Electronic Supplementary Material (ESI) for Polymer Chemistry.

Supporting Information:

Copper Complexes: Effect of Ligands on Their Photoinitiation Efficiencies in Radical Polymerization Reactions under Visible Lights.

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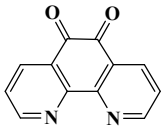
Preparation of Copper Complexes

All reagents and solvents were purchased from Aldrich or Alfa Aesar and used as received without further purification. Mass spectroscopy was performed by the Spectropole of Aix-Marseille University. ESI mass spectral analyses were recorded with a 3200 QTRAP (Applied Biosystems SCIEX) mass spectrometer. The HRMS mass spectral analysis was performed with a QStar Elite (Applied Biosystems SCIEX) mass spectrometer. Elemental analyses were recorded with a Thermo Finnigan EA 1112 elemental analysis apparatus driven by the Eager 300 software. ^{1}H and ^{13}C NMR spectra were determined at room temperature in 5 mm o.d. tubes on a Bruker Avance 400 spectrometer of the Spectropole: ^{1}H (400 MHz) and ^{13}C (100 MHz). The ^{1}H chemical shifts were referenced to the solvent peak $CDCl_3$ (7.26 ppm), DMSO (2.49 ppm) and the ^{13}C chemical shifts were referenced to the solvent peak $CDCl_3$ (77 ppm), DMSO (49.5 ppm). All these dyes were prepared with analytical purity up to accepted standards for new organic compounds (>98%) which was checked by high field NMR analysis. 2,9-Dibutyl-1,10-phenanthroline [T. Ishi-i, K. Yaguma, R. Kuwahara, Y. Taguri, S. Mataka, Org. Lett., 2006, 8, 585-588] and 4,4'-dimethyl-6,6'-diphenyl-2,2'-bipyrimidine [Q.-D. Liu, R. Wang, S. Wang, *Dalton Trans*. 2004, 2073-2079] were synthesized as previously reported, without modifications and in similar yields.

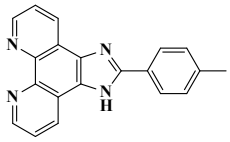
Synthesis of 1,10-phenanthroline-5,6-dione



Chemical Formula: $C_{12}H_6N_2O_2$
Exact Mass: 210,0429
Molecular Weight: 210,1882

To an ice-cold mixture of concentrated H_2SO_4 95% (10 mL) and HNO_3 (5 mL) was added to 1,10-phenanthroline (1 g, 5.5 mmol) and KBr (1 g, 8.4 mmol). The mixture was heated at reflux for 3 h. The hot yellow solution was poured over 500 mL of ice and neutralized carefully with sodium hydroxide until neutral to slightly acidic pH. Extraction with $CHCl_3$ followed by drying with Na_2SO_4 and removal of solvent gave 1,10-phenanthroline-5,6-dione (1.5 g, 96% yield). NMR analyses were consistent with those previously reported [J. P. Nietfeld, R. L. Schwiderski, T. P. Gonnella, S. C. Rasmussen, J. Org. Chem. 2011, 76, 6383–6388]. ^{1}H NMR (DMSO-d_6) δ (ppm): 7.58 (dd, 2H, J = 4.7 Hz, J = 8.0 Hz), 8.48 (dd, 2H, J = 1.8 Hz, J = 8.0 Hz), 9.11 (dd, 2H, J = 4.7 Hz, J = 1.8 Hz); ^{13}C NMR (DMSO-d_6) δ (ppm): 125.8, 128.3, 137.5, 153.2, 156.3, 178.9; HRMS (ESI MS) m/z: theor: 210.0429 found: 210.0431 ($M^{+\cdot}$ detected).

Synthesis of 2-(p-tolyl)-1H-imidazo[4,5-f][1,10]phenanthroline (TolylPhen)

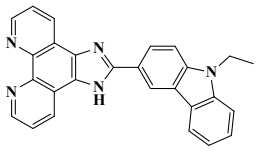


Chemical Formula: $C_{20}H_{14}N_4$
Exact Mass: 310,1218
Molecular Weight: 310,3520

1,10-Phenanthroline-5,6-dione (2.1 g, 10 mmol), *p*-tolualdehyde (1.6 mL, 1.68 g, 14 mmol) and ammonium acetate (15.5 g, 200 mmol) were refluxed overnight in degassed acetic acid (40 mL) under N_2 overnight. The reaction mixture was diluted with water (20 mL) and neutralized with NH_4OH to give a precipitate of the product which was filtered, washed with dilute NH_4OH (pH = 8), water and ether and dried in vacuum. The ligand was purified by column chromatography (SiO_2) using ethanol as the eluent. NMR analyses were consistent with those previously reported [N. M. Shavaleev, H. Adams, J. A. Weinstein, *Inorg. Chim. Acta* 360 (2007) 700-704]. ^{1}H NMR (DMSO-d_6) δ (ppm): 2.42 (s, 3H),

3.00-3.75 (brs, 1H, NH), 7.41 (d, 2H, J = 7.5 Hz), 7.82 (q, 2H, J = 4.2 Hz), 8.21 (d, 2H, J = 8.1 Hz), 8.95 (d, 2H, J = 7.9 Hz), 9.03 (d, 2H, J = 2.1 Hz); Anal. Calcd for $C_{20}H_{14}N_4$ (%): C, 77.4; H, 4.5; N, 18.1%; Found: C, 77.3; H, 4.7; N, 17.8%; HRMS (ESI MS) m/z: theor: 310.1218 found: 310.1215 ($M^{+\cdot}$ detected).

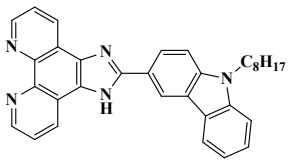
Synthesis of 2-(9-ethyl-9H-carbazol-3-yl)-1H-imidazo[4,5-f][1,10]phenanthroline (EtCarbPhen)



Chemical Formula: $C_{27}H_{19}N_5$
Exact Mass: 413,1640
Molecular Weight: 413,4733

1,10-Phenanthroline-5,6-dione (2.1 g, 10 mmol), 9-octyl-9*H*-carbazole-3-carbaldehyde (3.12 g, 14 mmol) and ammonium acetate (15.5 g, 200 mmol) were refluxed overnight in degassed acetic acid (40 mL) under N_2 overnight. The reaction mixture was diluted with water (20 mL) and neutralized with NH_4OH to give a precipitate of the product which was filtered, washed with dilute NH_4OH (pH = 8), water and ether and dried in vacuum. The ligand was purified by column chromatography (SiO_2) using ethanol as the eluent (3.06 g, 94 % yield). NMR characterizations were consistent with those previously reported [X. W. Huang, X. J. Chen, J. L. Shen, G. J. Su, J. Coord. Chem., 2013, 63, 1570-1581]. ^{1}H NMR (DMSO-d_6) δ (ppm): 1.40 (t, 3H, J = 7.2 Hz), 4.55 (q, 2H, J = 7.2 Hz), 7.35 (d, 2H, J = 6.8 Hz), 7.57 (td, 1H, J = 8.1 Hz, J = 0.9 Hz), 7.74 (d, 2H, J = 7.4 Hz), 7.84-7.88 (m, 2H), 8.32-8.36 (m, 3H), 9.08-9.12 (m, 4H); Anal. Calcd for $C_{27}H_{19}N_5$ (%): C, 78.5; H, 4.6; N, 16.9% Found: C, 78.3; H, 4.8; N, 16.6%; HRMS (ESI MS) m/z: theor: 413.1640 found: 413.1643 ($M^{+\cdot}$ detected).

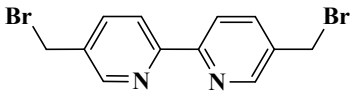
Synthesis of 2-(9-octyl-9H-carbazol-3-yl)-1H-imidazo[4,5-f][1,10]phenanthroline (OctCarbPhen)



Chemical Formula: $C_{33}H_{31}N_5$
Exact Mass: 497,2579
Molecular Weight: 497,6327

1,10-Phenanthroline-5,6-dione (2.1 g, 10 mmol), 9-octyl-9H-carbazole-3-carbaldehyde (4.3 g, 14 mmol) and ammonium acetate (15.5 g, 200 mmol) were refluxed overnight in degassed acetic acid (40 mL) under N_2 overnight. The reaction mixture was diluted with water (20 mL) and neutralized with NH_4OH to give a precipitate of the product which was filtered, washed with dilute NH_4OH (pH = 8), water and ether and dried in vacuum. The ligand was purified by column chromatography (SiO_2) using CH_2Cl_2:ethanol 1:1 as the eluent (3.98 g, 80% yield). ^{1}H NMR (DMSO-d_6) δ (ppm): 0.79 (t, 3H, J = 6.5 Hz), 1.08-1.40 (m, 12H), 1.77-1.81 (m, 2H), 4.40 (t, 2H, J = 7.2 Hz), 6.70 (brs, 1H, NH), 7.24-7.32 (m, 2H), 7.48 (td, 1H, J = 8.1 Hz, J = 0.9 Hz), 7.61 (d, 1H, J = 7.4 Hz), 7.75-7.85 (m, 2H), 8.26 (d, 1H, J = 8.7 Hz), 8.50 (d, 1H, J = 8.4 Hz), 9.08-9.12 (m, 3H); Anal. Calcd for $C_{33}H_{31}N_5$ (%): C, 79.6; H, 6.3; N, 14.1%; Found: C, 79.4; H, 6.5; N, 13.8%; HRMS (ESI MS) m/z: theor: 497.2579 found: 497.2577 ($M^{+\cdot}$ detected).

