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Luminescent Dinuclear Cu(I) Complexes Containing Rigid Tetraphosphine Ligands

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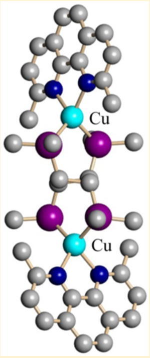
Supporting Information

ABSTRACT: The synthesis and the photophysics of three dinuclear copper(I) complexes containing bis(bidentate)phosphine ligands are described. The steric constraint imposed by tetrakis(di(2-methoxyphenyl)-phosphanyl)cyclobutane) (o-MeO-dppcb) in combination with 2,9-dimethyl-1,10-phenanthroline in one of the complexes leads to interesting photophysical properties. The compound shows an intense emission at room temperature in deoxygenated acetonitrile solution ($\Phi = 49\%$) and a long excited-state lifetime (13.8 μs). Interestingly, at low temperature, 77 K, the emission maximum shifts to lower energy, and the excited-state lifetime increases. This observation leads to the conclusion that a mixing between the excited triplet and singlet states is possible and that the degree of mixing and population of state strongly depends on temperature, as the energy difference is quite small. The electroluminescent properties of this compound were therefore tested in light-emitting electrochemical cells (LEECs), proving that the bright emission can also be obtained by electrically driven population of the singlet state.



■ INTRODUCTION

Among luminescent transition metal complexes, copper(I) compounds have attracted considerable interest for a variety of applications, from solar-energy conversion,[1] luminescence-based sensors,[2] and probes for biological systems[3] to optoelectronic applications[4,5] such as organic light-emitting devices (OLEDs)[6−16] or light-emitting electrochemical cells (LEECs).[17−20] Because of its abundance on earth crust, copper is relatively cheap and therefore offers a very attractive alternative to the most successfully employed heavy transition metals such as ruthenium, platinum, osmium, or iridium. However, emission intensity from copper(I) complexes is generally weak in solution. The reason for such behavior must be found in the geometry of these complexes.

Luminescent copper(I) complexes are characterized by a distorted tetrahedral ground-state geometry, since the d^{10} electronic shell is completely filled.[21] Upon excitation, metal-centered (MC) transitions cannot occur; therefore, the only transitions involving the metal are either metal-to-ligand charge transfer (MLCT) or, rarely, ligand-to-metal charge transfer (LMCT). Consequently, the excited metal complex undergoes a large structural change, leading to a more flattened geometry. This geometric distortion allows coordination of solvent molecules or coordinating ions to stabilize the square-based pyramidal geometry of Cu(II) and favors nonradiative pathways, facilitating relaxation back to the ground state.[22−24]

Using bulky ligands, that provide sterical hindrance, the geometrical distortion in the excited state is less favorable to occur, and the luminescent properties are enhanced.[25−27] Successful steric congestion and increasing rigidity around the copper(I) metal center has been achieved in mixed-ligand systems where two coordination sites are occupied by chelating phosphine, which suppresses ligand dissociation.[28,29] Among heteroleptic [Cu(NN)(PP)] complexes, those with bis[2-(diphenylphosphino)phenyl]ether (DPEphos) exhibit improved photophysical properties and stability were tested in OLEDs.[6−14]

To reach high stability of the copper(I) complexes in their excited state, increasing interest has been given not only to diverse sterically hindered substituents, but also to the design and synthesis of heteroleptic Cu(I) complexes with novel molecular architecture of polyphosphine[14,2b] as well as heterodonor PN ligands.[30,31] The geometrical requirements and the electronic properties of these chelating ligands resulted in very high luminescence quantum yields of the relative coordinated copper(I) complexes.[2b,14,31]

Recently, conformationally rigid bis(bidentate) phosphines have been used in heterometallic dinuclear species, where the steric pressure produces unusual characteristics of the excited states. In fact long lifetimes of the excited states and intense photoluminescence can be detected.[32] In the perspectives of developing materials with appealing photophysical properties for optoelectronic applications, rigid bis(bidentate)phosphine ligands have been employed to synthesize homodimetallic copper(I) complexes.

In this work, we present the syntheses and the photophysical and electrochemical properties of three new homodimetallic

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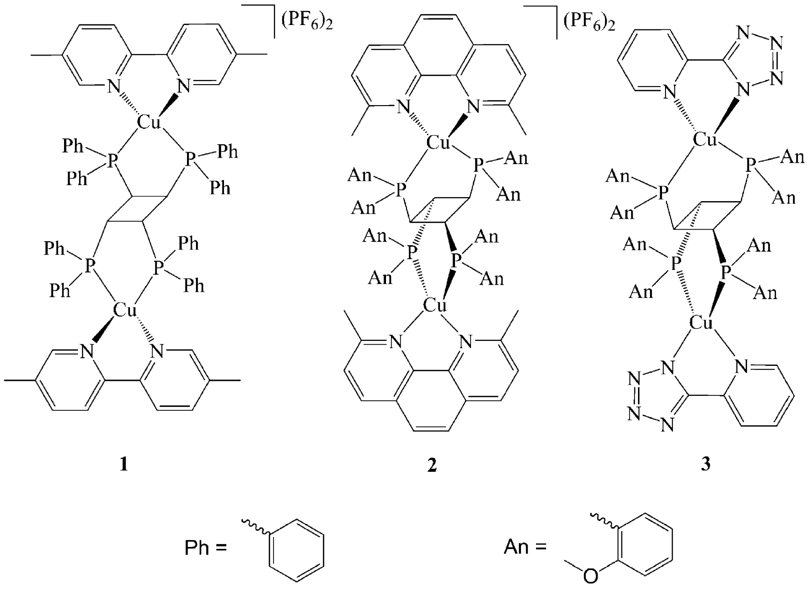
Scheme 1. Molecular Structures of the Three Investigated Homodimetallic Cu(I) Complexes



copper(I) complexes. A positively charged complex, **1**, was synthesized using the tetrakis(diphenylphosphanyl)cyclobutane (dppcb) and bis(5-methylpyridine) as ancillary ligand. The other charged complex, **2**, possesses tetrakis(di(2-methoxyphenyl)phosphanyl)cyclobutane) (o-MeO-dppcb) and has as ancillary ligands 2,9-dimethyl-1,10-phenanthroline. In the attempt to have a luminescent neutral complex, **3**, a 5-(2′-pyridyl)-1*H*-1,2,3,4-tetrazole was coordinated to the Cu(I) ion in place of the phenanthroline. All the investigated compounds are schematically presented in Scheme 1. The introduction of 2-methoxyphenyl substituents on the phosphorus donor atoms of the bis(chelating) ligand significantly enhances the luminescence properties of the corresponding copper(I) complexes, due to a favorable combination of electronic and sterical effects, allowing one of the presented complexes, **2**, to have high emission quantum yield in solution. Because of the interesting brightness of the emission, compound **2** was tested as dopant in solution-processed LEECs, and the main results are herein reported.

■ EXPERIMENTAL SECTION

General Information and Materials. Solvents for spectroscopic measurements were supplied by Merck (Uvasol). When necessary, they were purified according to the standard procedure.[33] Dichloromethane was distilled over CaH_2. All air- and water-sensitive experiments were carried out in standard glassware under an inert nitrogen atmosphere using standard vacuum line techniques. The ligands dppcb and *o*-MeO-dppcb were prepared as described earlier.[34,35] CuCl, 5,5′-dimethyl-2,2′-bipyridine (dmbpy), 2,9-dimethyl-1,10-phenanthroline (Neocuproine), 5-(2′-pyridyl)-1*H*-1,2,3,4-tetrazole, and $TlPF_6$ were obtained commercially.

