

Modulation of emission properties of phosphine-sulfonate ligand containing copper complexes playing with solvato-, thermo-, and mechanochromism

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Modulation of phosphine sulfonate ligands containing copper complexes emission properties: playing with solvato-, thermo-, and mechanochromism

Antoine Vacher,[a] Anissa Amar,[b] Franck Camerel,[a] Yann Molard,[a] Camille Latouche,[c] Thierry Roisnel,[a] Vincent Dorcet,[a] Abdou Boucekkine,[a*] Huriye Akdas-Kiliç [a*] and Mathieu Achard [a*]

Modulations of various neutral phosphine containing copper(I) complexes exhibiting phosphorescence and TADF are easily achieved by solvent modification restricting intramolecular rotation or by modifying the L-X phosphine-sulfonate chelate. This concept is not limited to solvent as the addition of metallic salts also led to the formation of original well-defined photoluminescent K_2CuLX_3 and $KCuL_2X_2$ cuprate complexes.

Introduction

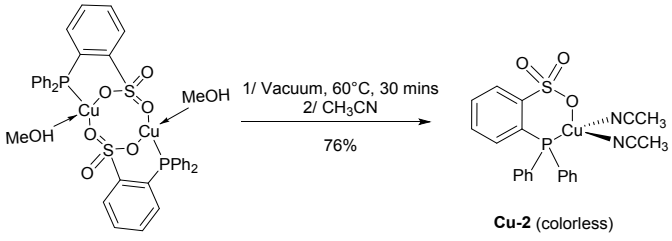
Since the seminal independent observations of Boudin[1a] on eosin and Lewis[1b] on fluorescein of a second long-lived luminescence in viscous/rigid media, delayed fluorescence has attracted a lot of interests. This temperature dependent phenomenon is not limited to organic molecules and re-examination of this concept by McMillin with well-defined copper complexes demonstrated that the emission processes arise from the two close S_1 and T_1 excited states leading to the so-called Thermally Activated Delayed Fluorescence (TADF), thus allowing the development of organic and inorganic materials to harvest both singlet and triplet excitons.[2,3,1d] Owing to their possible application in OLEDs as sensor and due to the low cost and abundancy of first row transition metal complexes, copper complexes exhibiting TADF and/or phosphorescence have received a lot of interest as promising alternatives to triplet harvesters based on precious metals.[4,5] Thus, lots of attention has been paid to a careful design of various cationic and neutral mono-, di- and multi-nuclear cuprous complexes to tune their photophysical properties and to minimize geometry distortion in the excited state.[2-11] In contrast cuprate complexes have been far less investigated and usually led to halo bridged coordination polymers[12]. Noteworthy that due to the side presence of Cu(I) in copper perovskite defects, this material exhibit green photoluminescence.[13]

In our quest to develop sustainable approaches to obtain efficient and photoresponsive luminescent molecules,[14] in this article, we present the preparation of various original neutral copper(I) and cuprates(I) complexes arising from the treatment of phosphine-benzenesulfonic acids with solvents and metal salts. Photophysical properties of the synthesized complexes are also investigated.

Results and discussions

Complex **Cu-2** (**Scheme 1**) was easily synthesized from our **Cu-1**[14a] complex after removal of the coordinated methanol molecules under vacuum followed by the addition of acetonitrile. This simple reaction affords colourless crystals of **Cu-2** in 76% isolated yield. Interestingly, whereas X-ray structure determination highlights the formation of a tetracoordinated mononuclear copper(I) complex bearing two acetonitrile ligands along with 2 lattice acetonitrile molecules restricting rotation of one exocyclic P-Ph bond (**Figure 1** and **Figure S3**), NMR analyses in CD_3CN and cyclic voltammetry demonstrate the presence of a dimer in acetonitrile solution (**Figure S1**;**S2**). The nature of the phosphine plays an important role on the formation of the bi- and mono-nuclear species in the solid state. Replacement of the Murray ligand in **Cu-1** by the

