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Highly efficient and recyclable pre-catalysts based on mono- and dinuclear heteroleptic Cu(I) dithio- PPh_3 complexes to produce variety of glycoconjugate triazoles

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ABSTRACT

Highly efficient and reusable pre-formed mono- and dinuclear heteroleptic copper(I) dithiocarbamate and dithiocarbimate complex based catalysts, **[Cu(PPh$_3$)$_2$(L)]** and **[Cu$_2$(PPh$_3$)$_4$(L)]** (L = *N*-(4-methylpyridyl)-*N*-(3-methylpyridyl)dithiocarbamate$^-$ L^1 **1**, N-methylfuryl-*N*-methylthiophenedithiocarbamate- L^2 **2**; 4-chlorobenzenesulfonyl dithiocarbimate^{2-} L^3 **3**, 4-bromobenzenesulfonyldithiocarbimate^{2-} L^4 **4**) have been utilized in the cycloaddition reactions of azide and alkyne to form a variety of glycoconjugate triazoles in Click chemistry. These new pre-catalysts have been characterized by elemental (C, H, N) analysis, IR, UV–vis., ^{1}H, ^{13}C{^{1}H}, and ^{31}P{^{1}H} NMR spectroscopy and their structures have been revealed by X-ray crystallography. In the structures of (**1**,**2**)/(**3**,**4**) the copper atoms are situated within a four coordinate (P_2S_2)/(P_2NS) distorted tetrahedral geometry. Notably in the dinuclear complexes **3** and **4,** the dithiocarbimate ligands are bonded in a S, S- chelating mode to one copper atom and simultaneously bridge the other copper centre via N, S- donor atoms. **1**-**4** are strongly luminescent in CH_2Cl_2 solution at room temperature.

1. Introduction

Novel catalytic activities of low valent electron rich transition metal phosphine complexes have been extensively explored. The introduction of the Click concept by Sharpless [1] and Meldal [2] in which copper(I) assisted cycloaddition reactions of azides and alkynes produce triazoles has revolutionized research in diverse chemical disciplines, such as drug discovery, synthetic polymers, fluorescent imaging and material science [3–5]. In comparison to the *in situ* generation of copper(I) species by the treatment of Cu(II) salts with sodium ascorbate reductant [6], use of pre-formed copper(I) complexes is more advantageous because it facilitates the reaction under mild conditions and avoids the addition of reducing agents. Here the ligating moieties protect the oxidation/ reduction of Cu(II) centres and modify the activity of the Cu (I) centres [7]. Among many copper(I) complexes used for this reaction, the N-heterocyclic carbenes (NHCs) [8], mild basic amines and other O/ S and P donor ligands [9–10] have been frequently reported. The copper centres together with the ligands play key roles in the catalytic transformations. The best developed systems are those with heterocyclic carbene and phosphine ligands.

Many catalytic transformations using metal thiolato complexes have been extensively studied [11]. By comparison research involving copper(I) complexes assisted Click chemistry for the cycloaddition reactions of azides and alkynes with the O/S donor ligands is rare [12]. It has been reported that in this reaction dinuclear Cu(I) complexes have more potential than mononuclear complexes because of the synergic effect due to the appropriate proximity of the metal centres. This has been corroborated by DFT calculations [13].

Generally, the copper(I) catalyzed 1, 3-dipolar cycloaddition reaction is considered to be a step wise process dissimilar from [3 + 2]-cycloaddition reactions and does not proceed through concerted way. Previously, this stepwise mechanistic study was confirmed by the DFT calculations and kinetic evidences [13a–c]. However, recently the previous predicted π,σ- biscopper acetylide and a 3,5-bismetalated