Fourier-mode $^{31}P\{^1H\}$, $^{13}C\{^1H\}$, and ^1H NMR spectra were obtained using a Bruker DPX-300 spectrometer (internal deuterium lock) at 298 K. Positive chemical shifts are downfield from the standards: 85% H_3PO_4 for the $^{31}P\{^1H\}$ resonances and tetramethylsilane, $Si(CH_3)_4$, for the $^{13}C\{^1H\}$ and ^1H resonances. Fast atom bombardment mass spectrometry (FAB-MS) measurements were obtained on a Finnigan MAT-95 spectrometer, using 3-nitrobenzylalcohol (NOBA) as matrix. Elemental analyses were performed using a PerkinElmer Model 2400 C, H, N elemental analyzer.

Syntheses. *[Cu$_2$(dmbpy)$_2$(dppcb)](PF$_6$)$_2$ (**1**).* Under argon, dppcb (80.0 mg, 0.101 mmol) was dissolved in degassed acetonitrile (20 mL). Copper(I) chloride (20.0 mg, 0.202 mmol) was added in solid form to this solution, and the reaction mixture was stirred for 1 h at ambient temperature. Then thalliumhexafluorophosphate (70.5 mg, 0.202 mmol) was added in solid form to the colorless suspension, and the mixture was stirred for 16 h at 70 °C. Afterward, the suspension was filtered to remove precipitated TlCl, and dmbpy (37.2 mg, 0.202 mmol) was added to the filtrate in solid form. After 1 h of stirring, the product was completely precipitated via the addition of diethyl ether, filtered off, and dried *in vacuo*, to give $[Cu_2(dmbpy)_2(dppcb)](PF_6)_2$ as a yellow powder (Yield: 130.5 mg, 81.9%). $C_{76}H_{68}Cu_2F_{12}N_4P_6$ (1578.32): calc. C 57.84, H 4.34, N 3.55; found C 57.73, H 4.40, N 3.49%. mp: 300 °C dec; positive ion FAB-MS: m/z (m/z_{calcd}) = 1433.41 (1433.36) $[M\text{-}PF_6]^+$. $^{31}P\{^1H\}$ NMR (121.495 MHz, MeCN): δ 5.43 (s). ^1H NMR (300 MHz, MeCN-d_3): δ 2.13 (s, 6H, CH_3-$C_{12}H_{12}N_2$); 2.63 (s, 6H, CH_3-$C_{12}H_{12}N_2$); 4.53 (s, 4H, CH-C_4H_4); 6.80−7.37 (m, 40H, CH-Ph + 2H, CH-$C_{12}H_{12}N_2$); 7.87 (s, 5H, CH-$C_{12}H_{12}N_2$); 8.17 (s, 5H, CH-$C_{12}H_{12}N_2$). The solubility of **1** in common solvents like MeCN, CH_2Cl_2, or *N*,*N*-dimethylformamide (DMF) is too low for $^{13}C\{^1H\}$ NMR measurements.

*[Cu$_2$(Neocuproine)$_2$(o-MeO-dppcb)](PF$_6$)$_2$ (**2**).* Copper(I) chloride (11.5 mg, 0.116 mmol) and Neocuproine (24.2 mg, 0.116 mmol) were dissolved in degassed acetonitrile (30 mL) under argon. This solution was stirred for 15 min and then added dropwise to a solution of *o*-MeO-dppcb (60 mg, 0.058 mmol) and thalliumhexafluorophosphate (40.5 mg, 0.116 mmol) in 30 mL of degassed acetonitrile. The mixture was further stirred for 2 h, and the insoluble thallium chloride was separated by filtration. The solution was concentrated, and the yellow product was precipitated with an excess of diethyl ether and filtered to give [Cu$_2$(Neocuproine)$_2$(*o*-MeO-dppcb)][PF$_6$]$_2$ as a yellow solid (Yield: 85.9 mg, 79.3%). $C_{88}H_{84}Cu_2F_{12}N_4O_8P_6$ (1866.52): calc. C 56.63, H 4.54, N 3.00; found C 56.71, H 4.59, N 2.93%. mp: 305 °C; positive ion FAB-MS: m/z (m/z_{calcd}) = 1719.35 (1719.54) $[M\text{-}2H\text{-}PF_6]^+$, 1574.61 (1574.58) $[M\text{-}2H\text{-}2PF_6]^+$. $^{31}P\{^1H\}$ NMR (121.495 MHz, ACN-d_3): δ −1.79 (s). ^1H NMR (300 MHz, ACN-d_3): δ 1.85 (s, 12H, CH_3-$C_{14}H_{12}N_2$); 2.56 (s, 12H, -OCH_3); 2.95 (s, 12H, -OCH_3); 4.73 (t, ^3J(H,H) = 11.5 Hz, 4H, CH-C_4H_4); 6.16 (t, $^3J(H,H)$ = 7.4 Hz, 4H, CH-An); 6.25 (d, $^3J(H,H)$ = 8.1 Hz, 4H, CH-An); 6.43 (d, $^3J(H,H)$ = 6.9 Hz, 4H, CH-An); 6.78 (m, 8H, CH-An); 7.08 (t, $^3J(H,H)$ = 7.8 Hz, 4H, CH-An); 7.42 (t, $^3J(H,H)$ = 7.8 Hz, 4H, CH-$C_{14}H_{12}N_2$); 7.80 (m, 8H, CH-An); 8.16 (s, 4H, CH-$C_{14}H_{12}N_2$); 8.64 (d, $^3J(H,H)$ = 8.3 Hz, 4H, CH-$C_{14}H_{12}N_2$). $^{13}C\{^1H\}$ NMR (75.476 MHz, ACN-d_3): δ 28.9 (s, $CH_3-C_{14}H_{12}N_2$); 35.6 (s, $CH-C_4H_4$); 36.3 (s, $CH-C_4H_4$); 53.5 (s, -OCH_3); 55.4 (s, -OCH_3); 111.1 (s, CH-An); 113.1 (s, C-$C_{14}H_{12}N_2$), 120.5 (s, CH-An); 123.4, 132.1 (s, C-$C_{14}H_{12}N_2$); 133.8, 134.7 (s, CH-An); 136.3, 137.1 (s, C-$C_{14}H_{12}N_2$);

137.8 (s, CH-An); 161.7 (s, C=N−$C_{14}H_{12}N_2$); 162.7 (s, C=C-OCH_3). Suitable crystals for X-ray crystal structure analysis were obtained by crystallization from acetonitrile against diethyl ether.