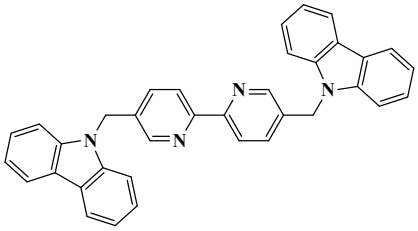
Synthesis of 5,5'-dibromomethyl-2,2'-bipyridine



Chemical Formula: $C_{12}H_{10}Br_2N_2$
Exact Mass: 339,9211
Molecular Weight: 342,0292

5,5'-dimethyl-2,2'-bipyridine (1 g, 5.43 mmol), *N*-bromosuccinimide (2 g, 11.23 mmol) were suspended in chloroform (50 mL), followed by an addition of AIBN (20 mg). The reaction mixture was refluxed overnight and cooled. The succinimide was removed from the reaction mixture by filtration and the filtrate was cooled at 0°C for 2h. The residue was purified by column chromatography (SiO_2, pentane/CH_2Cl_2 : 9:1). The solid was recrystallized in a mixture of chloroform and pentane and isolated as colourless crystals (1.56 g, 84% yield). ^{1}H NMR ($CDCl_3$) δ (ppm): 4.54 (s, 4H), 7.86 (dd, 2H, J = 1.8 Hz, J = 7.9 Hz), 8.41 (d, 2H, J = 7.9 Hz), 8.70 (d, 2H, J = 1.8 Hz); ^{13}C NMR ($CDCl_3$) δ (ppm): 29.4, 121.2, 133.3, 137.7, 149.3, 155.2; HRMS (ESI MS) m/z: theor: 339.9211 found: 339.9209 ($M^{+\cdot}$ detected).

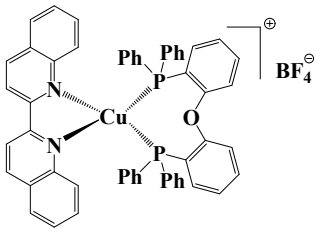
Synthesis of 5,5'-bis((9H-carbazol-9-yl)methyl)-2,2'-bipyridine



Chemical Formula: $C_{36}H_{26}N_4$
Exact Mass: 514,2157
Molecular Weight: 514,6184

To carbazole (1.08 g, 5.98 mmol, 2.2 eq.) in 30 mL dry THF was added 0.3 g NaH (60% dispersion in mineral oil). After 20 min, 5,5'-*bis*(bromomethyl)-2,2'-bipyridine (1.0 g, 2.93 mmol) was added and the reaction mixture was heated at 60°C overnight. After cooling, the reaction mixture was quenched onto ice, and an insoluble precipitated formed. It was filtered and dried. It was used without any further purification. ^{1}H NMR (DMSO-d_6) δ (ppm): 5.49 (s, 4H), 7.24 (t, 4H, J = 7.3 Hz), 7.33 (d, 4H, J = 7.9 Hz), 7.41 (t, 4H, J = 7.5 Hz), 7.43 (d, 2H, J = 7.7 Hz), 8.11 (d, 2H, J = 7.7 Hz), 8.19 (d, 4H, J = 8.1 Hz), 8.43 (s, 2H); Anal. Calcd for $C_{36}H_{26}N_4$ (%): C, 84.0; H, 5.1; N, 10.9%; Found: C, 80.1; H, 5.3; N, 10.8%; HRMS (ESI MS) m/z: theor: 514.2157 found: 514.2155 ($M^{+\cdot}$ detected).

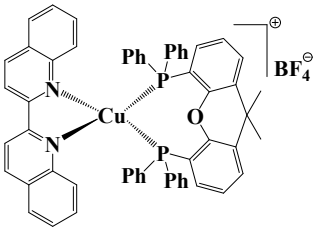
Synthesis of [Cu(2,2'-biquinoline)(DPEphos)]BF_4 ***A3***



A mixture of [Cu(CH_3CN)$_4$]BF_4 (310 mg, 1 mmol) and *bis*[2-(diphenylphosphino)phenyl]ether (540 mg, 1 mmol) in dichloromethane (200 mL) was stirred at 25 °C for 2 h and then treated with a solution of 2,2'-biquinoline (256 mg, 1 mmol) in 50 mL of dichloromethane. This reaction mixture was stirred for an additional 1 h and filtered and the clear yellow filtrate concentrated to ca. 5 mL. Addition of pentane precipitated the complex which was filtered, washed several times with pentane and dried under vacuum (832 mg, 88 % yield). ^{1}H NMR (DMSO-d_6) δ (ppm): 6.79-6.91 (m, 16H), 7.11-7.21 (m, 12H), 7.40 (td, 2H, J = 8.2 Hz, J = 2.1 Hz), 7.47 (t, 2H, J = 7.7 Hz), 7.89 (d, 2H, J = 8.1 Hz), 8.24 (d,

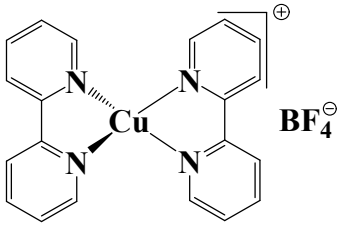
2H, J = 8.6 Hz), 8.48 (d, 2H, J = 8.7 Hz), 8.57 (d, 2H, J = 8.7 Hz); ^{13}C NMR (DMSO-d_6) δ (ppm): 120.0, 120.3, 124.8, 125.2, 125.36-125.41 (m), 128.1, 128.4 (t, J = 4.7 Hz), 129.1, 129.6, 129.8, 130.0, 131.0 (t, J = 17.0 Hz), 132.3, 132.7 (t, J = 7.7 Hz), 134.2, 139.6, 145.6, 152.6 (t, J = 2.3 Hz), 158.7 (t, J = 6.1 Hz); ^{31}P NMR (DMSO-d_6) δ (ppm): -15.80; HRMS (ESI MS) m/z: theor: 857.1906 found: 857.1902 ($M^{+\cdot}$ detected).

Synthesis of [Cu(2,2'-biquinoline)(XantPhos)]BF_4 ***A4***



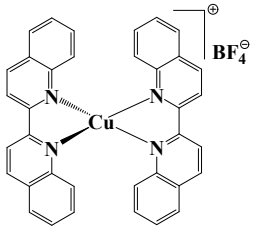
In a round bottom flask was added [Cu(CH_3CN)$_4$]BF_4 (93 mg, 0.4 mmol) and Xantphos (231 mg, 0.4 mmol) and dissolved in THF (74 mL). The solution was allowed to stir at room temperature for 1h and a solution of 2,2'-biquinoline (102 mg, 0.4 mmol) in THF (9 mL) was added in one portion. The resulting solution was stirred for an additional hour. Addition of dichloromethane (5 mL) followed by addition of pentane precipitated the complex. It was filtered off, washed several times with water and dried under vacuum (337 mg, 82 % yield). ^{1}H NMR (DMSO-d_6) δ (ppm): 1.75 (s, 3H), 1.87 (s, 3H), 6.55-6.58 (m, 2H), 6.80-6.95 (m, 8H), 7.07-7.38 (m, 16H), 7.55-7.67 (m, 2H), 7.77-7.79 (m, 2H), 7.90-7.92 (m, 2H), 8.09-8.11 (m, 2H), 8.83 (s, 4H); ^{13}C NMR (DMSO-d_6) δ (ppm): 25.1, 28.1, 36.0, 120.1, 120.4, 125.7, 128.0, 128.5, 128.7 (t, J = 4.5 Hz), 129.9, 130.1, 130.6 (t, J = 16.4 Hz), 132.4 (t, J = 7.7 Hz), 133.8, 139.7, 145.0, 152.3, 154.3 (t, J = 7.2 Hz); ^{31}P NMR (DMSO-d_6) δ (ppm): -11.80; HRMS (ESI MS) m/z: theor: 897.2225 found: 897.2222 ($M^{+\cdot}$ detected).

Synthesis of [Cu(bpy)$_2$]BF_4 ***A5***



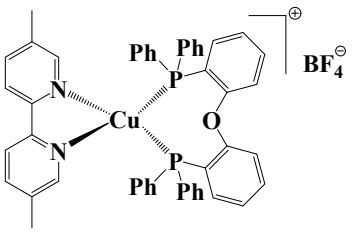
To 2,2'-dipyridyl *bpy* (1 g, 6.40 mmol) in MeOH (50 mL) was added in one portion $Cu(CH_3CN)_4.BF_4$ (1g, 3.20 mmol) and the solution was stirred at 45°C overnight. The solution was concentrated under reduced pressure. Addition of a minimum of DCM and addition of pentane precipitated a solid which was filtered off, washed with pentane and dried under vacuum (1.27 g, 86% yield). ^{1}H NMR (DMSO-d_6) δ (ppm): 7.99 (t, 2H, J = 8.3 Hz), 8.10 (dd, 2H, J = 2.2 Hz, J = 8.4 Hz), 8.42 (t, 2H, J = 8.0 Hz), 8.91 (d, 2H, J = 2.2 Hz); Anal. Calcd for $C_{20}H_{16}BCuF_4N_4$ (%): C, 51.9; H, 3.5; N, 12.1%; Found: C, 52.1; H, 3.6; N, 11.8%; HRMS (ESI MS) m/z: theor: 375.0665 found: 375.0662 ($M^{+\cdot}$ detected).