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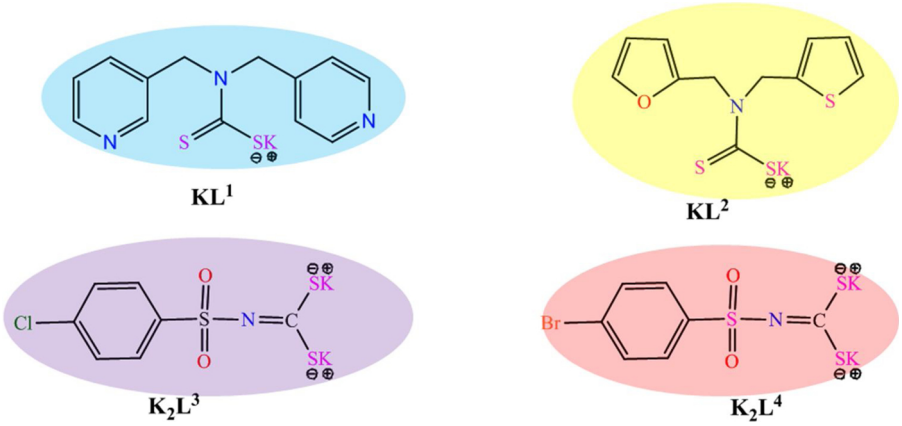


Scheme 1. Potassium salts of the dithiocarbamate and dithiocarbimate ligands used in this work.

triazole complex intermediates were isolated by Bertand research group [14] and supported the previous reports.

The chemistry of transition metal dithiocarbamates including that with Cu(II) has been extensively investigated due to their myriad of diverse applications in magnetic, optical, agricultural and industrial areas [15–17]. Heteroleptic Cu(I) complexes [Cu(phosphine)(L)] have attracted considerable attention because of their important optical properties and their use as sensitizers in solar cells and biological imaging [18], but despite synthetic versatility and structural simplicity, to the best of our knowledge heteroleptic copper(I) dithiocarbamate and dithiocarbimate complexes have not yet been investigated under the Click approach. Motivated by these facts, in this contribution the synthesis, crystal structures, luminescent characteristics and catalytic efficiency for the synthesis of glycoconjugate triazoles, new mono- and dinuclear Cu(I) complexes **1**-**4** utilizing dithiocarbamate/dithiocarbimate (Scheme 1) in conjunction with PPh_3 ligands were undertaken. The present work was pursued considering the following points : (i) the modification of the ligand framework by varying the substituents on the dithio unit and using of sterically demanding PPh_3 which may substantially modify electronic and steric properties together with the chemical reactivity of the complexes which are crucial for the development of promising Click catalysts, (ii) the incorporation of electron rich moieties, Py(N) in the 3- and 4- positions may enhance conjugation in the molecule, hence affect the catalytic activities and luminescent characteristics of the complexes, (iii) in spite of some common features, the monoanionic dithiocarbamate and dianionic dithiocarbimate ligands differ significantly in their structure and properties. Generally heteroleptic Cu(I) dithiocarbamate complexes bearing bulky phosphine ligands are mononuclear [16a,b] in which identical S,S- donor atoms are bonded to the metal in a bidentate mode while, though rare, the analogous dithiocarbimate complexes are dinuclear [17a] where the dithiocarbimate group is attached to the metal via the S,S-/S,N- donor atoms in a chelating as well as bridging mode. This difference in bonding behavior is attributed to the dominant resonance forms, $\mathbf{R_2N^+=CS_2^{2-}}$ and $\mathbf{RSO_2N=CS_2^{2-}}$ exhibited respectively in their complexes. Furthermore, in the dithiocarbamate complexes electron delocalization occurs via CN, CS_2 and MS_2 bonds whereas in the dithiocarbimates it is present via CS_2, CN and aromatic SO_2 groups. The difference in their bonding and electronic properties may significantly influence the catalytic activities and luminescent properties of their complexes, (iv) Cu(I), d^{10} dithio-ligand complexes with Cu-S bonds formed with the soft Cu(I) and S donors are generally thermodynamically more stable and less labile in comparison to the Cu-N bond formed with hard N donors. This fact also increases their hydrolytic stability hence improves the purity, reproducibility and catalytic activities and (v) often dinuclear Cu(I) complexes display better catalytic activity than mono-nuclear complexes due to the synergic effect of two Cu(I) ions.