[Cu_2{5-(2′-pyridyl)-1H-1,2,3,4-tetrazolato-κN^1}$_2$(o-MeO-dppcb)] (3). Copper(I) chloride (5.7 mg, 0.058 mmol) was dissolved in degassed acetonitrile (20 mL) under argon, and solid thalliumhexafluorophosphate (20.3 mg, 0.058 mmol) was added with vigorous stirring. After half an hour of reaction time at ambient temperature a white precipitate was filtered. The filtrate was added to a solution of *o*-MeO-dppcb (30.0 mg, 0.0290 mmol) in degassed acetonitrile (30 mL), and the resulting solution was stirred for 2 h at ambient temperature. To produce deprotonated pyridine tetrazole (PyN_4), PyN_4 (8.5 mg, 0.058 mmol) was dissolved in degassed acetonitrile (10 mL) under argon, and LiOH (1.4 mg, 0.058 mmol) dissolved in degassed water (24 μL) was added with vigorous stirring. This solution was stirred for further 40 min, and then the solvent was completely removed. The obtained solid was dissolved in degassed MeOH (5 mL) and then added to the above solution of [$Cu_2(MeCN)_3$(*o*-MeO-dppcb)]$(PF_6)_2$. The resulting yellow solution was stirred for 2 h and then evaporated to dryness to give [Cu_2{5-(2′-pyridyl)-1*H*-1,2,3,4-tetrazolato-κN^1}$_2$(*o*-MeO-dppcb)] as a light yellow powder (Yield: 24.4 mg, 58.0%). $C_{72}H_{68}Cu_2N_{10}O_8P_4$ (1452.38): calc. C 59.54, H 4.72, N 9.64; found C 59.46, H 4.77, N 9.59%. mp > 360 °C; positive ion FAB-MS: m/z (m/z_{calcd}) = 1452.15 (1452.38) $[M]^+$, 1306.14 (1306.25) $[M+H-(PyN_4)]^+$. $^{31}P\{^1H\}$ NMR (121.495 MHz, MeCN): δ −3.27 (s). ^1H NMR (300 MHz, CD_2Cl_2): δ 2.92 (s, 12H, -OCH_3); 3.00 (s, 12H, -OCH_3); 4.42 (br s, 4H, *C*H-C_4H_4); 6.56 (m, 16H, *C*H-An + 2H, *C*H-$C_6H_4N_5$); 7.25 (br s, 16H, *C*H-An); 8.08 (s, 4H, *C*H-$C_6H_4N_5$); 8.50 (s, 2H, *C*H-$C_6H_4N_5$). The solubility of **3** in common solvents like MeCN, CH_2Cl_2, or DMF is too low for $^{13}C\{^1H\}$ NMR measurements.

UV−vis Spectroscopy. Characterization methods, techniques, spectroscopic instruments, and tools were thoroughly described in previous papers.[36]

Electrochemistry. The electrochemical characterization, cyclic voltammetry (CV), and differential pulse voltammetry (DPV) was performed in acetonitrile (ACN)/0.1 M tetrabutylammonium hexafluorophosphate ($TBAPF_6$) or DMF/0.1 M $TBAPF_6$. The use of different solvents was due to a different solubility of the investigated complexes. The concentration of the samples was 1 mM for compound **1** and 1.5 mM for compound **2**. ACN (Acros Organics, 99.8%, extra dry over molecular sieves) and DMF (Sigma-Aldrich, Chromasolv Plus, 99.9%) were used as received without any further purification. $TBAPF_6$ (electrochemical grade, 99%, Fluka) was used as the supporting electrolyte, which was recrystallized from a 1:1 ethanol/water solution and dried at 60 °C under vacuum.

Details of the electrochemical experiments and a description of the electrochemical workstation and methods have been previously reported.[37] The reference electrode was calibrated at the end of each experiment against the ferrocene/ferricenium couple (Fc/Fc^+), whose formal potential against the KCl saturated calomel electrode (SCE) is 0.450 V in ACN and 0.464 V in DMF. In the following, all potential values are reported against the SCE.

X-ray Crystallography. Selected bond lengths, bond angles, and intramolecular contact distances are given in the Supporting Information. Details of data collection, refinement, and corrections were described in previous papers.[38]

Device Fabrication. The solution-processed LEEC device was made on a glass substrate, with a 120 nm transparent indium tin oxide (ITO) layer as the bottom electrode. A detailed description of procedures, materials, and tools was reported in previous papers.[36c]

■ RESULTS AND DISCUSSION

Electronic Absorption. The UV−vis absorption spectra of compounds **1**, **2**, and **3** were recorded at room temperature in acetonitrile solutions, where N_2 was purged for several minutes before dissolving the complexes. The molar absorption coefficients ε were calculated, and the spectra are displayed in Figure 1.

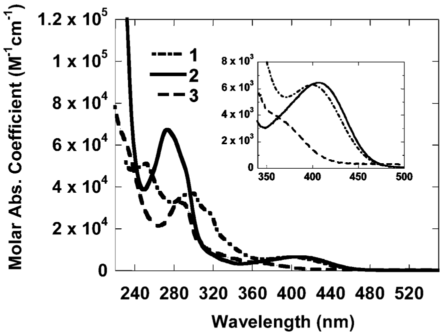


Figure 1. Electronic absorption spectra recorded in acetonitrile solutions ([C] ≈ 2 × 10^{-5} M) of compounds **1** (dot-dashed line), **2** (solid line), and **3** (dashed line). (inset) The low-energy bands are magnified.

The absorption bands in the UV region (220−290 nm) are dominated by spin-allowed intraligand transitions (^{1}IL). In this region the three dinuclear complexes have the more intense π−π* transitions occurring on the ancillary ligands and the weaker intraligand charge-transfer states, involving the phosphorus atoms and their aromatic substituents. It is well-known that aryl-phosphines, when not coordinated, have a transition called n−$a_π$, which involves the promotion of one electron from the lone pair orbital (n) on P to an empty antibonding orbital of π origin ($a_π$) located on the aromatic ring.[39] Upon coordination of aromatic phosphines, the lone pair on P is used for σ-bonding to the metal. The transition n−$a_π$ is then converted to a σ−$a_π$ transition and can be labeled as intraligand charge transfer, ILCT.[40] At longer wavelength, 350−450 nm, singlet metal-to-ligand charge transfer, MLCT, states are populated. In particular the broad band centered at 410 nm (ε = 6 × 10^3 M^{-1} cm^{-1}) for compound **1** is typical for ^{1}MLCT transitions from d orbitals on the copper(I) metal center to empty π* orbitals localized on the 5,5′-dimethyl-2,2′-bipyridine (dmbpy).[41] For compound **2** the metal-to-ligand charge transfer occurs with the involvement of the π* orbitals localized on the 2,9-dimethyl-1,10-phenanthroline at 420 nm (ε = 5.9 × 10^3 M^{-1} cm^{-1}), in analogy to homoleptic phenanthrolines copper(I) compounds.[42] The singlet MLCT transition for compound **3** is much less intense in comparison with the MLCT bands of the other compounds (ε = 3.8 × 10^3 M^{-1} cm^{-1}). Moreover since the lowest unoccupied molecular orbital (LUMO) of the pyridine tetrazole is much higher in energy, it occurs at higher energy (λ = 365 nm). All the data are collected in Table 1.

Emission at Room Temperature. At room temperature, only compounds **2** and **3** were found to be emissive. Their photophysics was studied in two spectroscopic solvents of different polarity, namely, acetonitrile (ACN) and dichloromethane (DCM). Each solution was degassed by three cycles of freeze−pump−thaw. The excitation and the emission spectra of these compounds in deaerated ACN and DCM are shown, respectively, in Figures 2 and 3.