Synthesis of [Cu(2,2'-biquinoline)]BF_4 ***A6***



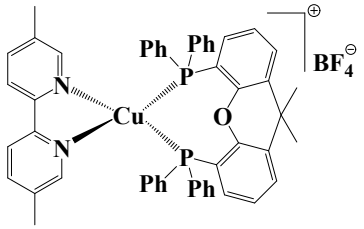
To 2,2'-biquinoline (1 g, 3.90 mmol) in 50 mL MeOH was added in one portion $Cu(CH_3CN)_4.BF_4$ (613 mg, 1.95 mmol) of and the solution was stirred at 45°C overnight. The solution was concentrated under reduced pressure. Addition of a minimum of CH_2Cl_2 and addition of pentane precipitated a solid which was filtered off, washed with pentane and dried under vacuum (957 mg, 74% yield). ^{1}H NMR ($CDCl_3$) δ (ppm): 7.32-7.35 (t, 4H, J = 6.6 Hz), 7.44-7.46 (t, 4H, J = 7.0 Hz), 7.67 (d, 4H, J = 7.9 Hz), 7.94 (d, 4H, J = 7.3 Hz), 8.80 (d, 4H, J = 8.0 Hz), 8.96 (d, 4H, J = 8.0 Hz); ^{13}C NMR ($CDCl_3$) δ (ppm): 120.2, 127.8, 128.1, 128.7, 129.9, 131.3, 139.3, 145.8, 152.4; HRMS (ESI MS) m/z: theor: 575.1291 found: 575.1292 ($M^{+\cdot}$ detected).

Synthesis of [Cu(dimethylbpy)(DPEphos)]BF_4 ***B1***



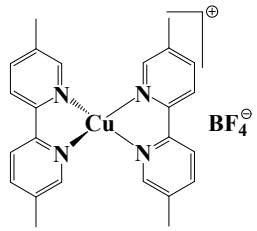
A mixture of $[Cu(CH_3CN)_4]BF_4$ (310 mg, 1 mmol) and *bis*[2-(diphenylphosphino)phenyl]ether (540 mg, 1 mmol) in dichloromethane (200 mL) was stirred at 25 °C for 2 h and then treated with a solution of 5,5'-dimethyl-2,2'-bipyridine (183 mg, 1 mmol) in 50 mL of dichloromethane. This reaction mixture was stirred for an additional 1 h and filtered and the clear yellow filtrate concentrated to ca. 5 mL. Addition of dichloromethane (5 mL) followed by addition of pentane precipitated the complex. It was filtered off, washed several times with water and dried under vacuum (698 mg, 80 % yield). ^{1}H NMR ($CDCl_3$) δ (ppm): 2.12 (s, 6H), 6.74-6.77 (m, 2H), 6.95-7.08 (m, 12H), 7.19 (t, 8H, J = 7.3 Hz), 7.28-7.33 (m, 6H), 7.76 (d, 2H, J = 8.1 Hz), 8.05 (s, 2H), 8.26 (d, 2H, J = 8.3 Hz); ^{13}C NMR ($CDCl_3$) δ (ppm): 18.0, 53.4, 120.1 (t, J = 2.2 Hz), 121.7, 123.7 (t, J = 14.3 Hz), 125.0 (t, J = 2.2 Hz), 128.6 (t, J = 5.0 Hz), 129.9, 130.6 (t, J = 17 Hz), 131.9, 132.9 (t, J = 8.2 Hz), 134.1, 135.6, 138.9, 149.2-149.3 (m), 158.0 (t, J = 6.1 Hz); ^{31}P NMR ($CDCl_3$) δ (ppm): - 10.77; HRMS (ESI MS) m/z: theor: 785.1906 found: 785.1902 ($M^{+\cdot}$ detected).

Synthesis of [Cu(dimethylbpy)(Xantphos)]BF_4 ***B2***



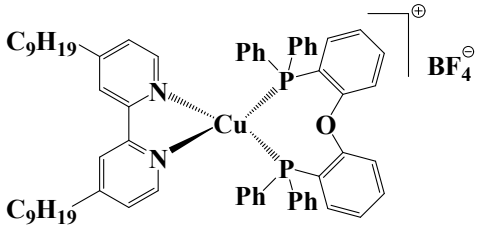
In a round bottom flask was added $[Cu(CH_3CN)_4]BF_4$ (93 mg, 0.4 mmol) and Xantphos (231 mg, 0.4 mmol) and dissolved in THF (74 mL). The solution was allowed to stir at room temperature for 1h and a solution of 5,5'-dimethyl-2,2'-bipyridine (74 mg, 0.4 mmol) in THF (9 mL) was added in one portion. The resulting solution was stirred for an additional hour. Addition of dichloromethane (5 mL) followed by addition of pentane precipitated the complex. It was filtered off, washed several times with water and dried under vacuum (325 mg, 88 % yield). ^{1}H NMR ($CDCl_3$) δ (ppm): 1.43 (s, 6H), 2.07 (s, 6H), 6.45-6.48 (m, 2H), 6.90-6.93 (m, 8H), 7.10-7.25 (m, 16H), 7.65-7.67 (m, 4H), 7.82 (d, 2H, J =7.1 Hz), 8.41 (d, 2H, J = 7.8 Hz); ^{13}C NMR ($CDCl_3$) δ (ppm): 30.1, 34.0, 119.7 (t, J = 13.5 Hz), 122.1, 125.0, 125.2, 126.7, 127.8-127.9 (m), 128.5 (t, J = 4.7 Hz), 129.7, 130.8-131.0 (m), 132.5 (t, J = 8.0 Hz), 133.6 (t, J = 10.3 Hz), 135.6 (d, J = 3.5 Hz), 137.1-137.2 (m), 139.2, 148.6, 149.2, 151.3, 153.8, 154.7 (t, J = 6.1 Hz); ^{31}P NMR ($CDCl_3$) δ (ppm): -11.05; HRMS (ESI MS) m/z: theor: 825.2219 found: 825.2215 ($M^{+\cdot}$ detected).

Synthesis of [Cu(diMeBpy)$_2$]BF$_4$ ***B3***



To 5,5'-dimethyl-2,2'-bipyridine (1 g, 5.43 mmol) in MeOH (50 mL) was added in one portion Cu(CH$_3$CN)$_4$.BF$_4$ (0.85 g, 2.71 mmol) and the solution was stirred at 45°C overnight. Addition of a minimum of DCM and addition of pentane precipitated a green solid which was filtered off, washed with pentane and dried under vacuum (1.15 g, 82% yield). ^{1}H NMR (DMSO-d$_6$) δ (ppm): 21.3 (s, 12H), 7.65 (dd, 4H, J = 7.9 Hz, J = 1.2 Hz), 8.28-8.41 (m, 4H), 8.52 (s, 4H); Anal. Calcd for C$_{24}$H$_{24}$BCuF$_4$N$_4$ (%): C, 55.6; H, 4.7; N, 10.8%; Found: C, 55.8; H, 4.6; N, 10.8%; HRMS (ESI MS) m/z: theor: 431.1291 found: 431.1295 ($M^{+\cdot}$ detected).

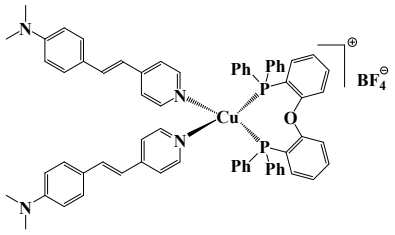
Synthesis of [Cu(dinonylbpy)(DPEphos)]BF$_4$ ***C1***



A mixture of [Cu(CH$_3$CN)$_4$]BF$_4$ (310 mg, 1 mmol) and *bis*[2-(diphenylphosphino)phenyl]ether (540 mg, 1 mmol) in dichloromethane (200 mL) was stirred at 25 °C for 2 h and then treated with a solution of 9,9'-dinonylbipyridine (409 mg, 1 mmol) in 50 mL of dichloromethane. This reaction mixture was stirred for an additional 1 h and filtered and the clear yellow filtrate concentrated to ca. 5 mL. Addition of pentane precipitated the complex which was filtered, washed several times with pentane and dried under vacuum (922 mg, 84 % yield). ^{1}H NMR (CDCl$_3$) δ (ppm): 0.87 (t, 6H, J = 6.5 Hz), 1.15-1.45 (m, 24H), 1.61-1.75 (m, 4H), 2.77 (t, 4H, J = 7.5 Hz), 6.73-6.75 (m, 2H), 6.94-7.10 (m, 14H), 7.16-7.19 (m, 8H), 7.26-7.33 (m, 6H), 8.12 (s, 2H), 8.25 (d, 2H, J = 5.2 Hz); ^{13}C NMR (CDCl$_3$) δ (ppm): 13.9, 22.5, 29.0, 29.1, 29.3, 29.35, 30.2, 31.7, 35.2, 120.3, 122.1, 123.8 (t, J = 14.5 Hz), 124.9, 125.7, 128.6 (t, J = Hz), 129.9, 130.7 (t, J = 4.7 Hz), 131.8, 132.9 (t, J = 8.2 Hz), 134.1, 148.9, 151.6 (t,

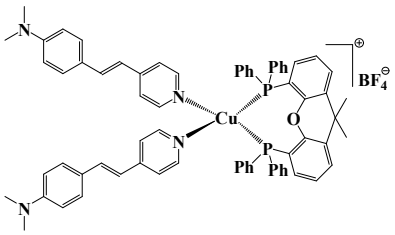
H = 2.0 Hz), 154.9, 158.2, (t, J = 6.2 Hz); ^{31}P NMR ($CDCl_3$) δ (ppm): -11.42; HRMS (ESI MS) m/z: theor: 1009.4410 found: 1009.4409 ($M^{+\cdot}$ detected).