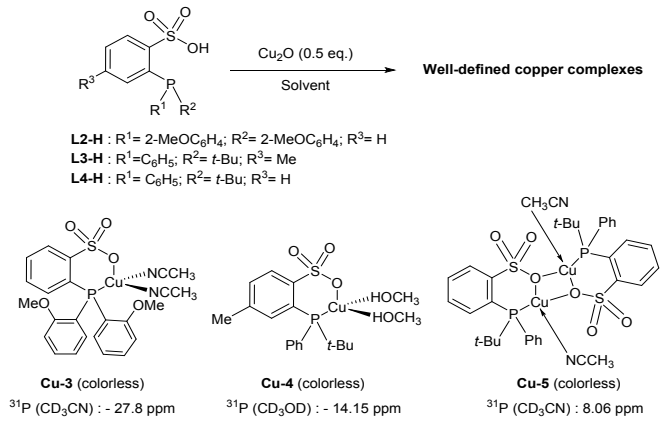
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Cu-1 (colorless)
^{31}P (CD_3OD) : - 5.36 ppm

Cu-2 (colorless)
^{31}P (CD_3CN) : - 11.07 ppm

Scheme 1. Facile access to the acetonitrile containing mononuclear complex **Cu-2** from the methanol containing dimer **Cu-1**.



Cu-3 (colorless)
^{31}P (CD_3CN) : - 27.8 ppm

Cu-4 (colorless)
^{31}P (CD_3OD) : - 14.15 ppm

Cu-5 (colorless)
^{31}P (CD_3CN) : 8.06 ppm

Scheme 2. Impact of the chelate and solvent on nuclearity.

sterically hindered Drent ligand **L2-H**[15] (**Scheme 2**) known to shield the metallic centre resulted in the formation of an unstable species in methanol. In contrast to this result, when the reaction was conducted in acetonitrile moderately stable **Cu-3** was isolated as a mononuclear complex. Interestingly, when the reaction was carried out with our previously *t*-Bu based phosphine-sulfonate precursor **L4-H**,[16] we were able to isolate a dinuclear copper(I) complex where the coordinated oxygen atoms play the role of bridging ligands to form a diamond core four membered metallacycle **Cu-5** reminiscent to the observation of a dimer form from **Cu-2** in acetonitrile. The crystal structures for all the synthesized complexes confirm the crucial pyramidal trigonal planar geometry on the copper metallic centres (**Figure 1**).[17,18] The synthesized colourless complexes exhibit photoluminescence in the solid state (**Table 1**). The spectrum envelopes are broad and featureless for complexes from **Cu-1** to **Cu-5** at room temperature and consistent with emission from the ^{3}MLCT state. We observed that the emission bands of complexes containing acetonitrile

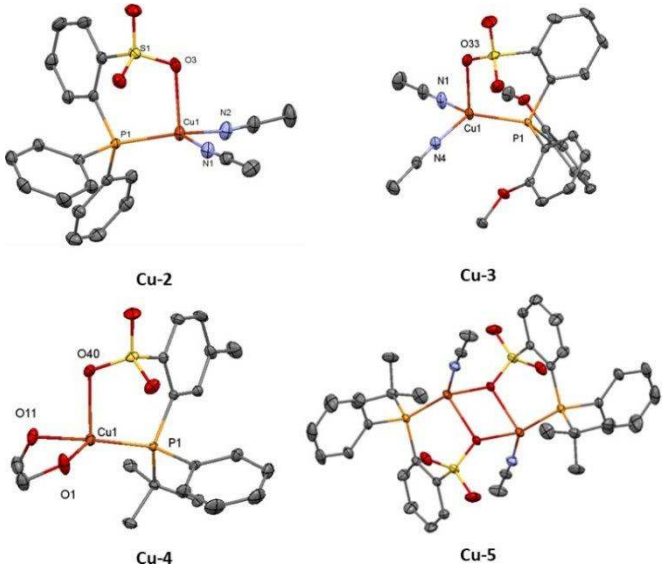


Figure 1. X-ray structures of **Cu-2**.2CH_3CN; **Cu-3**.1CH_3CN; **Cu-4**; **Cu-5**. lattice solvent molecules and hydrogens have been omitted for clarity. CCDC 1857809, CCDC 1857826, CCDC 1857827 and CCDC 1857812 contain the supplementary crystallographic data for **Cu-2**, **Cu-3**, **Cu-4** and **Cu-5**.

ligands are broader and occur in the yellow region, whereas the methanol containing complexes emit in the blue-green area (**Table 1**). Compared to the complexes **Cu-1**, **Cu-2** and **Cu-3** featuring aryl phosphine-sulfonate chelates, the alkyl phosphine-sulfonate containing complexes **Cu-4** and **Cu-5** afforded lower emission quantum yield. Notably, the flat dinuclear **Cu-5** species with the shortest Cu-Cu distance (3.34 Å) where π-π stacking interaction occurs between the MeCN ligand and the Ar-SO_3 moiety letting the exocyclic P-C bonds unrestricted led to the weakest emissive complex with a dual emission presumably arising from ^{3}MLCT and ^{3}CC excited states or a vibronic fine structure from a single excited state (**Table 1**).[10c,19] The presence of both solvent lattice and ligand in the corresponding structures suggests reduced vibrational quenching and prevents structural relaxation upon excitation.