In each solvent, the excitation spectrum for the two compounds perfectly matches their relative absorption spectra. The two Cu(I) complexes show bright luminescence, with emission maxima at 554 nm in ACN and at 555 nm in DCM for compound **2**, and at 579 nm in ACN and at 555 nm in DCM for compound **3**. The difference in behavior of the two complexes evidences a more present CT nature of the luminescent level for **3**, while the lack of solvatochromism

Table 1. Photophysical Data for Cu(I) Complexes at Room and Low Temperatures

	absorption[a]	emission in deareated solutions at 298 K					emission, 77 K[b]	
	λ (nm) ($\varepsilon \times 10^{-3}$ M^{-1} cm^{-1})[c]	λ_{max} (nm)	$\Phi^{d} \times 10^{2}$	τ (μs)	k_r (10^4 s^{-1})	k_{nr} (10^4 s^{-1})	λ_{max} (nm)	τ (μs)
1[e]	254 (50.01)						645	0.355
	301(36.69)							
	318(26.93, sh)							
	410(6.01)							
2	277(65.85)	554[a]	39[a], 49[e]	13.8[a]	2.8	4.4	560	634
	293(46.89, sh)	555[f]						
	420(5.89)							
3	230(62.33)	579[a]	0.40[a]	0.475[a]	0.83	208	570	3.64
	285(32.89)	555[f]	1.53[f]					
	334(6.98)							
	365(3.8)							

[a] Data in CH_3CN at room temperature. [b] Data at 77 K are recorded in EtOH/MeOH (4/1) (v/v) rigid matrix. [c] The term sh indicates shoulder. [d] Quantum yield values in solution were calculated with the relative method, using, as standards, $Ir(ppy)_3$ in degassed toluene for compound **2** and $Ru(bipy)_3Cl_2{\cdot}6H_2O$ in water for compound **3**. [e] Calculated with the integrated sphere. [f] Data in CH_2Cl_2 at room temperature.

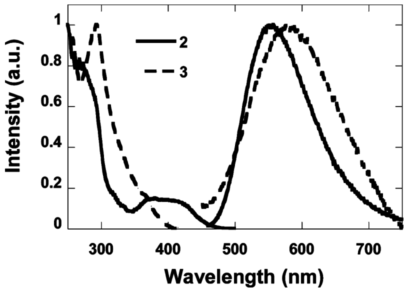


Figure 2. Normalized excitation (left) and emission (right) spectra recorded in degassed acetonitrile at room temperature of compounds **2** (solid line) [λ_{exc} = 400 nm; λ_{em} = 560 nm] and **3** (dashed line) [λ_{exc} = 300 nm; λ_{em} = 580 nm].

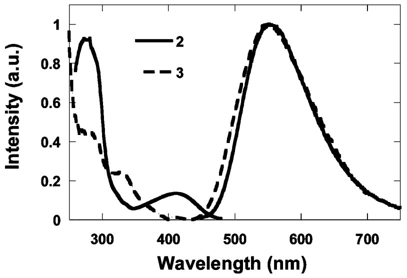


Figure 3. Normalized excitation (left) and emission (right) spectra recorded in degassed dichloromethane at room temperature of compounds **2** (solid line) [λ_{exc} = 400 nm; λ_{em} = 560 nm] and **3** (dashed line) [λ_{exc} = 300 nm; λ_{em} = 550 nm].

and long excited-state lifetime (see below) suggests a different nature of the excited state for compound **2** or at least a strong mixing of the CT state with an LC level. The assignment of the MLCT nature is suggested by the Supporting Information that the emissions are broad and do not show any structured bands, as expected for copper(I) complexes,[43] confirmed also by electrochemical data (see below). Emission quantum yields were measured for both compounds in deaerated ACN solutions. Compound **2** showed an unusually good quantum yield, when calculated with the relative method using $Ir(ppy)_3$ (ppy = 2-phenylpyridine) in toluene as standard (Φ = 0.97)[44] and with the absolute method of the integrating sphere.[45] The obtained values are surprisingly high for a copper(I) complex since they are, respectively, of 0.39 and 0.49. The different values arise from the uncertainties present in both methods for the evaluation of the quantum yields.[46] Quantum yield for compound **3** was measured with the relative method using $Ru(bipy)_3Cl_2{\cdot}6H_2O$ (bipy = 2,2′-bipyridine) in aerated water as standard (Φ = 0.040).[47] The values in DCM and in ACN are much lower than those found for complex **2**, and they are, respectively, 0.015 and 0.004. One possible reason for this low quantum yield might be related to the more pronounced distortion of the molecular geometry in the excited state when the ancillary ligand is the 5-(2′-pyridyl)-1*H*-1,2,3,4-tetrazole, as there are no hindered substituents. This could lead to an easier access of solvent molecules and in particular to coordinating solvent such as ACN.

Excited-state lifetimes were measured in acetonitrile, and their values are obtained from a monoexponential fit giving 13.8 μs for **2** and 0.475 μs for **3**. From the photoluminescence quantum yield and the lifetime values the radiative and nonradiative rate constants were estimated, and they are summarized, together with all the other photophysical data, in Table 1.

Emission at 77 K in EtOH/MeOH (4:1) Glass. The three copper(I) dinuclear complexes studied in this work show luminescence at 77 K in ethanol/methanol (4:1, v/v) glass. The emission spectra are shown in Figure 4. The luminescence of the three copper(I) dimers at 77 K exhibit a broad orange-red structureless emission, with maxima at 645 nm for **1**, at 560 nm for **2**, and at 570 nm for **3**. A red shift upon cooling is evident

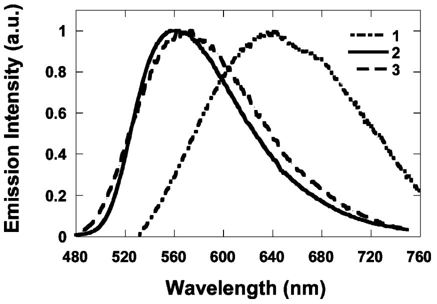


Figure 4. Low-temperature (77 K) emission spectra in EtOH/MeOH (4:1) (v/v) rigid matrix of compounds **1** (dot-dashed line) [λ_{exc} = 440 nm], **2** (solid line) [λ_{exc} = 400 nm], and **3** (dashed line) [λ_{exc} = 320 nm].

for compound **2** even if it is only of few nanometers, corresponding to 193 cm^{-1}. Interestingly, compound **3** also shows a small red shift if compared with the room-temperature emission in DCM, but the shift is negligible when compared with the polar ACN solution.