Synthesis of [Cu(DAST)$_2$(DPEphos)]BF$_4$ ***D1***



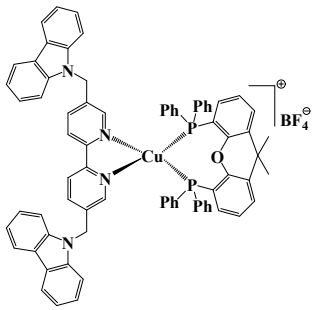
A mixture of $[Cu(CH_3CN)_4]BF_4$ (310 mg, 1 mmol) and *bis*[2-(diphenylphosphino)phenyl]ether (540 mg, 1 mmol) in dichloromethane (200 mL) was stirred at 25 °C for 2 h and then treated with a solution of (*E*)-*N,N*-dimethyl-4-(2-(pyridin-4-yl)vinyl)aniline (DAST) (448 mg, 2 mmol) in 50 mL of dichloromethane. This reaction mixture was stirred for an additional 1 h and filtered and the clear yellow filtrate concentrated to ca. 5 mL. Addition of pentane precipitated the complex which was filtered, washed several times with pentane and dried under vacuum (933 mg, 82 % yield). ^{1}H NMR ($CDCl_3$) δ (ppm): 3.02 (s, 12H), 6.11-6.14 (m, 4H), 6.79 (d, 4H, J = Hz), 7.16-7.21 (m, 4H), 7.29-7.39 (m, 8H), 7.47-7.62 (m, 22H), 7.92 (d, 2H, J = Hz), 8.01-8.08 (m, 4H); ^{13}C NMR ($CDCl_3$) δ (ppm): 25.1, 30.6, 67.0, 112.0, 117.7, 119.7 (d, J = 5.6 Hz), 122.6, 123.5, 123.8, 123.9, 124.5, 128.2 (dd, J = 12.0 Hz, J = 33.9 Hz), 130.0, 131.3-131.6 (m), 133.3 (d, J = 6.6 Hz), 134.0, 140.8, 141.6, 151.8, 158.1; ^{31}P NMR ($CDCl_3$) δ (ppm): - 23.6; HRMS (ESI MS) m/z: theor: 1049.3533 found: 1049.3538 ($M^{+\cdot}$ detected).

Synthesis of [Cu(DAST)$_2$(Xantphos)]BF$_4$ ***D2***



In a round bottom flask was added $[Cu(CH_3CN)_4]BF_4$ (93 mg, 0.4 mmol) and Xantphos (231 mg, 0.4 mmol) and dissolved in THF (74 mL). The solution was allowed to stir at room temperature for 1h and a solution of (E)-N,N-dimethyl-4-(2-(pyridin-4-yl)vinyl)aniline (DAST) (179 mg, 0.8 mmol) in THF (9 mL) was added in one portion. The resulting solution was stirred for an additional hour. The solvent was removed under reduced pressure. Addition of dichloromethane (5 mL) followed by addition of pentane precipitated the complex. It was filtered off, washed several times with pentane and dried under vacuum (419 mg, 89 % yield). ^{1}H NMR ($CDCl_3$) δ (ppm): 1.59 (s, 6H), 3.02 (s, 12H), 6.54 (m, 2H), 6.79 (d, 4H, J = Hz), 7.17-7.22 (m, 4H), 7.28-7.37 (m, 16H), 7.43-7.47 (m, 12H), 7.61 (d, 4H, J = Hz), 7.69 (d, 2H, J = Hz), 7.90 (d, 2H, J = Hz); ^{13}C NMR ($CDCl_3$) δ (ppm): 28.3, 32.5, 35.3, 111.9, 117.7, 120.6 (t, J = 12.7 Hz), 122.6, 124.4, 127.1, 128.4 (t, J = 4.4 Hz), 128.9-129.1 (m), 129.7, 130.0, 130.7, 131.9 (t, J = 15.1 Hz), 132.9, 133.4 (t, J = 1.6 Hz), 141.1, 141.4, 151.8, 153.7; ^{31}P NMR ($CDCl_3$) δ (ppm): - 20.0; HRMS (ESI MS) m/z: theor: 1089.3846 found: 1089.3844 ($M^{+\cdot}$ detected).

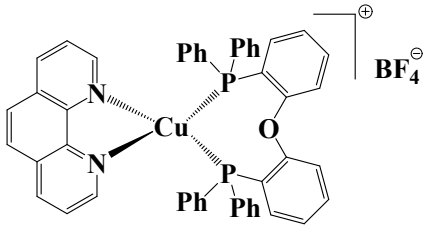
Synthesis of [Cu(diCarbBpy)(Xantphos)]BF_4 ***E2***



In a round bottom flask was added $[Cu(CH_3CN)_4]BF_4$ (93 mg, 0.4 mmol) and Xantphos (231 mg, 0.4 mmol) and dissolved in THF (74 mL). The solution was allowed to stir at room temperature for 1h and a solution of 5,5'-*bis*((9*H*-carbazol-9-yl)methyl)-2,2'-bipyridine (206 mg, 0.4 mmol) in THF (9 mL) was added in one portion. The resulting solution was stirred for an additional hour. Addition of dichloromethane (5 mL) followed by addition of pentane precipitated the complex. It was filtered off, washed several times with pentane and dried under vacuum (422 mg, 85 % yield). ^{1}H NMR ($CDCl_3$) δ (ppm): 1.60 (s, 6H),5.19 (s, 4H), 6.48-6.54 (m, 4H), 6.85-6.95 (m, 14H), 7.03 (t, 2H, J = 7.7 Hz), 7.15-7.20 (m, 14H), 7.44-7.48 (m, 4H), 7.61 (s, 2H), 7.78 (d, 2H, J = 8.3 Hz), 8.04-8.07 (m, 4H), 8.24 (d, 2H, J = 8.3 Hz); ^{13}C NMR ($CDCl_3$) δ (ppm): 27.8, 43.9, 108.4, 111.0, 119.0, 119.7, 120.0, 120.5, 123.1, 125.0 (t, J = 4.7 Hz), 125.7, 126.2, 126.7, 128.7 (t, J = 5.0 Hz), 129.8, 130.6, 130.8, 132.4 (t, J =

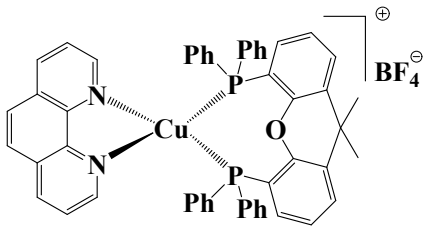
8.2 Hz), 133.8, 135.8, 137.6, 139.7, 140.1, 146.5, 150.8, 154.8; ^{31}P NMR ($CDCl_3$) δ (ppm): - 11.98; HRMS (ESI MS) m/z: theor: 1155.3376 found: 1155.3376 ($M^{+\cdot}$ detected).

Synthesis of [Cu(phen)(DPEphos)]BF_4 ***F1***



A mixture of [$Cu(CH_3CN)_4$]BF_4 (310 mg, 1 mmol) and *bis*[2-(diphenylphosphino)phenyl]ether (540 mg, 1 mmol) in dichloromethane (200 mL) was stirred at 25 °C for 2 h and then treated with a solution of 1,10-phenanthroline monohydrate (200 mg, 1 mmol) in dichloromethane (50 mL). This reaction mixture was stirred for an additional 1 h and filtered and the clear yellow filtrate concentrated to ca. 5 mL. Addition of pentane precipitated the complex which was filtered, washed several times with pentane and dried under vacuum (610 mg, 70 % yield). NMR characterizations were consistent with those previously reported [S.-M. Kuang, D. G. Cuttell, D. R. McMillin, P. E. Fanwick, R. A. Walton, Inorg. Chem. 2002, 41, 3313-3322]. ^{1}H NMR ($CDCl_3$) δ (ppm): 6.77-6.79 (m, 2H), 6.95-6.99 (m, 10H), 7.05-7.13 (m, 10H), 7.23 (t, 4H, J = 7.4 Hz), 7.29-7.33 (m, 2H), 7.71-7.74 (m, 2H), 8.04 (s, 2H), 8.52 (d, 2H, J = 8.0 Hz), 8.76 (d, 2H, J = 4.5 Hz); ^{13}C NMR ($CDCl_3$) δ (ppm): 120.2, 123.6 (t, J = 8.7 Hz), 124.9 (d, J = 5.1 Hz), 127.1, 128.5 (t, J = 4.7 Hz), 129.3, 129.9, 130.4 (t, J = 17.1 Hz), 131.9, 132.7 (t, J = 8.2 Hz), 134.0, 137.3, 142.9 (d, J = 1.7 Hz), 149.4, 158.2 (t, J = 6.1 Hz); ^{31}P NMR ($CDCl_3$) δ (ppm): -10.63; HRMS (ESI MS) m/z: theor: 781.1593 found: 781.1594 ($M^{+\cdot}$ detected).