DFT computations have been performed using the B3PW91 functional[20-22] together with the LANL2DZ basis set [23] augmented with polarization functions using the gaussian09 program. [24] Solvent effects (MeOH) were considered using implicit solvent (PCM) [25] together with explicit molecules in the calculations. The frontier MOs of the complex **Cu-1** are depicted in **Figure 2**.

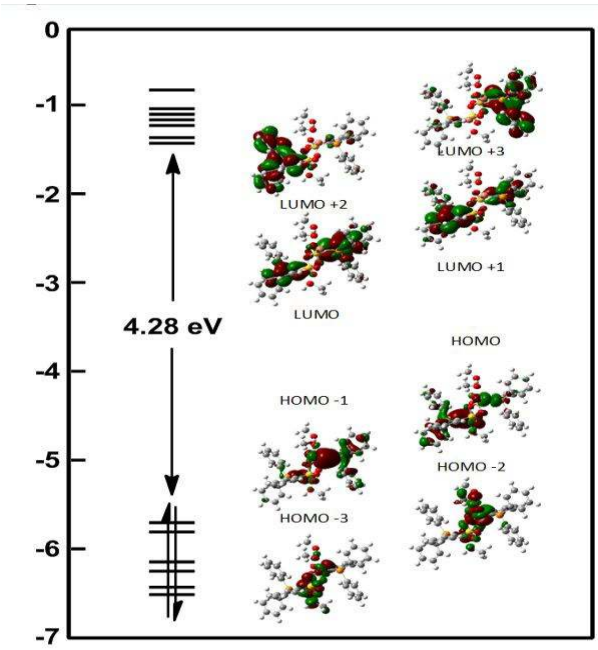


Figure 2: frontier MO diagram of complex **Cu-1**.

The HOMO and HOMO-1, which are very close in energy (-5.96 *vs*. -5.88 eV), are rather similar and exhibit a strong 3*d* orbital metallic character (>52%) as well as HOMO-2 and HOMO-3. On the opposite, the LUMO and LUMO +1, which are also quasi-degenerate, are clearly localized on the P-Ph_3 moieties.

Considering the UV-vis spectra, compound **Cu-1** exhibits an absorption in solution (MeOH) at 260 nm. In **Table 2**, are given the results of the TD-DFT computations of its electronic spectrum, namely the wavelengths and oscillator strengths as well as the transitions involved in the excitations, using the B3PW91 functional and the CAM-B3LYP one. [25-26] As it can be seen in **Table 2** the computed absorption wavelength using the CAM-B3LYP functional compares well with the observed one. On the contrary the B3PW91 computation overestimates the absorption wavelength This result is not surprising since the involved transitions are HOMO-1 → LUMO and HOMO → LUMO+1 which possess a long distance charge transfer MLCT character which are more accurately described by the range separated functional CAM-B3LYP. These HOMO to LUMO transitions are assigned to be metal to ligand charge-transfer (MLCT) confirming the previous assignment and the crucial role of solvent molecules. (*vide supra)*.

Table 1 Experimental and calculated optical data.

Complex	λ_{abs}(nm)[a]	λ_{em}(nm)		Φ[b]	τ (μs)[c]		k_r(298K) [s^{-1}]	τ(T_1) [μs][d]	τ(S_1) [μs][d]	$\Delta E_{(S1-T1)}$ [eV][d]
		78K	298K		78 K	298 K				
Cu-1	244, 290,330	515	515	0.51	57	2;9 (2.99)	170.10^3	59	0.139	0.05
Cu-2			568	0.34		2.0	170.10^3			
Cu-3			550	0.40						
Cu-4			522	0.12						
Cu-5	230,280		560;600	0.06						
Cu-6	262,298,320,362	508	515	0.60	76	8	75.10^3	76	0.048	0.10
Cu-7	262, 298, 474	593	568	0.10	107	1;10 (3.0)	33.10^3	105	0.080	0.07

[a] in solid state at 298K. [b] in solid state at 298K. [c] number in parenthesis corresponds to $\tau_{av}=(B_1/(B_1+B_2))\ \tau_1+(B_2/(B_1+B_2))\ \tau_2$, in which B_1 and B_2 are relative amplitude for τ_1 and τ_2, respectively. [d] Calculated from the fit of the decay curves with the equation provided in ref. 8a.