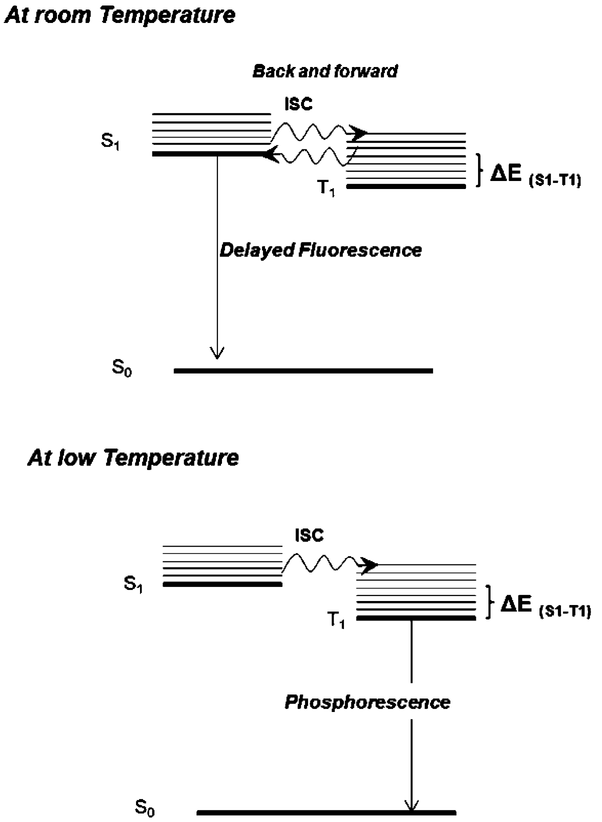
Observing almost no shift or even a red shift upon freezing the matrix is not usual. In fact, a blue shift is normally observed for MLCT transitions with higher dipole moment in the excited state, since the lack of reorganization of the solvent, and thus the destabilization of the state, leads to higher energy emission. Otherwise the situation is reversed when the excited state is less polar than the ground state.

As expected, excited-state lifetimes were found distinctly longer, since the decrease in temperature slows down the nonradiative processes related to motion or vibration of the ligands. Compound **1** exhibits luminescence only at low temperature and has a lifetime of 0.335 μs; compound **2** has an incredibly long excited-state lifetime of 634 μs, whereas compound **3** has an excited-state lifetime of 3.64 μs. Studying the lifetimes of the excited state with deeper insight gives a hint about the nature of the emissive states involved in the transitions. Compound **2** has a distinctly longer lifetime at 77 K that could be due to the shift of the equilibrium from a CT state to a LC state since the destabilization of the CT state. However, this hypothesis would not explain the red shift since the LC level is not sensitive to the solvent. Therefore, the observed behavior must be related to an equilibrium between the singlet and triplet MLCT state having at room temperature an emission from an equilibrated thermally populated singlet state, while at low temperature the emissive state is a triplet. All the photophysical data in solution at room temperature and at 77 K are summarized in Table 1.

Delayed Fluorescence Phenomenon for Compound 2. From the analysis of the photophysical data for the three copper(I) dinuclear species at room and low temperature, it is evident how the photoluminescence of **2** has a not-expected bathochromic shift at low temperature of 193 cm^{-1} in energy, with a large increase of the lifetime (see Table 1). As already mentioned, this behavior suggests the existence of two emissive excited states, where the one at higher energy can be populated at room temperature. This phenomenon was already observed and is known as delayed fluorescence,[48,49] since the higher energy state is a singlet in nature. The steady-state emission of a variety of phenanthrolines-based copper(I) complexes was indeed described as an equilibrium between two different excited states in thermal communication.[42,50−53] A qualitative representation of the energy levels involved is given in Scheme 2.

Vibrational relaxations are assumed to be rapid compared to electronic relaxation, and they are not shown; the same is true for the nonradiative pathways. Similarly to the reported complexes,[48−53] compound **2** shows a room-temperature emission at higher energy than at 77 K. Moreover the 13.8 μs of the excited-state lifetime at room temperature is not as short as it should be if it were due to a normal perturbed fluorescence. When the system becomes more rigid by decreasing the temperature, the decay lifetime becomes distinctly longer, but this increase cannot be addressed only to an inhibited nonradiative transition, and the emission maximum is red-shifted. This decrease in the emission energy must be related to a population of a different state. The simplest explanation of this temperature dependence is that these two states have similar energies, and the population of the upper level, the singlet, is thermally activated. In copper(I) complexes these two involved states are more likely ^{1}MLCT and ^{3}MLCT states, but the mixing with ^{3}LC states cannot be excluded.

Scheme 2. Diagram of the Relevant Energy States Showing Schematically the Intersystem Crossings (ISC) between the Singlet and the Triplet Excited States[a]



[a] The back ISC is thermally activated due to the small energy separation between these two states.

Thermally activated delayed fluorescence has been observed for some copper(I) complexes with small energy gaps between the S_1 and T_1 states. Compound **2** shows a completely comparable behavior with related complexes.[48b] Since for those phosphine-containing copper(I) complexes the occurrence of delayed fluorescence has been exhaustively proved,[48−50] the similarity of these species strongly suggests that delayed fluorescence also occurs in the case of **2**. However, only a qualitative interpretation of the temperature dependence of the emission maximum can be done at this stage.

Electrochemistry of Compounds 1 and 2. The CV of compound **1** (see Figure S1 in the Supporting Information) shows two successive irreversible processes in the negative range at −2.37 and −2.57 V versus SCE. The first reduction process is irreversible when varying the scan rate from 0.02 to 5 V s^{-1}. Both the former and latter processes in the negative scan are most probably associated with the reduction of the dmbpy ligands. In the positive scan two irreversible oxidation processes are observed (see Table 2). The first process at +0.85 V can be due to the oxidation of the Cu(I) metal center, as previously observed in other Cu(I) complexes, while the second one at +1.33 V can be associated with the oxidation of the phosphine moiety in the ligand. The highest occupied molecular orbital

Table 2. Electrochemical Data for Compounds 1 and 2

	CV					DPV		
	E_{ox} (CuI/CuII) (V)	E_{ox} (phosph) (V)	E_{red} (V)	HOMO (eV)	LUMO (eV)	E_{ox} (CuI/CuII) (V)	E_{ox} (phosph) (V)	E_{red} (1) (V)
1[a]	0.85	1.33	−2.37 −2.57	−5.19	−1.97	0.70	1.07	−2.29 −2.51
2[a]	1.18	1.38	−1.7	−5.52	−2.64	1.17	1.38	−1.7

[a] Data were recorded in DMF/0.1 M $TBAPF_6$ for **1**, and in CH_3CN/0.1 M $TBAPF_6$ for **2**.

(HOMO) and LUMO energy levels are calculated referring to the energy level of the Fc/Fc$^+$ couple.[54]

The CV of **2** (see Figure S3 in the Supporting Information) shows a quasi-reversible process in the negative scan occurring at −1.70 V, which can be associated with the reduction of the polyaromatic ligand. The peak-to-peak distance, ΔE_p, is about 85 mV at a scan rate of 0.1−0.5 V s^{-1}. In the positive scan, two redox processes are observed. The first one, at +1.18 V, is a quasireversible oxidation ($\Delta E_p \approx 75$ mV) that can be associated with the Cu(I) metal center. The second one, at approximately +1.4 V, is irreversible and can be associated with the oxidation of the bis(bidentate)phosphine. It is worth noticing that the intensity of the peak current, related to the oxidation of the metal core, is about half of that observed for the reduction of the ligand. Both quasireversible redox processes in the positive and negative scan were studied by varying the scan rate in the range of 0.1−5 V s^{-1}, and the peak currents were found to depend linearly on the square root of the scan rate as expected for a diffusion-controlled redox process.[55]

Since the coordination modes of dppcb and o-MeO-dppcb are totally different, because of difference of their absolute configurations (Scheme 1), the structural differences can affect the redox potential.

Because of its neutral charge, compound **3** showed less solubility in these common solvents for electrochemical analysis, and therefore its electrochemistry could not be measured. Differential pulse voltammetry was also performed to gain a better resolution of the redox processes occurring in the two homodinuclear copper(I) complexes. The voltammetric curves (CV and DPV) of the dinuclear copper(I) complexes are shown in the Supporting Information. The electrochemical data are reported in Table 2.