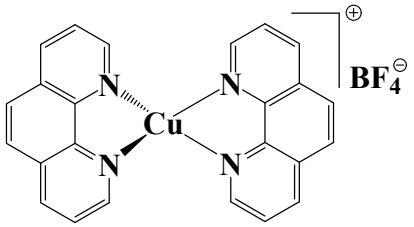
Synthesis of [Cu(phen)(Xantphos)]BF_4 ***F2***



In a round bottom flask was added [$Cu(CH_3CN)_4$]BF_4 (93 mg, 0.4 mmol) and Xantphos (231 mg, 0.4 mmol) and dissolved in THF (74 mL). The solution was allowed to stir at room temperature for

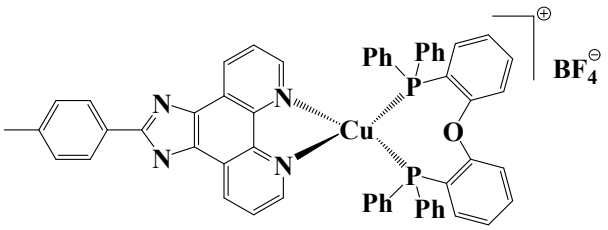
1h and a solution of 1,10-phenanthroline (72 mg, 0.4 mmol) in THF (9 mL) was added in one portion. The resulting solution was stirred for an additional hour. The solvent was removed under reduced pressure. Addition of dichloromethane (5 mL) followed by addition of pentane precipitated the complex. It was filtered off, washed several times with water and dried under vacuum (335 mg, 92 % yield). ^{1}H NMR ($CDCl_3$) δ (ppm): 1.34 (s, 6H), 6.48-6.50 (m, 2H), 6.75-7.05 (m, 14H), 7.07-7.18 (m, 8H), 7.59-7.67 (m, 4H), 7.98 (s, 2H), 8.36 (s, 2H), 8.49 (d, 2H, J = 7.8 Hz); ^{13}C NMR ($CDCl_3$) δ (ppm): 29.5, 30.2, 36.0, 119.5 (t, J = 13.7 Hz), 125.0, 125.2, 125.4, 127.2, 127.4, 128.5 (t, J = 4.6 Hz), 129.6, 129.7, 130.9-131.2 (m), 132.5, 133.8, 143.0, 148.8, 151.4, 154.7 (t, J = 6.2 Hz); ^{31}P NMR ($CDCl_3$) δ (ppm): -11.93; HRMS (ESI MS) m/z: theor: 821.1906 found: 821.1904 ($M^{+\cdot}$ detected).

Synthesis of $[Cu(phen)_2]BF_4$ ***F3***



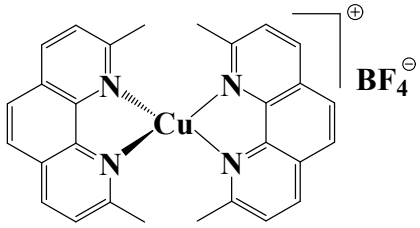
To 1 g (5.55 mmol) of phenanthroline in 50 mL MeOH was added in one portion 873 mg (2.77 mmol) of $Cu(CH_3CN)_4.BF_4$ and the solution was stirred at 45°C overnight. Addition of a minimum of DCM and addition of pentane precipitated a green solid which was filtered off, washed with pentane and dried under vacuum (1.30 g, 92% yield). Anal. Calcd for $C_{24}H_{16}BCuF_4N_4$ (%): C, 56.4; H, 3.2; N, 11.0%; Found: C, 56.6; H, 3.3; N, 10.8%; HRMS (ESI MS) m/z: theor: 423.0665 found: 423.0666 ($M^{+\cdot}$ detected).

Synthesis of $[Cu(TolylPhen)(DPEphos)]BF_4$ ***F4***



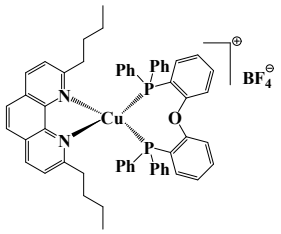
A mixture of $[Cu(CH_3CN)_4]BF_4$ (310 mg, 1 mmol) and *bis*[2-(diphenylphosphino)phenyl]ether (540 mg, 1 mmol) in dichloromethane (200 mL) was stirred at 25 °C for 2 h and then treated with a solution of 2-(p-tolyl)-1H-imidazo[4,5-f][1,10]phenanthroline (*TolylPhen*) (310 mg, 1 mmol) in 50 mL of dichloromethane. The reaction was stirred at room temperature overnight. The solvent was removed under reduced pressure. Addition of dichloromethane (5 mL) followed by addition of pentane precipitated the complex. It was filtered off, washed several times with water and dried under vacuum (939 mg, 94 % yield). ^{1}H NMR (DMSO-d_6) δ (ppm): 2.46 (s, 3H), 6.77-6.79 (m, 2H), 6.99-7.05 (m, 12H), 7.17-7.19 (m, 5H), 7.27-7.33 (m, 5H), 7.43 (d, 2H, J = 7.5 Hz), 7.87 (q, 2H, J = 4.2 Hz), 8.12 (s, 2H), 8.21 (d, 2H, J = 8.1 Hz), 8.25 (d, 2H, J = 5.2 Hz), 8.95 (d, 2H, J = 7.9 Hz), 9.03 (d, 2H, J = 2.1 Hz); Anal. Calcd for $C_{56}H_{42}BCuF_4N_4OP_2$ (%): C, 67.3; H, 4.2; N, 5.6%; Found: C, 67.4; H, 4.3; N, 5.8%; HRMS (ESI MS) m/z: theor: 911.2124 found: 911.2122 ($M^{+\cdot}$ detected).

Synthesis of Cu(neo)$_2$.BF$_4$ ***G3***



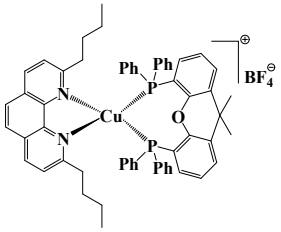
To a solution of neocuproine (1 g, 4.80 mmol) in MeOH (50 mL) was added in one portion $Cu(CH_3CN)_4.BF_4$ (755 mg, 2.71 mmol). The solution was stirred at 45°C overnight. The solution was concentrated under reduced pressure. Dissolution in a minimum of dichloromethane (DCM) followed by addition of pentane precipitated a green solid which was filtered off, washed with pentane and dried under vacuum (1.50 g, 97% yield). ^{1}H NMR ($CDCl_3$) δ (ppm): 2.43 (s, 12H), 7.79 (d, 4H, J = 8.3 Hz), 8.03 (s, 4H), 8.51 (d, 4H, J = 8.3 Hz); ^{13}C NMR ($CDCl_3$) δ (ppm): 25.8, 125.6, 126.1, 127.7, 137.4, 143.0, 157.7; HRMS (ESI MS) m/z: theor: 479.1291 found: 479.1290 ($M^{+\cdot}$ detected).

Synthesis of [Cu(diBuPhen)(DPEphos)]BF$_4$ ***H1***



A mixture of $[Cu(CH_3CN)_4]BF_4$ (246 mg, 1.06 mmol) and *bis*[2-(diphenyl-phosphino)phenyl]ether (570 mg, 1.06 mmol) in dichloromethane (200 mL) was stirred at 25 °C for 2 h and then treated with a solution of 2,9-dibutyl-1,10-phenanthroline diBuPhen (0.464 g, 1.59 mmol) in 50 mL of dichloromethane. This reaction mixture was stirred for an additional 1 h and filtered and the clear yellow filtrate concentrated to ca. 5 mL. Addition of dichloromethane (5 mL) followed by addition of pentane precipitated the complex. It was filtered off, washed several times with water and dried under vacuum (884 mg, 85 % yield). ^{1}H NMR ($CDCl_3$) δ (ppm): 0.88 (t, 6H, *J* = 7.6 Hz, CH_3), 1.26-1.30 (m, 4H, CH_2CH_3), 1.91 (quint, 4H, *J* = 7.6 Hz, $ArCH_2CH_2$), 2.82 (t, 4H, *J* = 7.6 Hz, $ArCH_2$), 6.76-6.78 (m, 2H), 6.94-7.02 (m, 14H), 7.18-7.33 (m, 12H), 7.65 (d, 2H, J = 8.4 Hz), 7.90 (s, 2H), 8.46 (d, 2H, J = 8.4 Hz); ^{13}C NMR ($CDCl_3$) δ (ppm): 13.7, 22.2, 30.5, 40.6, 120.2, 123.4, 125.0, 125.5 (t, J = 13.5 Hz), 126.1, 128.0, 128.6 (t, J = 4.6 Hz), 128.7-128.9 (m), 129.8, 131.2-131.3 (m), 131.3 (t, J = 16.1 Hz), 132.1, 132.8 (t, J = 7.9 Hz), 133.4, 133.4-133.5 (m), 134.0, 138.2, 142.9, 157.9, 162.6; ^{31}P NMR ($CDCl_3$) δ (ppm): -14.55; HRMS (ESI MS) m/z: theor: 893.2845 found: 893.2848 ($M^{+\cdot}$ detected).

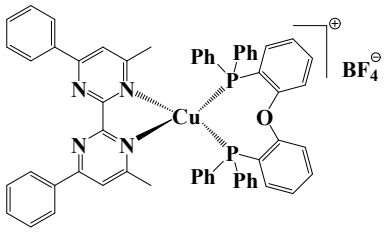
Synthesis of [Cu(diBuPhen)(Xantphos)]BF_4 ***H2***



In a round bottom flask was added $[Cu(CH_3CN)_4]BF_4$ (93 mg, 0.4 mmol) and Xantphos (231 mg, 0.4 mmol) and dissolved in THF (74 mL). The solution was allowed to stir at room temperature for 1h and a solution of 2,9-dibutyl-1,10-phenanthroline diBuPhen (234 mg, 0.8 mmol) in THF (9 mL) was added in one portion. The resulting solution was stirred for an additional hour. Addition of dichloromethane (5 mL) followed by addition of pentane precipitated the complex. It was filtered off, washed several times with water and dried under vacuum (359 mg, 88 % yield). ^{1}H NMR ($CDCl_3$) δ

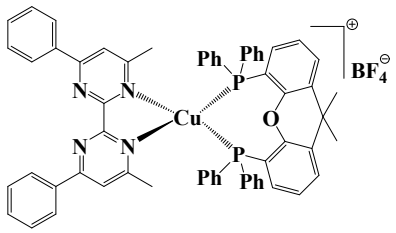
(ppm): 0.88 (t, 6H, J = 7.6 Hz, CH_3), 1.26-1.30 (m, 4H, CH_2CH_3), 1.79 (s, 6H), 1.91 (quint, 4H, J = 7.6 Hz, $ArCH_2CH_2$), 3.19 (t, 4H, J = 7.6 Hz, $ArCH_2$), 6.94-6.98 (m, 2H), 6.99-7.02 (m, 14H), 7.18-7.33 (m, 6H), 7.51 (d, 2H, J = 8.2 Hz), 7.57 (d, 2H, J = 8.4 Hz), 7.64 (d, 2H, J = 7.8 Hz), 7.84 (s, 2H), 8.41 (d, 2H, J = 8.4 Hz); ^{13}C NMR ($CDCl_3$) δ (ppm): 13.7, 13.9, 14.0, 22.2, 30.3, 40.8, 67.8, 121.8 (t, J = 12.3 Hz), 122.4, 123.0, 124.8, 125.2, 127.0, 127.8, 128.4 (t, J = 9.8 Hz), 129.8, 130.2, 131.1 (t, J = 15.9 Hz), 132.7 (t, J = 7.7 Hz), 133.81-133.84 (m), 136.2, 138.0, 142.7 (t, J = 1.7 Hz), 145.2, 154.8 (t, J = 6.7 Hz), 161.5; ^{31}P NMR ($CDCl_3$) δ (ppm): -13.04; HRMS (ESI MS) m/z: theor: 933.3158 found: 933.3154 ($M^{+\cdot}$ detected).