2. Experimental

2.1. Materials and measurements

The synthesis of the complexes was performed in aerobic conditions. Solvents dichloromethane, methanol and dimethylformamide (DMF) were distilled and dried according to known methods. The chemicals, $Cu(NO_3)_2{\cdot}3H_2O$ (SDFCL), *para*-Cl or Br substituted benzenesulfonamide, 4-pyridine carboxyaldehyde, 3-picolylamine (all sigma-Aldrich), KOH, $NaBH_4$ and carbon disulfide (Merck), triphenylphosphine (Spectrochem) and 2-thiophenecarboxyaldehyde (Avra) were used as received. The ligands N-(4-methylpyridyl)-N-(3-methylpyridyl) dithiocarbamate (KL^1), N-methylfuryl-*N*-methylthiophene dithiocarbamate (KL^2) / 4-chlorobenzenesulfonyl dithiocarbimate (K_2L^3) and 4-bromobenzenesulfonyl dithiocarbimate (K_2L^4) were prepared by the reaction of appropriate secondary amines/sulfonamide, KOH and carbon disulfide in THF/ DMF according to literature procedure [16,19]. The starting compound $[Cu(PPh_3)_2NO_3]$ was synthesized by the reported method [20].

The melting points of the complexes were measured with a Gallenkamp apparatus in open capillaries and are uncorrected. The experimental details regarding elemental (C, H, N) analysis, IR as KBr pellet, UV–vis and photoluminescence spectra are the same as described earlier [12c]. NMR (^1H, $^{13}C\{^1H\}$,$^{31}P\{^1H\}$) spectra were recorded on a JEOl ECZ500 MHz FT NMR in DMSO-d_6 /$CDCl_3$. Chemical shifts are noted in ppm downfield from internal *TMS* and *J* values in Hz. Thin-layer chromatography (TLC) was accomplished using 60 F254 silica gel, pre-coated on aluminum plates and revealed with either a UV lamp (λ_{max} = 254 nm) or a specific color reagent (iodine vapors) or by spraying with methanolic H_2SO_4 solution and subsequent charring by heating at 100 °C.

2.2. Crystallography

Single crystal X-ray data for complexes **1**-**4** were collected with an Oxford Diffraction X-calibur CCD diffractometer using Mo-*Kα* radiation at temperatures of 150(2) K for **1**, **2**, **4** 293(2) K for **3**. Data reduction for **1**–**4** was performed using the CrysAlis program [21]. The structures were solved by direct methods using SHELXS-97 [22] and refined on F^2 by full-matrix least-squares technique using SHELXL 2016-6 [23]. Non-hydrogen atoms were refined anisotropically and hydrogen atoms were geometrically fixed with thermal parameters equivalent to 1.2 times that of the atom to which they were bonded. Diagrams for the complexes were prepared using *Olex2* [24] and Mercury [25] software. In **2,** one five-membered ring is identified as furan with the oxygen disordered between two positions in the ratio 0.89(2), 0.11(2), while the other five-membered ring is disordered between furan and thiophene with the ratio of S/CH 0.47(2), 0.53(2). In **3** and **4**, some phenyl rings of

PPh_3 ligands are disordered. In **3**, four of the phenyl rings were disordered over two orientations. These were refined as rigid groups with occupation factors of x and 1-x, with x values of 0.49(3), 0.62(4), 0.53(4), 0.64(4). In **4**, three of the phenyl rings were disordered over two orientations. **3** and **4** are isomorphous and as the data for **4** was poor, details of the structure are provided in the ESI. Complexes **1**-**4** crystallized with 0.5 CH_2Cl_2, 0.5H_2O; CH_3OH, 1.5H_2O; 0.25CH_2Cl_2, H_2O and 0.5CH_2Cl_2, 2.5H_2O solvent molecules respectively. The crystal data of **1**-**4** have been deposited at the Cambridge Crystallographic Data Centre, the reference numbers CCDC1867082-1867085.