Crystal Structure of $[Cu_2(Neocuproine)_2(o\text{-}MeO\text{-}dppcb)][PF_6]_2$ (2). To the best of our knowledge the crystal structure of **2** is unique and shows the combination of two Cu(I) centers by a fused 6−4−6-membered ring system. The asymmetric unit of the crystal structure of **2** contains the metal complex dication and two $[PF_6]^-$ anions. Views of **2** are shown in Figures 5 and 6, and selected bond lengths, bond angles, and intramolecular contact distances are given in the captions of those Figures and in the Supporting Information. A discussion of the structure properties of **2**, related to its photophysical behavior, might help understanding the surprisingly high luminescence quantum yield and lifetime. Two effects can be taken into consideration.

First, as displayed in Figure 6 the methoxy groups of two 2-methoxyphenyl rings hinder the solvent molecules to approach the Cu(1) metal center. The corresponding Cu(1)···O(2) and Cu(1)···O(4) contact distances are 3.307(3) and 3.308(3) Å, respectively. Comparable attractive interactions at the Cu(2) center show Cu(2)···O(5) and Cu(2)···O(8) contact distances of 3.545(3) and 3.322(3) Å, respectively. The approach of solvent molecules is further blocked by the methyl groups of Neocuproine (see Figure 6). It is well-known that in the case of Cu(I) a flattening distortion caused by excitation of the Cu(I) center makes the nucleophilic attack of a solvent molecule possible.[26] However, from Figure 6 it is clear that neither a flattening distortion nor a nucleophilic attack is possible due to the very high "steric pressure" at the Cu(I) center. As a consequence this channel of energy release is hindered in **2**, and hence the emission lifetime becomes 13.8 μs at ambient temperature, which is very long compared with similar compounds. The same is true for the surprisingly high emission quantum yield of 0.49.

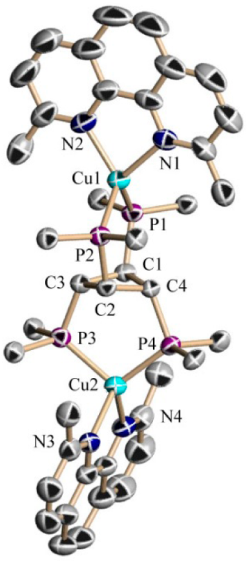


Figure 5. Perspective view of the cation of **2**. Thermal ellipsoids are shown at the 30% level. Hydrogen atoms are omitted, and only the ipso carbon atoms of the 2-methoxyphenyl rings are shown for clarity. Selected bond lengths (Å) and angles (deg): Cu(1)−P(1) = 2.2578(11), Cu(1)−P(2) = 2.2682(11), Cu(1)−N(1) = 2.125(4), Cu(1)−N(2) = 2.083(3), Cu(2)−P(3) = 2.2715(11), Cu(2)−P(4) = 2.2561(12), Cu(2)−N(3) = 2.095(3), Cu(2)−N(4) = 2.082(3), C(1)−C(3) = 1.576(5), C(1)−C(4) = 1.559(5), C(2)−C(3) = 1.596(5), C(2)−C(4) = 1.579(5); P(1)−Cu(1)−P(2) = 102.31(4), N(1)−Cu(1)−N(2) = 80.92(15), P(3)−Cu(2)−P(4) = 103.21(4), N(3)−Cu(2)−N(4) = 81.33(14).

Furthermore, the excited-state lifetime of **2** also increases very much at 77 K reaching 634 μs. This behavior suggests the existence of two emissive excited states and that the higher energy one can only be populated at room temperature. This phenomenon is known as delayed fluorescence[48,49] (see Scheme 2).

Electroluminescence Devices. Considering the promising PL quantum yield, compound **2** was selected to act as emitting material for LEECs. LEECs were fabricated with a very simple structure on ITO glass substrate, where a layer of compound **2** was sandwiched between the hole injection layer of poly(3,4-ethylenedioxythiophene) polystyrene sulfonate (40 nm) and the Al cathode (100 nm). Figure 7 shows the electro-

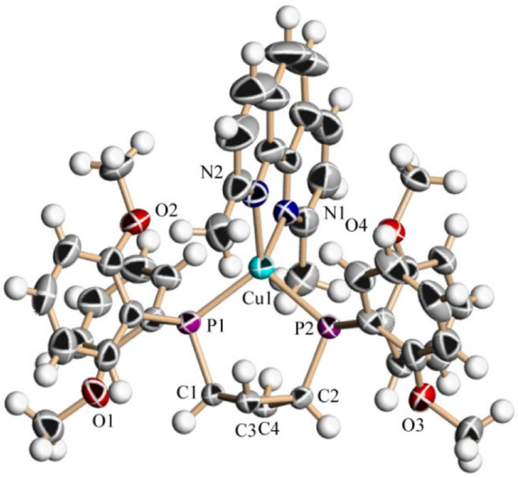


Figure 6. Perspective view of one Cu(I) coordination center of compound **2**. Thermal ellipsoids are shown at the 30% level. Because of unfavorable overlaps the second half of 2 is omitted for clarity. The close approaches of the oxygen atoms O(2) and O(4) of two methoxy groups of the two 2-methoxyphenyl rings of the o-MeO-dppcb ligand to the Cu(1) center can be clearly seen: Cu(1)···O(2) = 3.307(3), Cu(1))···O(4) = 3.308(3) Å. The second half of **2** shows comparable approaches: Cu(2)···O(5) = 3.545(3), Cu(2)···O(8) = 3.322(3) Å.

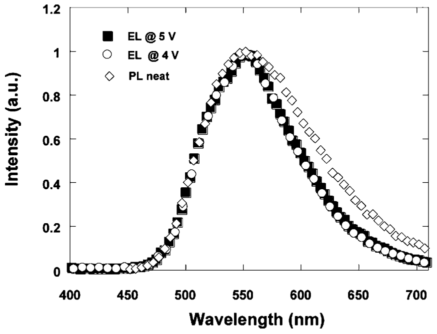


Figure 7. Electroluminescent spectra of **2**, recorded at applied voltage 4 and 5 V, are compared to photoluminescence spectrum of neat film.

luminescence spectra of a device driven at two different voltages: 4 and 5 V. The emission maximum is, respectively, at 553 nm and at 554 nm, as for the photoluminescence of the neat film, also reported for comparison in Figure 7.

Although the structure of the device was not optimized, the maximum luminance gave very promising results. The LEEC driven at 5 V shows a maximum luminance of 108 cd/m^2. Indeed this value shows an extraordinary brightness, unusual for copper(I)-based light-emitting electrochemical cells.[17,19,20]

The delayed fluorescence mechanism of compound **2** allows harvesting both singlet and triplet excitons in the device,[49a] leading to the first copper(I)-based LEEC with singlet harvesting effect. In Table 3, the electroluminescence properties of the LEEC device, made with compound **2** as emitting dopant, are summarized.

■ CONCLUSION

Three novel homodinuclear copper(I) complexes have been synthesized, and their photophysical and electrochemical properties have been studied. One of the complexes, compound **2**, showed an interesting photophysical behavior, which has been attributed to a temperature-dependent singlet−triplet equilibrium. An electroluminescent device, an LEEC, has been constructed to prove that this singlet emission can also be exploited in such simple electrically driven devices.