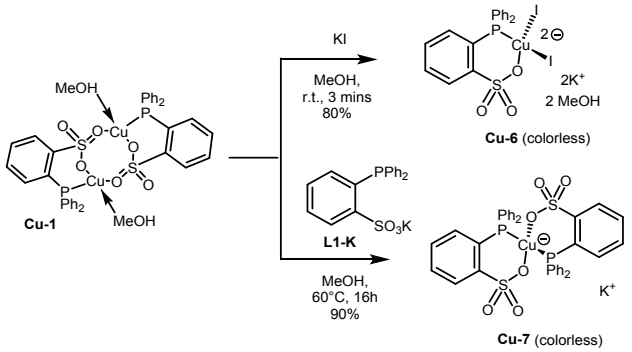
Table 2: TD-DFT computed UV-vis in solution (MeOH) of **Cu-1**. Computed oscillator strengths are given in square brackets.

	λ calc. (nm) [f]	Main transitions (weight)
B3PW91	339 [0.042]	HOMO-1 → LUMO (44%) HOMO → LUMO+1 (44%)
CAM-B3LYP	267 [0.132]	HOMO → LUMO+1 (42%) HOMO-1 → LUMO (41%)

Depending on the complex, the presence of uncoordinated solvent molecules in the crystal structure led to mechano-sensitive species. While **Cu-1**, **Cu-3** and **Cu-4** (Figure S7) are relatively stable in powder form compared to their crystal forms without any changes in their emission properties at room temperature, complex **Cu-2** loses after several minutes its emissivity upon grinding with a red shift of its emission (Figure S3, S4). Elemental analysis of room temperature vacuum dried **Cu-2** corroborates dimer formation. Additionally, thermal gravimetric analysis of crystals **Cu-2** highlights noticeable mass loss at room temperature within 5 minutes (**Figure S5**). Interestingly, a slight increase of temperature showed an endothermic phenomenon and a significant 11% mass loss at 55 °C. Taken together below 65°C, 14% mass loss suggests the loss of acetonitrile molecules on **Cu-2** including one coordinated solvent molecule responsible for the decrease of emissivity. [27] Interestingly, an unexpected phenomenon at 73 °C shows the additional loss of some acetonitrile ligand on the putative dimer leading to a new bright green emissive species.[27]

Noteworthy that and in contrast to **Cu-1**,[14a] **Cu-3** and **Cu-4**, reversible photoluminescence is not observed with powdered **Cu-2** after the addition of small amount of acetonitrile. In fact, redissolution followed by crystallization is required to fully restore **Cu-2** luminescent properties.[28]