2.3. Synthesis of mono-/dinuclear complexes [$Cu(PPh_3)_2(L)$]and [$Cu_2(PPh_3)_4(L)$] ($L = L^1$(**1**), L^2(**2**), L^3(**3**) and L^4(**4**))

All four heteroleptic complexes were synthesized by adopting similar procedures. To a 15 ml stirred methanol solution of the ligand K$\mathbf{L^1}$ (0.313 g, 1 mmol), K$\mathbf{L^2}$ (0.307 g, 1 mmol), $K_2\mathbf{L^3}$(0.172 g, 0.5 mmol) or $K_2\mathbf{L^4}$(0.194 g, 0.5 mmol) was added gradually a 10 ml CH_2Cl_2 solution of [$Cu(PPh_3)_2NO_3$] (0.650 g, 1 m mol) and the reaction was stirred for 5 h at room temperature in each case. The dark yellow solid products formed were filtered off, washed with methanol followed by diethyl ether and vacuum-dried. The light yellow needle shaped crystals were obtained within 2–3 weeks by the recrystallisation of the solid products in dichloromethane/methanol mixture.

2.4. Characterisation

1. Yield: (0.707 g, 82%). M.p.: 152–156 °C. $C_{49}H_{42}N_3P_2S_2Cu$ (862.52): calc. C 68.23, H 4.91, N 4.87%; found C 67.85, H 4.98, N 4.62%. IR (KBr, cm^{-1}): 1435 ($\nu_{C–N}$), 1095 ($\nu_{C–S}$). ^{1}H NMR (500.15 MHz, DMSO-d_6, ppm): δ 8.61-8.50 (d, 4H, C_5H_4N), 7.75–7.30 (m, 34 H, Ar-H + 4H, C_5H_4N), 5.15 (s, 4H, $-CH_2$-C_5H_4N).^{13}C{^{1}H} NMR (125.76 MHz, DMSO-d_6, ppm): δ 211.00 (CS_2), 149.26, 148.97, 137.07 123.98 (C_5H_4N), 135.61, 134.08, 132.86, 130.4, 129.00, 127.87 (C_6H_5), 54.3 ($-CH_2$-C_5H_4N), 51.8 ($-CH_2$-C_5H_4N). ^{31}P{^{1}H} (202.46 MHz, DMSO-d_6, ppm): δ -0.449 [$Cu(PPh_3)_2(L^1)$], 26.377 [$Cu(PPh_3)]^+$, 42.946 [$Cu(PPh_3)_3]^+$. UV–vis. (CH_2Cl_2, λ_{max} (nm), ε ($M^{-1}\,cm^{-1}$)): 260 (1.54×10^4), 310 (0.48×10^4).

2. Yield: (0.736 g, 86%). M.p.:148-152 °C. $C_{47}H_{40}S_3P_2NOCu$ (856.52): calc. C 65.91, H 4.71, N 1.64%; found C 65.83, H 4.78, N 1.62%. IR (KBr, cm^{-1}): 1455 ($\nu_{C–N}$), 1095 ($\nu_{C–S}$). ^{1}H NMR (500.15 MHz, DMSO-d_6, ppm): δ 6.88–7.50 (m, 30 H, C_6H_5), 6.35–6.40 (m, 3H, C_4H_3S), 6.23–6.34 (m, 3H, C_4H_3O), 5.20 (s, $-CH_2$-C_4H_3S), 5.28 (s, $-CH_2$-C_4H_3O).^{13}C{^{1}H} NMR (125.76 MHz, DMSO-d_6, ppm): δ 203.23 (CS_2), 107.73, 110.07, 125.37, 152.26 (C_4H_3O), 110.36, 110.76, 125.68, 141.69 (C_4H_3O), 126.27–127.01 (C_6H_5), 48.4 ($CH_2C_4H_3O$), 46.1 ($CH_2C_4H_3S$). ^{31}P{^{1}H} (202.47 MHz, DMSO-d_6, ppm): δ -0.997 [$Cu(PPh_3)_2(L^2)$], 29.868 [$Cu(PPh_3)]^+$, 43.971 [$Cu(PPh_3)_3]^+$. UV–vis. (CH_2Cl_2, λ_{max} (nm), ε ($M^{-1}\,cm^{-1}$)): 290 (1.10×10^4), 350 (0.43×10^4).