■ ASSOCIATED CONTENT

Supporting Information

X-ray crystallographic data of **2** in CIF format, selected bond lengths and bond angles. Cyclic and differential pulse voltammograms. This material is available free of charge via the Internet at http://pubs.acs.org.

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⊥These authors contributed equally. All authors have given approval to the final version of the manuscript.

Notes

The authors declare no competing financial interest.

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■ REFERENCES

(1) Alonso-Vante, N.; Nierengarten, J.-F.; Sauvage, J.-P. *J. Chem. Soc., Dalton Trans.* **1994**, 1649−1654.

(2) (a) Smith, C. S.; Mann, K. R. *Chem. Mater.* **2009**, *21*, 5042. (b) Smith, C. S.; Branham, C. W.; Marquardt, B. J.; Mann, K. R. *J. Am. Chem. Soc.* **2010**, *132*, 14079.

(3) (a) McMillin, D. R.; McNett, K. M. *Chem. Rev.* **1998**, *98*, 1201. (b) Starosta, R.; Florek, M.; Krol, J.; Puchalaska, M.; Kochel, A. *New J. Chem.* **2010**, *34*, 1441.

(4) Armaroli, N.; Accorsi, G.; Cardinali, F.; Listorti, A. *Top. Curr. Chem.* **2007**, *280*, 69.

(5) Evans, R. C.; Douglas, P.; Winscom, C. J. *Coord. Chem. Rev.* **2006**, *250*, 2093.

(6) Kuang, S.-M.; Cuttell, D. G.; McMillin, D. R.; Fanwick, P. E.; Walton, R. A. *Inorg. Chem.* **2002**, *41*, 3313.

Table 3. Electroluminescence Data for LEEC with Compound 2

compound	U (V)	$\lambda_{\text{max, EL}}$ (nm)	L_{max} (cd/m^2)	t_{on}[a] (h)	$t_{1/2}$[b] (h)	current efficacy (cd/A)	CIE[c] (x, y)
2	4	553	59.5	0.239	0.84	0.07	0.40, 0.57
	5	554	108	0.036	0.084	0.05	0.39, 0.54

[a] Time required to reach the maximal brightness. [b] Time to decay to the half of the maximal brightness. [c] CIE evaluated from the EL spectra.

(7) Zhang, Q.; Zhou, Q.; Cheng, Y.; Wang, L.; Ma, D.; Jing, X. *Adv. Mater.* **2004**, *16*, 432.

(8) McCormick, T.; Jia, W. L.; Wang, S. *Inorg. Chem.* **2006**, *45*, 147.

(9) Che, G.; Su, Z.; Li, W.; Chu, B.; Li, M.; Hu, Z.; Zhang, Z. *Appl. Phys. Lett.* **2006**, *89*, 103511.

(10) Zhang, Q.; Ding, J.; Cheng, Y.; Wang, L.; Xie, Z.; Jing, X.; Wang, F. *Adv. Mater.* **2007**, *17*, 2983.

(11) Si, Z.; Li, J.; Li, B.; Liu, S.; Li, W. *J. Lumin.* **2009**, *129*, 181.

(12) Min, J.; Zhang, Q.; Sun, W.; Cheng, Y.; Wang, L. *Dalton Trans.* **2011**, *40*, 686.

(13) Femoni, C.; Muzzioli, S.; Palazzi, A.; Stagni, S.; Zacchini, S.; Monti, F.; Accorsi, G.; Bolognesi, M.; Armaroli, N.; Massi, M.; Valenti, G.; Marcaccio, M. *Dalton Trans.* **2013**, *42*, 997.

(14) Hou, R.; Huang, T. H.; Wang, X. J.; Jiang, X. F.; Ni, Q. L.; Gui, L. C.; Fan, Y. J.; Tan, Y. L. *Dalton Trans.* **2011**, *40*, 7551.

(15) Igawa, S.; Hashimoto, M.; Kawata, I.; Yashima, M.; Hoshino, M.; Osawa, M. *J. Mater. Chem.* **2013**, *1*, 542.

(16) Osawa, M.; Kawata, I.; Ishii, R.; Igawa, S.; Hashimoto, M.; Hoshino, M. *J. Mater. Chem.* **2013**, *1*, 4375.

(17) Armaroli, N.; Accorsi, G.; Holler, M.; Moudam, O.; Nierengarten, J.-F.; Zhou, Z.; Wegh, R. T.; Welter, R. *Adv. Mater.* **2006**, *18*, 1313.

(18) Zhang, Q.; Zhou, Q.; Cheng, Y.; Wang, L.; Ma, D.; Jing, X.; Wang, F. *Adv. Funct. Mater.* **2006**, *16*, 1203.

(19) Wang, Y.-M.; Teng, F.; Hou, Y.-B.; Xu, Z.; Wang, Y.-S.; Fu, W.-F. *Appl. Phys. Lett.* **2005**, *87*, 233512.

(20) Costa, R. D.; Tordera, D.; Ortì, E.; Bolink, H. J.; Schönle, J.; Graber, S.; Housecroft, C. E.; Constable, E. C.; Zampese, J. A. *J. Mater. Chem.* **2011**, *21*, 16108.

(21) Scaltrito, D. V.; Thompson, D. W.; O'Callaghan, J. A.; Meyer, G. J. *Coord. Chem. Rev.* **2000**, *208*, 243.

(22) Eggleston, M. K.; McMillin, D. R.; Koenig, K. S.; Pallenberg, A. J. *Inorg. Chem.* **1997**, *36*, 172.

(23) Cunningham, C. T.; Cunningham, K. L. H.; Michalec, J. F.; McMillin, D. R. *Inorg. Chem.* **1999**, *38*, 4388.

(24) Rader, R. A.; McMillin, D. R.; Buckner, M. T.; Matthews, T. G.; Casadonte, D. J.; Lengel, R. K.; Whittaker, S. B.; Darmon, L. M.; Lytle, F. E. *J. Am. Chem. Soc.* **1981**, *103*, 5906.

(25) Miller, M. T.; Gantzel, P. K.; Karpishin, T. B. *J. Am. Chem. Soc.* **1999**, *121*, 4292.

(26) Armaroli, N. *Chem. Soc. Rev.* **2001**, *30*, 113.

(27) Cuttell, D. G.; Kuang, S.-M.; Fanwick, P. E.; McMillin, D. R.; Walton, R. A. *J. Am. Chem. Soc.* **2002**, *124*, 6.

(28) Manbeck, G. F.; Brennessel, W. W.; Eisenberg, R. *Inorg. Chem.* **2011**, *50*, 3431.

(29) Crestani, M. G.; Manbeck, G. F.; Brennessel, W. W.; McCormick, T. M.; Eisenberg, R. *Inorg. Chem.* **2011**, *50*, 7172.

(30) Harkins, S. B.; Peters, J. C. *J. Am. Chem. Soc.* **2005**, *127*, 2030.

(31) Li, Q. *Dalton Trans.* **2009**, 9388.