Coordinated solvent molecules on the resulting complexes **Cu-1** to **Cu-5** allow the development of tunable luminescent complexes which might be useful for sensing of solvent molecules *via* reversible photoluminescence.[5,14a,19,27] The drawback of this concept for other applications lies in the long time stability of some complexes towards slow degradation owing to the loss of solvent molecules. This would lead to the modification of the structural environment around the metallic center increasing vibrational quenching as well as structural distortion upon excitation. One way to solve this issue lies in the rigidification of the molecular scaffold by tailoring the electrostatic forces between the charged copper species and a metallic or an organic salt. Thus, taking advantage on the halo- and cyano-cuprate chemistry, **Cu-1** was next treated with metal salts.[12] Reaction of **Cu-1** with an excess of potassium iodide at room temperature led to the precipitation of the mixed cuprate A_2MLX_3 **Cu-6** as a dianion in 80% yield (**Scheme 3**). X-ray structural determination highlights the formation of **Cu-6** as a 2D-layered material with a minimal Cu-Cu distance of 6.9 Å (**Figure 3**, **Figure S20**). During the reaction of DPPBS **L1-K** with **Cu-1** complex in boiling methanol almost quantitative precipitation of the monoanionic cuprate AML_2X_2 **Cu-7** was obtained. Importantly, in both cases, the iodides do not play the role of bridging ligands and the photoluminescent properties of **Cu-6** and **Cu-7** are not sensitive to grinding or drying. For the three-air stable neutral and -ate complexes **Cu-1**, **Cu-6** and **Cu-7** in their powdered form, the emission lifetime increases around ten times from 298K to 78K (**Table 1** and **Figure 4**). The long emission lifetimes and high quantum yields exclude prompt fluorescence phenomena. The decay curves are largely monoexponential at 78K (**Figure S9**, **S16**, **S19**). Together with temperature increase, the decay times decrease for the three complexes and become biexponential for dimer **Cu-1** and **Cu-7**. Noteworthy that the emission spectra for **Cu-1**, **Cu-6** and **Cu-7** were not narrowed upon cooling which tend to exclude energy transfer between **Cu-1** dimers or **Cu-6** polymer or via other non-radiative processes (**Figure 4**).[12c] Whereas emission of **Cu-7** was , interestingly, red-shifted upon cooling, equivalent to about 742 cm^{-1} (0.09 eV) peak to peak, no noticeable modification of the emission wavelength was observed with **Cu-1**. Furthermore, one should notice that even a slight blue shift was observed with **Cu-6**. Owing to the slightly low-lying T_1 triplet state, copper complexes exhibiting TADF are usually characterized by a red shift in emission upon cooling. Nevertheless, similar absence of red shift were reported



Scheme 3. Preparation of the anionic and dianionic complexes **Cu-7** and **Cu-6** from **Cu-1**.

independently by Osawa and by Yersin, which do not exclude TADF processes.[17,29] Emission decay profile for **Cu-1** suggests that the pure triplet state $\tau(T_1)$ is reached below 78K. Small $\Delta E_{S_1-T_1}$ values were obtained by fitting the sigmoid decay curves which strongly support phosphorescence at low temperature and the occurrence of both phosphorescence and TADF processes upon temperature increase (**Table 1**).[8a] The biexponential decays for **Cu-1** and **Cu-7** tends to support these results. The monoexponential decay for **Cu-6** suggests essentially overlap due to fast equilibration processes owing to its rigid structure. This could prevent vibrational quenching or deactivation through structural distortion from the tetrahedral to quasi-square-planar coordination geometry (**Figure 4**).[17,19,29]

Conclusions

In conclusion, we prepared various photoluminescent copper(I) and cuprate(I) complexes by modification of the solvent or the metallic salt with water as the only side product of the overall synthesis. These results pave the way on the preparation of a true library of photoluminescent neutral and anionic complexes by varying the nature of the chelate, the solvent/gas or the metallic salt at the first or second stage of the synthesis to tune their optical properties. The use of other L,X chelating ligands with cuprates might afford interesting materials. Oxidation of the cuprates is underway in our laboratories.