3. Yield: (0.490 g, 68%), M.p. 118–122 °C. $C_{79}H_{64}NS_3O_2P_4ClCu_2$ (1441.99): calc. C 65.80, H 4.47, N 0.97%; Found: C 65.65, H 4.52, N 0.93%. IR (KBr, cm^{-1}): 1478 ν(C = N), 1306 $\nu_{asym}(SO_2)$, 1147 $\nu_{sym}(SO_2)$, 961 $\nu_{asym}(CS_2)$. ^{1}H NMR (500.15 MHz, DMSO-d_6, ppm): δ 7.67 (d, 2H,ClC_6H_4), 7.28 (d, 2H,ClC_6H_4), 7.54-7.65(m, 60 H, C_6H_5). ^{13}C{^{1}H} NMR (125.76 MHz, DMSO-d_6, ppm):δ 205.12 (CS_2), 133.99, 133.83, 129.30, 129.06 (ClC_6H_4), 129.40–133.21(C_6H_5).^{31}P{^{1}H} (202.47 MHz, DMSO-d_6, ppm): δ -3.297 [$Cu_2(PPh_3)_4(L^3)$], 26.211 [$Cu(PPh_3)]^+$, 42.919 [$Cu(PPh_3)_3]^+$. UV–vis. (CH_2Cl_2, λ_{max} (nm), ε ($M^{-1}\,cm^{-1}$)): 250 (1.02×10^4), 305 (1.07×10^4), 350 (1.02×10^4).

4. Yield: (0.476 g, 64%), M.p. 120–124 °C. $C_{79}H_{64}NS_3O_2P_4BrCu_2$ (1486.45): calc. C 63.83, H 4.34, N 0.94%; Found: C 63.55, H 4.48, N 0.90%. IR (KBr, cm^{-1}): 1480 ν(C = N), 1383 $\nu_{asym}(SO_2)$, 1158 $\nu_{sym}(SO_2)$, 1023 $\nu_{asym}(CS_2)$. ^{1}H NMR (500.15 MHz, $CDCl_3$, ppm): δ 7.72 (d, 2H, BrC_6H_4), 7.24(d, 2H,BrC_6H_4),7.25–7.68 (m, 60 H, C_6H_5).^{13}C{^{1}H} NMR (125.76 MHz, $CDCl_3$, ppm): δ 200.66 (CS_2), 133.67, 133.56, 128.51, 128.41 (BrC_6H_4), 128.77–132.09 (C_6H_5). ^{31}P{^{1}H} (202.47 MHz, $CDCl_3$, ppm): δ -0.083 [$Cu_2(PPh_3)_4(L^4)$], 29.813 [$Cu(PPh_3)]^+$, 43.944 [$Cu(PPh_3)_3]^+$. UV–vis. (CH_2Cl_2, λ_{max} (nm), ε ($M^{-1}\,cm^{-1}$)): 255 (1.06×10^4), 290 (1.05×10^4), 310 (1.02×10^4), 345 (0.96×10^4).

2.5. General procedure for synthesis of diverse glycoconjugates from pre-catalysts **1–4**

A solution of sugar azides **5** (1. 0 equivalent), alkyne **7** (1.2 equivalent) and pre-catalysts **1–4** (10 mol%) in the presence /absence of triethylamine in normal CH_2Cl_2 was stirred at room temparature in a closed vessel for 2–8 h. The reaction was monitored by TLC, and then after completion the mixture was concentrated *in vacuo* to obtain a crude residue which was further purified by silica gel (100–200 mesh) column chromatography to afford compound **8**.

3. Results and discussion

3.1. Synthesis and methods

The heteroleptic mono-/dinuclear dithiocarbamate and dithiocarbimate complexes [Cu ($PPh_3)_2$(**L**)] and [$Cu_2(PPh_3)_4$(**L**)] were prepared in good yield (Scheme S1), by treatment of a CH_2Cl_2 solution of [$Cu(PPh_3)_2NO_3$] with the methanolic solution of KL^1-KL^2/K_2L^3-K_2L^4 in 1:1/2:1 M ratio and characterized by spectroscopy and X-ray crystallography. The pre-formed complexes **1**-**4** have been investigated as catalysts for the synthesis of a variety of glycoconjugate triazoles under Click approach. Their photoluminescent characteristics have been studied.