Synthesis of [Cu(2,2'-bipyrimidine)(DPEphos)]BF_4 ***J1***



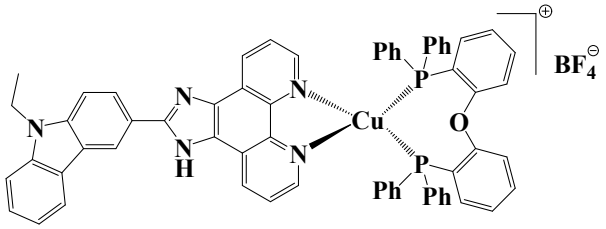
A mixture of $[Cu(CH_3CN)_4]BF_4$ (310 mg, 1 mmol) and *bis*[2-(diphenylphosphino)phenyl]ether (540 mg, 1 mmol) in 200 mL of dichloromethane was stirred at 25 °C for 2 h and then treated with a solution of 4,4'-dimethyl-6,6'-diphenyl-2,2'-bipyrimidine (339 mg, 1 mmol) in 50 mL of dichloromethane. This reaction mixture was stirred at room temperature overnight. The solution was concentrated to 1/3 of its initial volume and addition of pentane precipitated a light brown solid which was filtered off, washed with pentane and dried under vacuum. ^1H NMR ($CDCl_3$) δ (ppm): 2.32 (s, 6H), 6.76-7.31 (m, 30H), 7.52-7.65 (m, 4H), 7.93 (s, 2H), 8.37 (d, 4H, J = 7.5 Hz); ^{31}P NMR ($CDCl_3$) δ (ppm): -12.96; Anal. Calcd for $C_{58}H_{46}BCuF_4N_4OP_2$ (%): C, 67.8; H, 4.5; N, 5.5%; Found: C, 67.8; H, 4.6; N, 5.7%; HRMS (ESI MS) m/z: theor: 939.2437 found: 939.2438 ($M^{+\cdot}$ detected).

Synthesis of [Cu(2,2'-bipyrimidine)(Xantphos)]BF_4 ***J2***



In a round bottom flask was added $[Cu(CH_3CN)_4]BF_4$ (93 mg, 0.4 mmol) and Xantphos (231 mg, 0.4 mmol) and dissolved in THF (74 mL). The solution was allowed to stir at room temperature for 1h and a solution of 4,4'-dimethyl-6,6'-diphenyl-2,2'-bipyrimidine (135 mg, 0.4 mmol) in THF (9 mL) was added in one portion. The resulting solution was stirred at room temperature overnight. The solution was concentrated to 1/3 of its initial volume and addition of pentane precipitated a light brown solid which was filtered off, washed with pentane and dried under vacuum. ^{1}H NMR ($CDCl_3$) δ (ppm): 1.74 (s, 6H), 2.13 (s, 6H), 6.84-6.88 (m, 2H), 7.05-7.10 (m, 8H), 7.15 (t, 8H, J = 7.4 Hz), 7.21 (t, 2H, J = 7.6 Hz), 7.32 (t, 4H, J = 7.3 Hz), 7.58-7.59 (m, 6H), 7.66 (d, 2H, J = 7.8 Hz), 7.90 (s, 2H), 8.34-8.36 (m, 4H); ^{31}P NMR ($CDCl_3$) δ (ppm): - 12.71; Anal. Calcd for $C_{61}H_{50}BCuF_4N_4OP_2$ (%): C, 68.6; H, 4.7; N, 5.2%; Found: C, 68.8; H, 4.9; N, 5.5%; HRMS (ESI MS) m/z: theor: 979.2750 found: 979.2748 ($M^{+\cdot}$ detected).

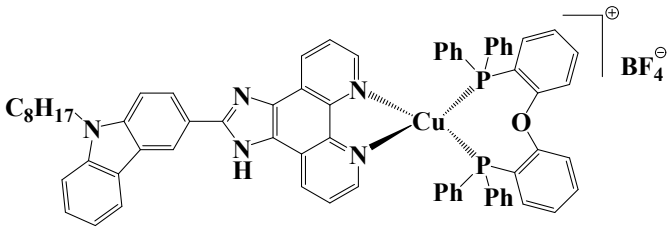
Synthesis of Cu(EtCarbPhen)(DPEphos)]BF_4 ***K1***



A mixture of $[Cu(CH_3CN)_4]BF_4$ (310 mg, 1 mmol) and *bis*[2-(diphenylphosphino)phenyl] ether (540 mg, 1 mmol) in 200 mL of dichloromethane was stirred at 25 °C for 2 h and then treated with a solution of 2-(9-ethyl-9H-carbazol-3-yl)-1H-imidazo[4,5-f][1,10]phenanthroline (*EtCarbPhen*) (414 mg, 1 mmol) in 50 mL of methanol. The reaction was stirred at room temperature overnight. The solvent was removed under reduced pressure. Dissolution in a minimum of THF followed by addition of pentane precipitated a light brown solid which was filtered off, washed with pentane and dried under vacuum (838 mg, 76% yield). ^{1}H NMR (DMSO-d_6) δ (ppm): 1.40 (t, 3H, J = 7.2 Hz), 4.54 (q, 2H, J = 7.2 Hz), 6.65-6.69 (m, 4H), 7.00-7.45 (m, 26H), 7.56 (td, 1H, J = 8.1 Hz, J = 0.9 Hz), 7.70 (d, 1H, J =

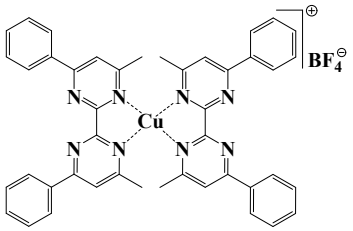
7.4 Hz), 7.91 (dd, 1H, J = 8.5 Hz, J = 1.4 Hz), 8.30-8.44 (m, 1H), 8.84 (d, 1H, J = 0.8 Hz), 9.08-9.12 (m, 2H); ^{31}P NMR (DMSO-d_6) δ (ppm): - 11.71; Anal. Calcd for $C_{63}H_{47}BCuF_4N_5OP_2$ (%): C, 68.6; H, 4.3; N, 6.3%; Found: C, 68.8; H, 4.5; N, 6.5%; HRMS (ESI MS) m/z: theor: 1014.2546 found: 1014.2548 ($M^{+\cdot}$ detected).

Synthesis of Cu(OctCarbPhen)(DPEphos)]BF_4 ***K2***



A mixture of $[Cu(CH_3CN)_4]BF_4$ (310 mg, 1 mmol) and *bis*[2-(diphenylphosphino)phenyl]ether (540 mg, 1 mmol) in 200 mL of dichloromethane was stirred at 25 °C for 2 h and then treated with a solution of 2-(9-octyl-9H-carbazol-3-yl)-1H-imidazo[4,5-f][1,10] phenanthroline (498 mg, 1 mmol) in 50 mL of dichloromethane. The reaction was stirred at room temperature overnight. The solvent was removed under reduced pressure. Dissolution in a minimum of THF followed by addition of pentane precipitated a light brown solid which was filtered off, washed with pentane and dried under vacuum (1.03g, 87% yield). 0.86 (t, 3H, J = 7.1 Hz), 1.20-1.38 (m, 10H), 1.79-1.87 (m, 2H), 4.28 (t, 2H, J = 7.3 Hz), 6.65-6.73 (m, 4H), 7.02-7.40 (m, 26H), 7.51 (td, 1H, J = 8.1 Hz, J = 0.9 Hz), 7.74 (d, 1H, J = 7.4 Hz), 7.95 (dd, 1H, J = 8.6 Hz, J = 1.2 Hz), 8.26-8.49 (m, 1H), 8.89 (d, 1H, J = 0.8 Hz), 9.06-9.13 (m, 2H); ^{31}P NMR (DMSO-d_6) δ (ppm): - 11.93; Anal. Calcd for $C_{69}H_{59}BCuF_4N_5OP_2$ (%): C, 69.8; H, 5.0; N, 5.9%; Found: C, 69.7; H, 5.1; N, 6.0%; HRMS (ESI MS) m/z: theor: 1098.3485 found: 1098.3488 ($M^{+\cdot}$ detected).