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Conflicts of interest

There are no conflicts of interest to declare

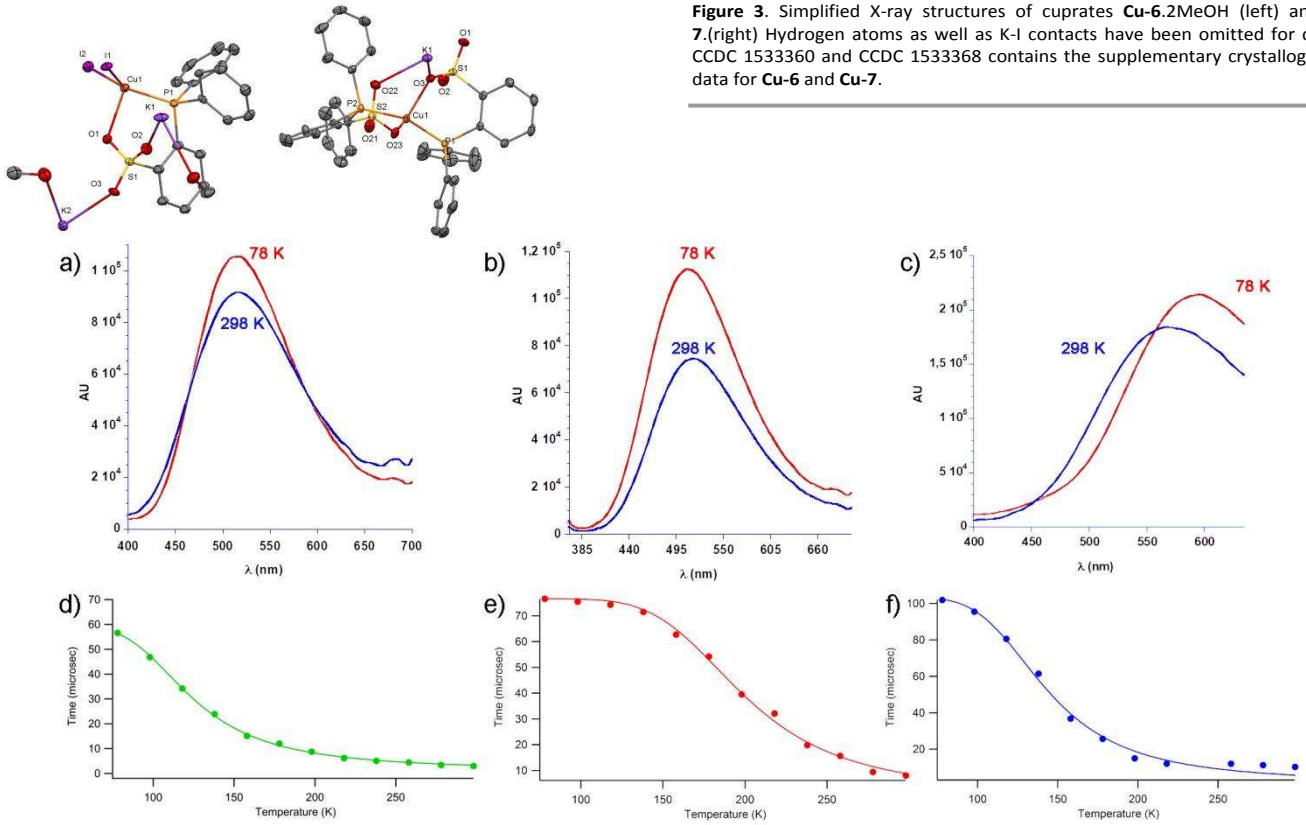


Figure 3. Simplified X-ray structures of cuprates **Cu-6**.2MeOH (left) and **Cu-7**.(right) Hydrogen atoms as well as K-I contacts have been omitted for clarity. CCDC 1533360 and CCDC 1533368 contains the supplementary crystallographic data for **Cu-6** and **Cu-7**.

Figure 4. Emission spectra at 78K and 298K of **Cu-1** (left), **Cu-6** (middle) and **Cu-7** (right) and emission decay profiles at different temperatures.

Experimental

General considerations

All reactions were carried out under argon atmosphere using Schlenk tube techniques. Unless stated, reagents were purchased from commercial sources and used as received. Acetonitrile, was dried using a MBraun Solvent Purification System. Methanol HPLC grade was degassed and used as received. NMR spectra were recorded at room temperature on a Bruker Avance (400 MHz) spectrometer and reported in ppm. Data are reported as follows: s=singlet, d=doublet, t=triplet, q=quartet, m=multiplet, br=broad. Coupling constants are reported in Hz. ^{13}C NMR spectra were recorded at 100.6 MHz on the same spectrometer and reported in ppm.

Synthesis of Cu-2

Cu-1 (200 mg, 0.22 mmol) was added to a Schlenk tube and stirred at 60°C under vacuum for 30 mins. The Schlenk was cooled at room temperature followed by the addition of acetonitrile (4 mL). The resulting mixture was then heated under stirring to dissolve the precipitate. The solution was then cooled at room temperature and then at -22 °C to afford colorless crystals of **Cu-2**. The solution was removed and the crystals of **Cu-2**.2CH_3CN (190 mg, 76%) were kept under argon atmosphere. In contrast to the crystal structure, NMR analyses and cyclic voltammetry support predominance of a dimer in acetonitrile solution. ^{1}H NMR (400 MHz, CD_3CN): δ 8.13-8.05 (m, 1H), 7.54-7.26 (m, 12H), 7.01 (t, *J*= 7.4 Hz, 1H), 2.15 (s, 3H); ^{31}P {1H} NMR (162 MHz, CD_3CN): -11.07; ^{13}C {1H} NMR (100 MHz, CD_3CN): δ 152.1 (d, *J*= 18.5 Hz), 135.6 (s), 134.3, 134.2, 134.0, 131.0, 130.7, 130.5, 129.6 (d, *J*= 9.2 Hz), 128.6 (d, *J*= 5.4 Hz). Elemental analysis for room temperature dried **Cu-2**-CH_3CN, theoretical: C, 53.87, H, 3.84, N, 3.14, S, 7.19, measured: C, 53.71, H, 3.88, N, 3.01, S, 7.27.