3.2. Spectroscopy

The IR spectra of dithiocarbamate complexes (**1**,**2**) display the ν(C—N) and ν(C—S) vibrations at 1435–1455 and 1095 cm^{-1} whereas in dithiocarbimate complexes (**3**,**4**) the appearance of ν(C═N), $\nu_{asym}(SO_2)$, $\nu_{sym}(SO_2)$ and $\nu_{asym}(CS_2)$ frequencies at 1480, 1306–1383, 1147–1158 and 998-1023 cm^{-1} respectively are diagnostic of ligand coordination in the complexes. Notably a perceptible increase in the ν(C—N) frequency of the complexes (**1**,**2**) as compared to the potassium salts of ligands (KL^1, KL^2) 1362-1398 cm^{-1} is concomitant with the dominant contribution of the resonance form $\mathbf{R_2N^+ = CS_2^{2-}}$ indicating enhancement of the C–N bond order (*vide infra*, crystal structures).

In the ^{1}H and ^{13}C {^{1}H} NMR spectra, complexes **1**-**4** show resonances characteristic of ligand functionalities and integrate well to the corresponding hydrogens. The ^{13}C NMR spectra of complexes (**1**,**2**) displayed a single up field resonance signal at δ(203.24, 211.00 ppm) for the NCS_2 carbon in comparison to the free dithiocarbamate ligand at δ(215.92, 218.48 ppm) because of the dominant contribution of $\mathbf{R_2N^+ = CS_2^{2-}}$ resonance form in the complexes. On the contrary the dithiocarbimate complexes (**3**, **4**) showed a downfield resonance at δ (200.67, 205.12 ppm) in comparison to the free dithiocarbimate ligands at δ (189.15, 197.41 ppm). This may be attributed to greater shielding of the NCS_2 carbon of dithiocarbamate complexes compared to free ligands while in dithiocarbimate complexes the NCS_2 carbon is less shielded than in the free ligands. In the ^{31}P NMR spectra of (**1**, **2**) the occurrence of a single resonanace signal at δ (-0.449, -0.997 ppm) is indicative of the equivalent nature of the PPh_3 ligands bonded to the copper atom. It is to be noted that the dinuclear dithiocarbimate complexes **3** and **4** show only one ^{31}P resonance at δ -3.297 and -0.083 ppm respectively instead of the expected two signals due to different coordination environments about the two copper centers, presumably the fluxional behavior of the ligand PPh_3 causes signal overlap at room temperature which results in only one broad signal. The appearance of two additional sharp resonances at δ (26.211–29.868 ppm) and (42.919–43.971 ppm) in all four complexes