Synthesis of [Cu(2,2'-bipyrimidine)$_2$]BF_4 ***L1***



A MeOH solution (15 mL) of $[Cu(CH_3CN)_4]BF_4$ (0.46 g, 1.46 mmol) was added to a THF solution (150 mL) of 4,4'-dimethyl-6,6'-diphenyl-2,2'-bipyrimidine (1 g, 2.95 mmol). A brown precipitate formed immediately upon addition of the copper solution. The solution was stirred at room temperature overnight. The solution was concentrated to the half of its initial volume, the precipitate was filtered off, washed several times with pentane and dried under vacuum (1.01 g, 84% yield). ^1H NMR (DMSO-d_6) δ (ppm): 2.53 (s, 12H), 7.70-7.78 (m, 12H), 8.45-8.65 (m, 12H); Anal. Calcd for $C_{44}H_{36}BCuF_4N_8$ (%): C, 63.9; H, 4.4; N, 13.6%; Found: C, 63.7; H, 4.7; N, 13.8%; HRMS (ESI MS) m/z: theor: 739.2353 found: 739.2355 ($M^{+\cdot}$ detected).

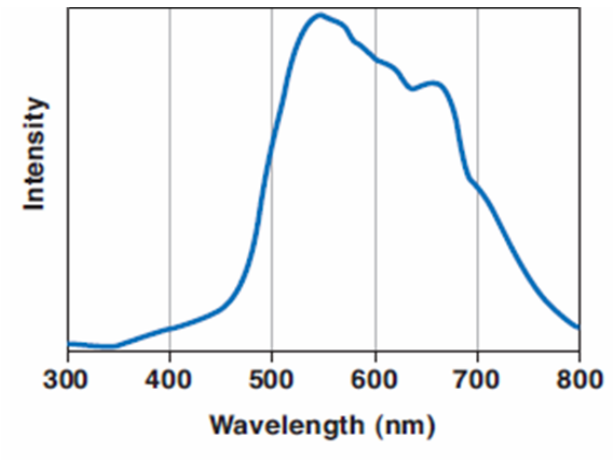
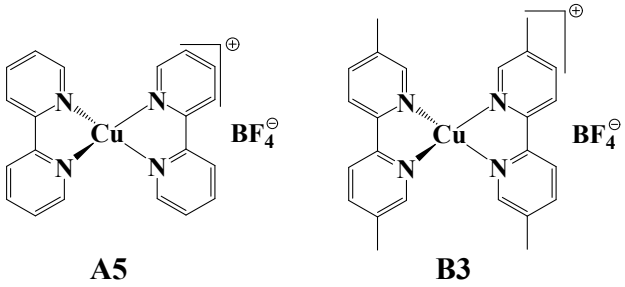


Figure S1. The emission spectrum of the halogen lamp.



Scheme S1. Chemical structures of the copper complexes (A5 and B3) that exhibit light absorption mainly in the UV range.

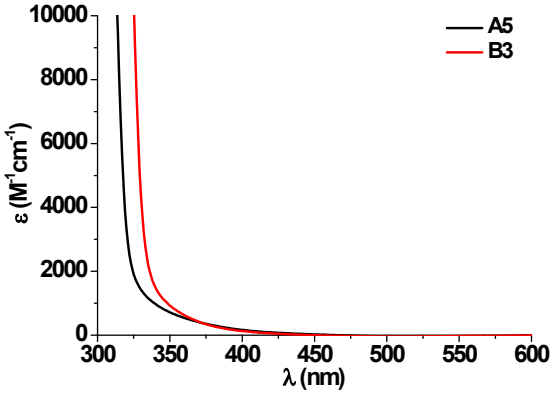
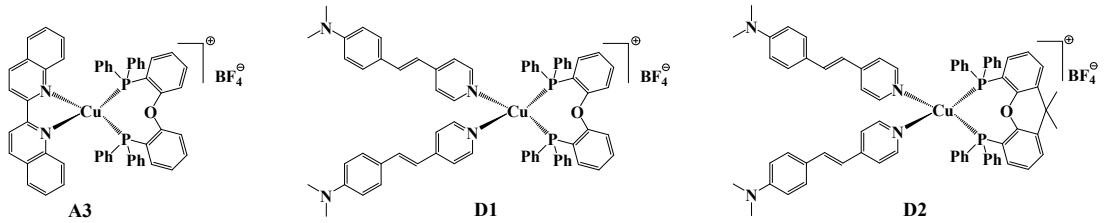


Figure S2. UV-vis absorption spectra of A5 and B3 in acetonitrile.



Scheme S2. Chemical structures of the copper complexes (A3, D1 and D2) that are not photostable in dichloromethane.

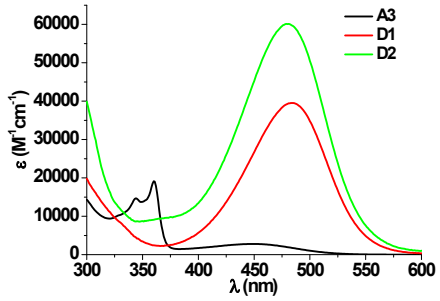


Figure S3. UV-vis absorption spectra of A3, D1 and D2 in dichloromethane.

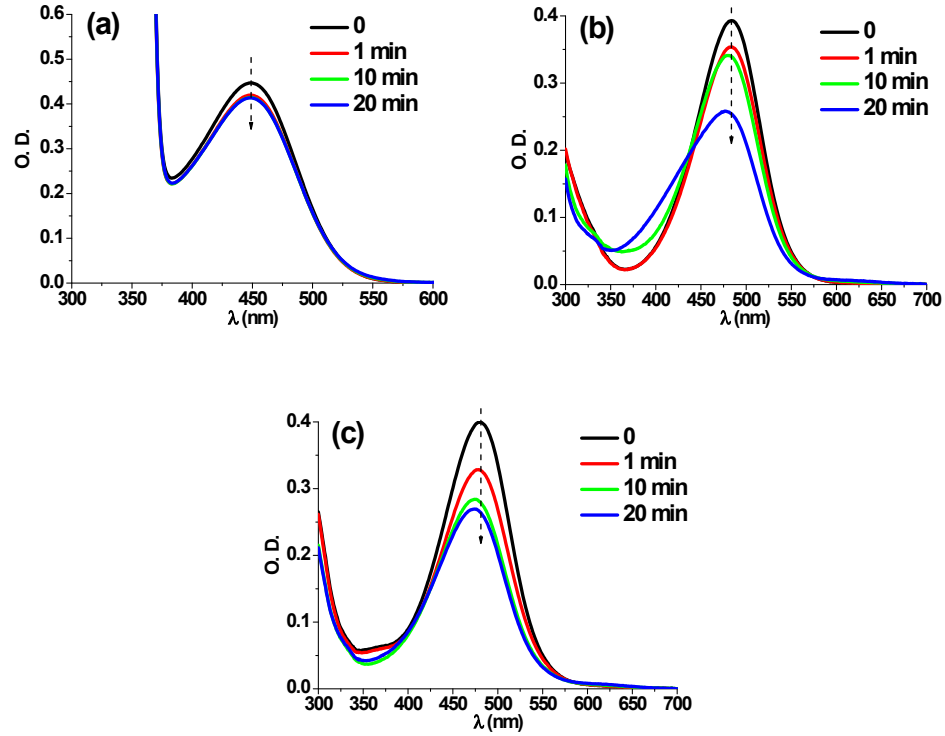
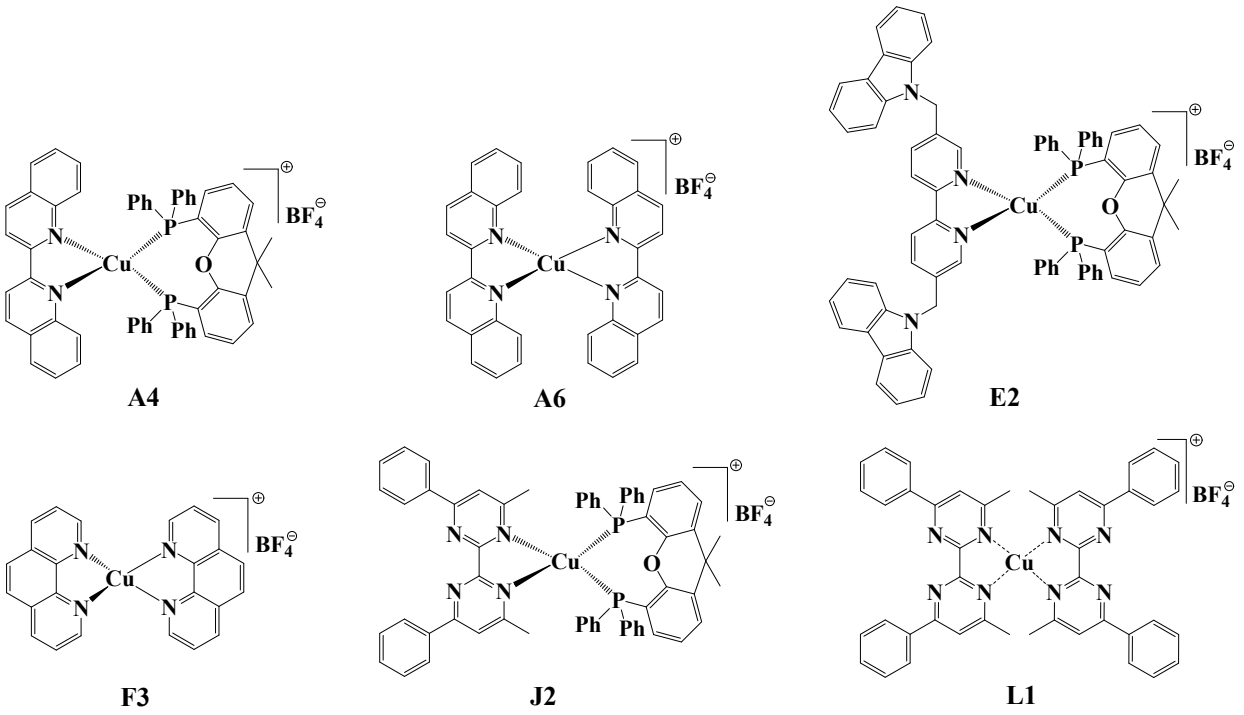


Figure S4. UV-vis spectra of (a) A3, (b) D1 and (c) D2 in dichloromethane after different irradiation time (halogen lamp).