(32) (a) Gutmann, R.; Eller, S.; Fesser, M.; van der Veer, W. E.; Dumfort, A.; Kopacka, H.; Müller, T.; Brüggeller, P. *Inorg. Chem. Commun.* **2007**, *10*, 1510. (b) Stampfl, T.; Gutmann, R.; Czermak, G.; Langes, C.; Dumfort, A.; Kopacka, H.; Ongania, K.-H.; Brüggeller, P. *Dalton Trans.* **2003**, 3425. (c) Trettenbrein, B.; Fessler, M.; Ruggenthaler, M.; Haringer, S.; Oberhuber, D.; Czermak, G.; Brüggeller, P.; Oberhauser, W. *Inorg. Chim. Acta* **2011**, *375*, 324. (d) Bachmann, C.; Gutmann, R.; Czermak, G.; Dumfort, A.; Eller, S.; Fessler, M.; Kopacka, H.; Ongania, K.-H.; Brüggeller, P. *Eur. J. Inorg. Chem.* **2007**, *2007*, 3227.

(33) Armarego, W. L. F.; Chai, C. L. L. *Purification of Laboratory Chemicals*, 5th ed.; Butterworth Heinemann, ElsevierScience: Bodmin, Cornwall, U.K., 2003.

(34) Oberhauser, W.; Bachmann, C.; Stampfl, T.; Haid, R.; Langes, C.; Kopacka, H.; Rieder, A.; Brüggeller, P. *Inorg. Chim. Acta* **1999**, *290*, 167.

(35) Fessler, M.; Czermak, G.; Eller, S.; Trettenbrein, B.; Brueggeller, P.; Bettucci, L.; Bianchini, C.; Meli, A.; Ienco, A.; Oberhauser, W. *Dalton Trans.* **2009**, 1859.

(36) (a) Barcina, J. O.; Herrero-Garcìa, N.; Cucinotta, F.; De Cola, L.; Contreras-Carballada, P.; Williams, R. M.; Guerrero-Martìnez, A. *Chem.—Eur. J.* **2010**, *116*, 6033. (b) Leenen, M. A. M.; Cucinotta, F.; Viani, L.; Mavrinskiy, A.; Pisula, W.; Gierschner, J.; Cornil, J.; Prodi-Schwab, A.; Thiem, H.; Müller, K.; De Cola, L. *J. Phys. Chem. B* **2010**, *114*, 14614. (c) Fernàndez-Hernàndez, J. M.; Yang, C.-H-; Beltràn, J. I.; Lemaur, V.; Polo, F.; Fröhlich, R.; Cornil, J.; De Cola, L. *J. Am. Chem. Soc.* **2011**, *133*, 10543. (d) Ramachandra, S.; Polo, F.; Edafe, F.; Schürmann, K. C.; Nijhuis, C. A.; Belser, P.; Reus, W. F.; Whitesides, G. M.; De Cola, L. *Pure Appl. Chem.* **2011**, *83*, 779.

(37) Mydlak, M.; Mauro, M.; Polo, F.; Felicetti, M.; Leonhardt; Diener, G.; De Cola, L.; Strassert, C. A. *Chem. Mater.* **2011**, *23*, 3659.

(38) Strabler, C.; Ortner, T.; Prock, J.; Granja, A.; Gutmann, R.; Kopacka, H.; Müller, T.; Brüggeller, P. *Eur. J. Inorg. Chem.* **2013**, *2013*, 5121.

(39) Kutal, C. *Coord. Chem. Rev.* **1990**, *99*, 213.

(40) Vogler, A.; Kunkely, H. *Coord. Chem. Rev.* **2002**, *230*, 243.

(41) Williams, R. M.; De Cola, L.; Hartl, F.; Lagref, J.-J.; Planeix, J.-M.; De Cian, A.; Hosseini, M. W. *Coord. Chem. Rev.* **2002**, *230*, 253.

(42) Blaskie, M. W.; McMillin, D. R. *Inorg. Chem.* **1980**, *19*, 3519.

(43) Armaroli, N.; Accorsi, G.; Cardinali, F.; Listorti, A. In *Photochemistry and Photophysics of Coordination Compounds I*, Springer: Berlin, Heidelberg, Germany, 2007; Vol. *280*, pp 69−115.

(44) Sajoto, T.; Djurovich, P. I.; Tamayo, A. B.; Oxgaard, J.; Goddard, W. A.; Thompson, M. E. *J. Am. Chem. Soc.* **2009**, *131*, 9813.

(45) de Mello, J. C.; Wittmann, H. F.; Friend, R. H. *Adv. Mater.* **1997**, *9*, 230.

(46) Würth, C.; Grabolle, M.; Pauli, J.; Spieles, M.; Resch-Genger, U. *Anal. Chem.* **2011**, *83*, 3431.

(47) Suzuki, K.; Kobayashi, A.; Kaneko, S.; Takehira, K.; Yoshihara, T.; Ishida, H.; Shiina, Y.; Oishi, S.; Tobita, S. *Phys. Chem. Chem. Phys.* **2009**, *11*, 9850.

(48) (a) Yersin, H.; Rausch, A. F.; Czerwieniec, R.; Hofbeck, T.; Fischer, T. *Coord. Chem. Rev.* **2011**, *255*, 2622. (b) Czerwieniec, R.; Yu, J.; Yersin, H. *Inorg. Chem.* **2011**, *50*, 8293. (c) Czerwieniec, R.; Yu, J.; Yersin, H. *Inorg. Chem.* **2012**, *51*, 1975. (d) Chen, X.-L.; Yu, R.; Zhang, Q.-K.; Zhou, L.-J.; Wu, X.-Y.; Zhang, Q.; Lu, C.-Z. *Chem. Mater.* **2013**, *25*, 3910.

(49) (a) Deaton, J. C.; Switalski, S. C.; Kondakov, D. Y.; Young, R. H.; Pawlik, T. D.; Giesen, D. J.; Harkins, S. B.; Miller, A. J. M.; Mickenberg, S. F.; Peters, J. C. *J. Am. Chem. Soc.* **2010**, *132*, 9499. (b) Zink, D. M.; Bächle, M.; Baumann, T.; Nieger, M.; Kühn, M.; Wang, C.; Klopper, W.; Monkowius, U.; Hofbeck, T.; Yersin, H.; Bräse, S. *Inorg. Chem.* **2013**, *52*, 2292. (c) Volz, D.; Zink, D. M.; Bocksrocker, T.; Friedrichs, J.; Nieger, M.; Baumann, T.; Lemmer, U.; Bräse, S. *Chem. Mater.* **2013**, *25*, 3414.

(50) Kirchhoff, J. R.; Gamache, R. E.; Blaskie, M. W.; Del Paggio, A. A.; Lengel, R. K.; McMillin, D. R. *Inorg. Chem.* **1983**, *22*, 2380.

(51) Casadonte, D. J.; McMillin, D. R. *Inorg. Chem.* **1987**, *26*, 3950.

(52) Felder, D.; Nierengarten, J.-F.; Barigelletti, F.; Ventura, B.; Armaroli, N. *J. Am. Chem. Soc.* **2001**, *123*, 6291.

(53) Kovalevsky, A. Y.; Gembicky, M.; Coppens, P. *Inorg. Chem.* **2004**, *43*, 8282.

(54) Thelakkat, M.; Schmidt, H.-W. *Adv. Mater.* **1998**, *10*, 219.

(55) Bard, A. J.; Faulkner, L. R. *ElectrochemicalMethods, Fundamentals and Applications*, 2nd ed.; Wiley: New York, 2001.