating systems (PISs) are mainly based on CuC/Iodonium salt (0.5/1% w/w) for both CP and FRP. The weight percent of the photoinitiating system is calculated from the monomer content. The photosensitive thin formulations ($\sim 25 \mu\text{m}$ of thickness) were deposited on BaF_2 pellets under air for the CP of EPOX while for the FRP of TMPTA and BisGMA/TEGDMA it was done in laminate (the formulation is sandwiched between two polypropylene films to reduce the O_2 inhibition). The 1.4 mm thick samples of BisGMA/TEGDMA were also polymerized under air.

The evolution of the epoxy group content and the double bond content of (meth)acrylate functions were continuously followed by real time FTIR spectroscopy (JASCO FTIR 4100) at about 790 cm^{-1} and 1630 cm^{-1} , respectively. The evolution of the methacrylate characteristic peak for the thick samples (1.4 mm) was followed in the near infrared range at $\sim 6160 \text{ cm}^{-1}$.

The procedure used to monitor the photopolymerization profile has been described in details in previous articles.^[3]

5/ Redox Potentials:

The CuC oxidation potentials (E_{ox} vs. SCE) were measured in acetonitrile by cyclic voltammetry with tetrabutyl-ammonium hexafluorophosphate 0.1 M as a supporting electrolyte. The free energy change ΔG_{et} for an electron transfer reaction was calculated from the classical Rehm-Weller equation (eq. 1) where E_{ox} , E_{red} , E^* and C are the oxidation potential of the electron donor, the reduction potential of the electron acceptor, the excited state energy level and the coulombic term for the initially formed ion pair, respectively.^[4] C is neglected as usually done in polar solvents.

$$\Delta G_{\text{et}} = E_{\text{ox}} - E_{\text{red}} - E^* + C \quad (\text{eq. 1})$$

6/ ESR spin trapping (ESR-ST) experiments:

The ESR-ST experiments were carried out using an X-Band spectrometer (Bruker EMX-Plus). LED@405nm was used as irradiation source for triggering the production of radicals at room temperature (RT) under N_2 saturated toluene/dichloromethane (90/10) and trapped by phenyl-*N-tert*-butylnitron (PBN) according to a procedure described elsewhere in detail.^[3a] The ESR spectra simulations were carried out with the PEST WINSIM program.

7/ Luminescence Experiments:

The luminescence properties of the compounds were studied using a JASCO FP-6200

Table 1. X-ray diffraction Data for CuC-3A·2(CH₂Cl₂), CuC-5·CH₂Cl₂, CuC-6 and CuC-7.

	CuC-3A	CuC-5	CuC-6	CuC-7
Chemical formula	C ₅₀ H ₃₉ CuN ₃ OP ₂ ·BF ₄ ·2(CH ₂ Cl ₂)	C ₄₄ H ₃₄ CuN ₄ O ₃ P ₂ ·BF ₄ ·CH ₂ Cl ₂	C ₂₈ H ₂₂ CuN ₆ ·BF ₄	C ₁₈ H ₁₂ CuF ₆ N ₆ ·BF ₄
M_r	1079.98	963.97	592.86	576.69
Crystal system, space group	Triclinic, <i>P-1</i>	Triclinic, <i>P-1</i>	Monoclinic, <i>P2₁/c</i>	Monoclinic, <i>P2₁/n</i>
Temperature (K)	223	293	293	293
a, b, c (Å)	13.4202 (2), 13.6037 (2), 16.3741 (3)	11.2058 (5), 14.4649 (6), 15.2793 (6)	12.19374 (9), 20.67859 (12), 10.92876 (9)	10.63580 (13), 9.58616 (10), 22.9954 (3)
α, β, γ (°)	70.5077 (16), 73.0432 (15),	67.032 (4), 82.767 (4),	108.0467 (8)	99.7158 (13)

	63.2685 (18)	77.773 (4)		
V (Å ³)	2480.99 (9)	2225.99 (18)	2620.11 (3)	2310.90 (5)
Z	2	2	4	4
Radiation type	Cu $K\alpha$	Mo $K\alpha$	Cu $K\alpha$	Cu $K\alpha$
μ (mm ⁻¹)	3.69	0.74	1.69	2.28
Crystal size (mm)	0.28 × 0.16 × 0.1	0.32 × 0.16 × 0.13	0.36 × 0.2 × 0.2	0.3 × 0.12 × 0.08
Data collection				
Diffractometer	SuperNova, Dual, Cu at zero, AtlasS2 diffractometer	SuperNova, Dual, Cu at zero, AtlasS2 diffractometer	SuperNova, Dual, Cu at zero, AtlasS2 diffractometer	SuperNova, Dual, Cu at zero, AtlasS2 diffractometer
Absorption correction	Multi-scan <i>CrysAlis PRO</i> , Agilent Technologies, Version 1.171.37.35 (release 13-08-2014 CrysAlis171 .NET) (compiled Aug 13 2014, 18:06:01) Empirical absorption correction using spherical harmonics, implemented in SCALE3 ABSPACK scaling algorithm.	Multi-scan <i>CrysAlis PRO</i> 1.171.38.43 (Rigaku Oxford Diffraction, 2015) Empirical absorption correction using spherical harmonics, implemented in SCALE3 ABSPACK scaling algorithm.	Multi-scan <i>CrysAlis PRO</i> , Agilent Technologies, Version 1.171.37.35 (release 13-08-2014 CrysAlis171 .NET) (compiled Aug 13 2014, 18:06:01) Empirical absorption correction using spherical harmonics, implemented in SCALE3 ABSPACK scaling algorithm.	Multi-scan <i>CrysAlis PRO</i> 1.171.38.43 (Rigaku Oxford Diffraction, 2015) Empirical absorption correction using spherical harmonics, implemented in SCALE3 ABSPACK scaling algorithm.
T_{\min} , T_{\max}	0.825, 1.000	0.729, 1.000	0.838, 1.000	0.700, 1.000
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	33640, 9099, 8456	28659, 9278, 7242	27280, 4825, 4522	23501, 4172, 3721
R_{int}	0.026	0.035	0.018	0.031
$(\sin \theta/\lambda)_{\text{max}}$ (Å ⁻¹)	0.605	0.663	0.605	0.600
Refinement				
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.037, 0.107, 1.06	0.053, 0.144, 1.03	0.040, 0.112, 1.06	0.059, 0.185, 1.04
No. of reflections	9099	9278	4825	4172
No. of parameters	685	559	361	352
H-atom treatment	H-atom parameters constrained	H-atom parameters constrained	H-atom parameters constrained	H-atom parameters constrained
$\Delta\rho_{\text{max}}$, $\Delta\rho_{\text{min}}$ (e Å ⁻³)	0.50, -0.50	0.98, -0.83	0.64, -0.43	0.46, -0.35

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