Scheme S3. Chemical structures of the copper complexes that are not very photoreactive with Iod in dichloromethane.

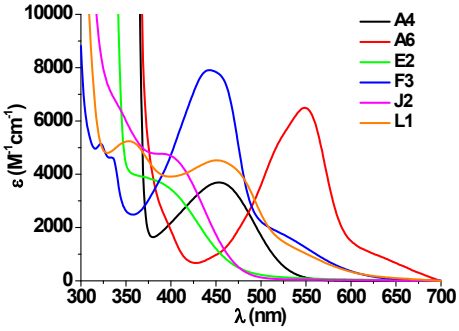


Figure S5. UV-vis absorption spectra of A4, A6, E2, F3, J2 and L1 in dichloromethane.

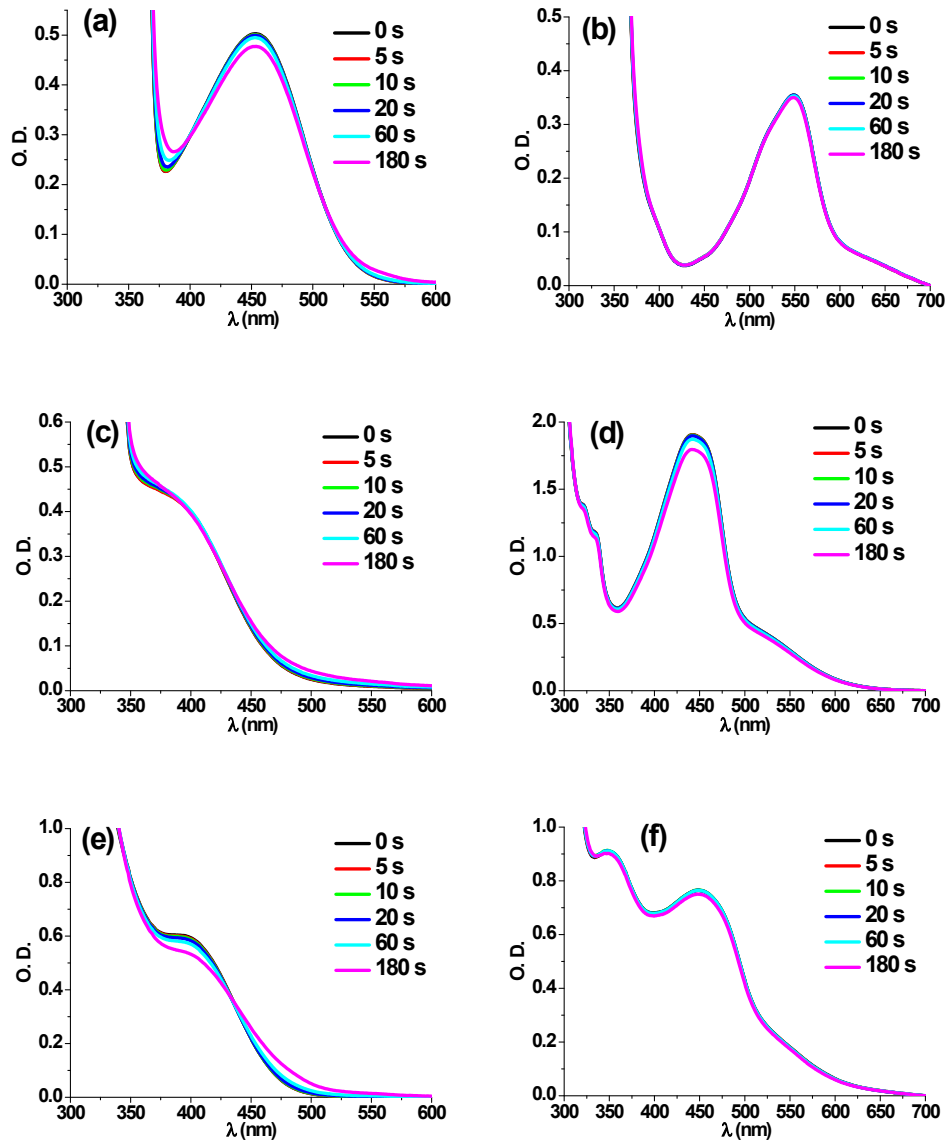


Figure S6. Steady state photolysis of (a) A4, (b) A6, (c) E2, (d) F3, (e) J2, and (f) L1 in the presence of Iod ([Iod] = 2.2 mM) in dichloromethane upon the visible light exposure; UV-vis spectra recorded at different irradiation time; A4, A6, F3, and L1 with the halogen lamp exposure; E2, and J2 with the laser diode at 405 nm exposure.

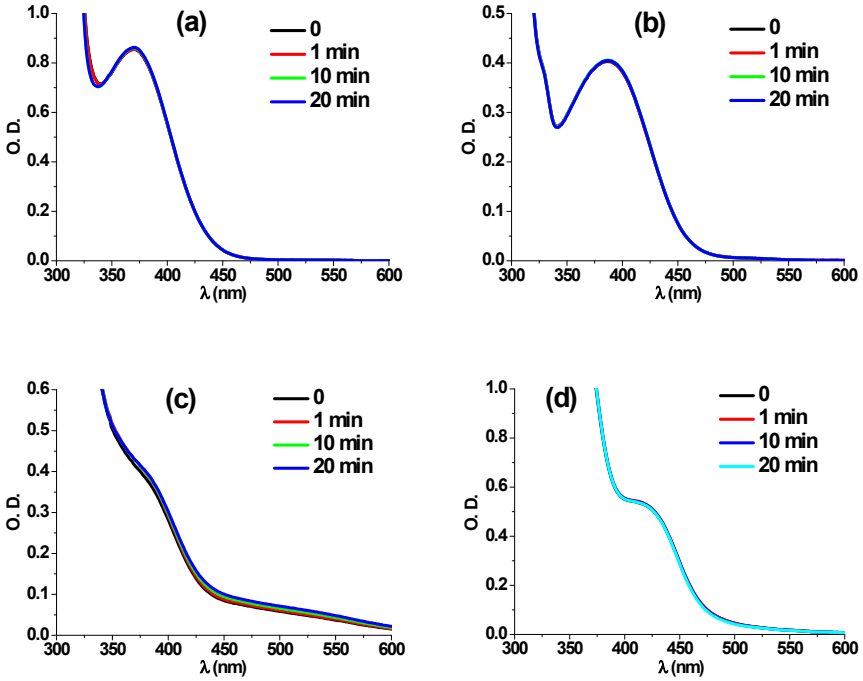


Figure S7. UV-vis spectra of (a) B2, (b) F2, (c) H1, and (d) K1 in dichloromethane after different irradiation (laser diode at 405 nm) time.

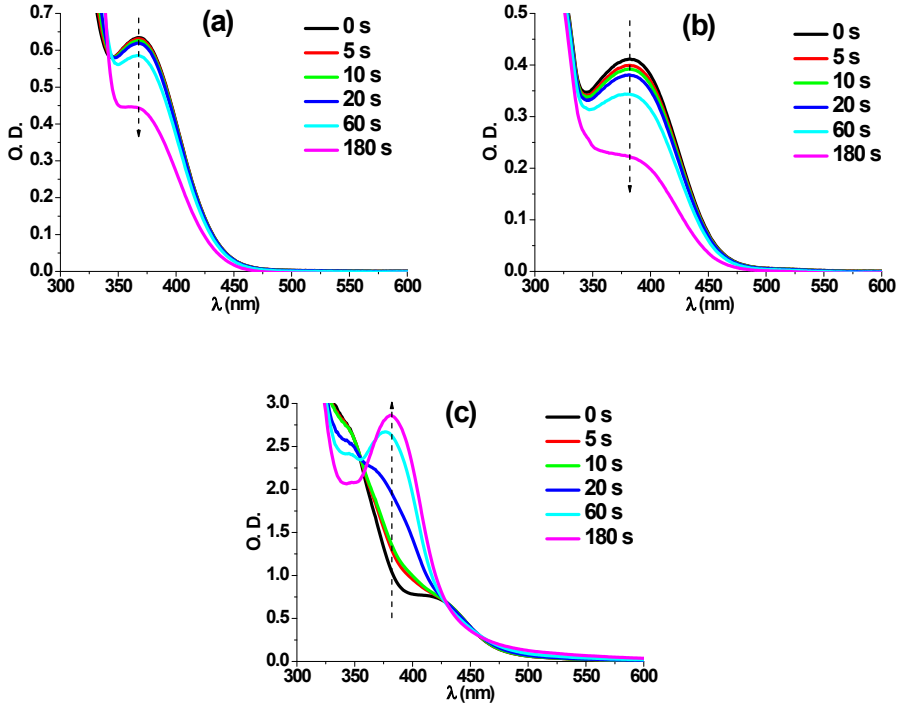


Figure S8. Steady state photolysis of (a) B2, (b) F2, and (c) K2 in the presence of Iod ([Iod] = 2.2 mM) in dichloromethane upon the laser diode at 405 nm exposure; UV-vis spectra recorded at different irradiation time.