Synthesis of Cu-3

Drent ligand 2-{bis(2-methoxyphenyl)phosphino}benzenesulphonic acid **L2-H** (135 mg, 0.33 mmol) and Cu_2O (24 mg, 0.16 mmol) were added in a Schlenk tube under an atmosphere of argon followed by the slow addition of degassed acetonitrile under stirring. Then, the resulting mixture was stirred for one hour at room temperature. The white precipitate was dissolved by the addition of extra acetonitrile followed by cannulation and concentration to afford colorless crystals of **Cu-3** (73 mg, 40%). ^{1}H NMR (400 MHz, CD_3CN): δ 8.10 (ddd, *J*= 7.8, 4.7, 1.4 Hz, 1H), 7.51-7.44 (m, 3H), 7.30 (td, *J*= 7.6, 1.4 Hz, 1H), 7.03 (dd, *J*= 8.3, 5.2 Hz, 2H), 6.97-6.88 (m, 3H), 6.71 (t, *J*= 8.5 Hz, 2H), 3.68 (s, 6H), 2.15 (s, 6H); ^{31}P {1H} NMR (162 MHz, CD_3CN): -27.8; ^{13}C {1H} NMR (100 MHz, CD_3CN): δ 161.7 (d, *J*= 9.1 Hz), 152.0 (d, *J*= 19.8 Hz), 135.5 (s), 134.8 (d, *J*= 3.9 Hz), 132.6 (s), 130.8 (s), 130.3 (d, *J*= 4.2 Hz), 130.2 (d, *J*= 30.8 Hz), 128.6 (d, *J*= 6.6 Hz), 121.7 (d, *J*= 6.1 Hz), 120.7 (d, *J*= 35 Hz), 111.9 (d, *J*= 3.5 Hz), 56.2 (s). Elemental analysis for **Cu-3**.1CH_3CN, theoretical: C, 52.47, H, 4.31, N, 3.99, S, 6.09, measured: C, 52.15, H, 4.10, N, 3.77, S, 5.74.

Synthesis of Cu-4

{tert-Butyl-4-Me-phenylphosphino}benzenesulfonic acid **L3-H** (100 mg, 0.29 mmol) and Cu_2O (22 mg, 0.15 mmol) were added in a Schlenk tube under an atmosphere of argon followed by the slow

addition of degassed methanol under stirring. Then, the resulting mixture was stirred for one hour at room temperature. The white precipitate was dissolved by the addition of methanol and moderate heating followed by cannulation. The resulting solution was concentrated to give air sensitive colorless crystals of **Cu-4** (71 mg, 52%). ^{1}H NMR (400 MHz, CD_3OD): δ 8.12 (ddd, *J*= 8.1, 4.3 Hz, 1H), 7.66-7.62 (m, 1H), 7.55 (ddd, *J*= 10.1, 6.3, 3.4 Hz, 2H), 7.43-7.34 (m, 4H), 3.35 (s, 6H), 2.42 (s, 3H), 1.33 (d, *J*= 15.5 Hz, 9H); ^{31}P {1H} NMR (162 MHz, CD_3OD): -14.15. Elemental analysis for **Cu-4**.2CH_3OH, theoretical: C, 47.85, H, 6.88, S, 6.08, measured: C, 47.64, H, 5.33, S, 7.06.

Synthesis of Cu-5

{tert-Butyl-phenylphosphino}benzenesulfonic acid **L4-H** (100 mg, 0.3 mmol) and Cu_2O (22 mg, 0.15 mmol) were added in a Schlenk tube under an atmosphere of argon followed by the slow addition of degassed methanol under stirring. Then, the resulting mixture was stirred for one hour at room temperature. The white precipitate was dissolved by the addition of methanol followed by cannulation and evaporated under vacuum at 60°C to yield a white precipitate. Addition of acetonitrile followed by concentration afforded colorless crystals of **Cu-5** dimer (60 mg, 45%). ^{1}H NMR (400 MHz, CD_3CN): δ 8.17-8.13 (m, 1H), 7.85-7.82 (m, 1H), 7.54-7.44 (m, 4H), 7.37-7.36 (m, 3H), 2.18 (s, 3H), 1.28 (d, *J*= 15 Hz, 9H); ^{31}P {1H} NMR (162 MHz, CD_3CN): 8.06; ^{13}C {1H} NMR (100 MHz, CD_3CN): δ 152.9 (d, *J*= 17.6 Hz), 135.8 (s), 134.6 (s), 134.2 (d, *J*= 14 Hz), 130.9 (s), 130.1, 130.0, 129.9, 129.9, 129.6 (d, *J*= 6.3 Hz), 128.9 (d, *J*= 9.2 Hz), 32.7 (d, *J*= 15.1 Hz), 29.0 (d, *J*= 10.6 Hz). Elemental analysis for **Cu-5**, theoretical: C, 50.76, H, 4.97, N, 3.29, S, 7.53, measured: C, 50.87, H, 4.97, N, 3.22, S, 7.26.

Synthesis of Cu-6

To a Schlenk tube, **Cu-1** dimer (45 mg, 0.05 mmol) was added to methanol mixture (3 mL) containing KI (27 mg, 0.16 mmol) and the resulting was stirred vigorously until the apparition of a white precipate of **Cu-6** polymer. The solution was quickly removed by cannulation and the white precipitate was dried under vacuum (59 mg, 80%). ^{1}H NMR (400 MHz, DMSO-d6): δ 8.00 (d, *J*= 7.7 Hz, 1H), 7.52 (t, *J*= 7.6 Hz, 1H), 7.43-7.28 (m, 11H), 6.93 (s, 1H), 4.09 (q, *J*= 5.3 Hz, 2H), 3.17 (d, *J*= 5.3 Hz, 6H); ^{31}P {1H} NMR (162 MHz, DMSO-d6): δ -11.67; ^{13}C {1H} NMR (100 MHz, DMSO-d6): δ 150.8-150.2 (m), 134.5-134.3 (m), 133.5 (s), 133.4 (s), 133.1-133.0 (m), 129.9 (s), 129.7 (s), 128.4 (s), 127.4-127.3 (m), 48.5 (s). HRMS-ESI: ($C_{18}H_{14}O_3IPSCu$) $[M\text{-}I^-]^-$: calcd.: 530.87476 m/z; found: 530.8743 (1 ppm). Elemental analysis for vacuum dried **Cu-6**, theoretical: C, 29.34, H, 1.92, S, 4.35, measured: C, 29.15; H, 2.04; S, 4.05.

Synthesis of Cu-7

Murray's ligand {diphenylphosphino}benzenesulfonic acid **L1-H** (66.5 mg, 0.2 mmol) and *t*-BuOK (23 mg, 0.2 mmol) were added in a Schlenk tube under an atmosphere of argon followed by the slow addition of degassed methanol. Then, the resulting mixture was stirred for half hour at room temperature followed by the addition of **Cu-1** dimer (85 mg, 0.1 mmol). The resulting mixture was heated at 60°C overnight. After cooling at room temperature, the solution was removed by cannulation and the white precipitate was dried under vacuum to give **Cu-7** (136 mg, 90%). ^{1}H NMR (400 MHz, DMSO-d6): δ 8.00 (d, *J*= 7.7 Hz, 2H), 7.52 (t, *J*= 7.6 Hz, 2H), 7.43-7.37 (m, 8H), 7.31-7.23 (m, 14H), 6.96 (d, *J*= 7.5 Hz, 2H); ^{31}P {1H} NMR (162 MHz, DMSO-d6): δ – 11.68 ; ^{13}C {1H} NMR (100 MHz, DMSO-d6): δ 150.8 (d, *J*= 6.5 Hz), 134.2 (s), 133.5 (s), 133.2 (d, *J*= 1.9 Hz), 129.8 (s), 129.6 (s), 128.3 (s), 127.3 (s). Elemental analysis for **Cu-7.**1CH_3OH., theoretical: C, 54.37, H, 3.95, S, 7.84, measured: C, 54.49, H, 3.51, S, 7.76.

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