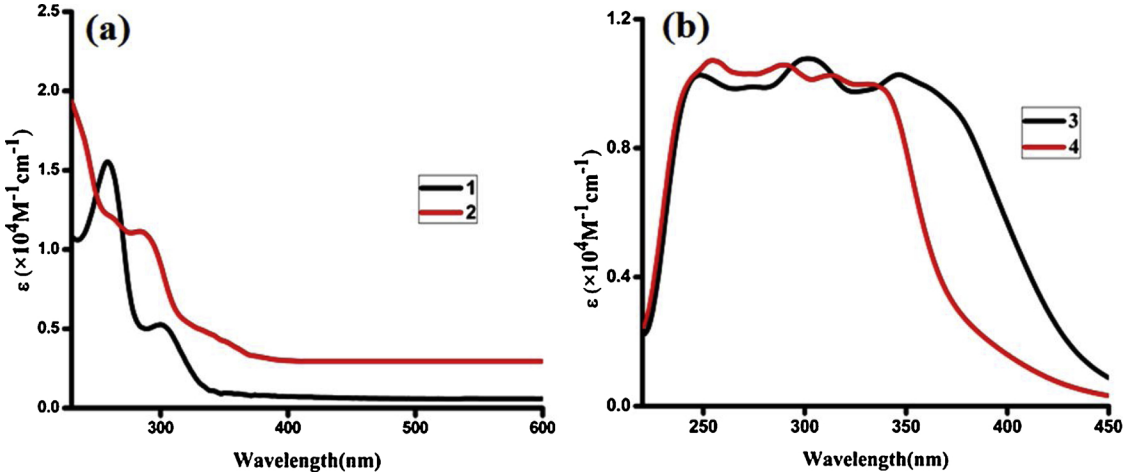


Fig. 1. Electronic absorption spectra in CH_2Cl_2 solution for **1**-**2** (a) and **3**-**4** (b).

shows the formation of $[Cu(PPh_3)]^+$ and $[Cu(PPh_3)_3]^+$ cationic species respectively via association/dissociation in solution. Cu(I) thiocarbamate [26] and thiophene-2-thiocarboxylate- phosphine complexes [26e] have been reported to form an equilibrium mixture of different cationic/anionic species via associative /dissociative process.

3.3. Electronic absorption and photoluminescence spectra

The d^{10} coinage metal complexes including clusters are becoming more important due to their intriguing optical and luminescent properties. The absorption spectra of the ligands (KL^1, KL^2) and (K_2L^3, K_2L^4) recorded in methanol (Fig. S1) show two absorptions near 250–260 nm (ε = 0.75–0.79 × $10^5 M^{-1} cm^{-1}$) and 300–325 nm (ε = 0.48–0.49 × $10^5 M^{-1} cm^{-1}$) while PPh_3 shows an absorption at 262 nm [27] which is assigned to intraligand, π–π* charge transfer transitions. The spectra of corresponding Cu(I) dithiocarbamate (**1**,**2**) and dithiocarbimate (**3**,**4**) complexes collected in CH_2Cl_2 (Fig. 1) show two absorptions at somewhat longer wavelengths near 260–290 nm (ε = 1.10–1.54 × $10^4 M^{-1} cm^{-1}$), 310–350 nm (ε = 0.43–0.48 × 10^4 $M^{-1} cm^{-1}$) and three to four bands near 250 nm (ε = 1.02–1.06 × 10^4 $M^{-1} cm^{-1}$), 290–310 nm (ε = 1.02–1.07 × 10^4 $M^{-1} cm^{-1}$) and 350 nm (ε = 0.96–1.02 × 10^4 $M^{-1} cm^{-1}$) respectively, the higher energy absorptions are assigned to ILCT transitions and those near 300 nm and above arise from a mixture of ILCT, π–π* and MLCT, d- π* transitions.

Under UV-irradiation all the complexes emit intense green light. When excited at 300 nm in CH_2Cl_2 solution at room temperature, complexes **1**-**4** show an intense broad unstructured emission band near 420–500 nm (Fig. 2) emanating most likely from the admixture of ILCT and MLCT states with a remarkable Stokes shift of 120- 200 nm because the free ligands are non- emissive/very weakly emissive. The comparable luminescent properties of the complexes may be attributed to only slight changes in their luminescent chromophores and minimal structural rearrangements in the ground and excited states of complexes which is probably fixed by the rigid ligand environments. Notably, highly intense photoluminescent characteristics of **1** and **4** arise due to Py-(N) on the 3- and 4 positions and p-bromo substituents of the dithio unit which enhance electron cloud hence conjugation in the molecule.

3.4. Crystal structures

Slow evaporation of a dichloromethane/methanol solution of the compound yielded single crystals of complexes **1**-**4**. The crystallographic details, selected bond distances and angles are given in Tables 1–3. The ORTEP drawings of a mononuclear **1** and dinuclear complex **3** are illustrated in Figs. 3 and 4 and those of **2** and **4** in ESI figure S2. Dimensions for **1**-**3** are given in Table 2. As the data for **4**, which is isomorphous with **3**, were not so good, dimensions are given in the ESI.

In the mononuclear complexes (**1**, **2**) the Cu(1) atoms are bonded to two sulphur atoms of a dithiocarbamate and phosphorus atoms of two PPh_3 ligands with Cu-S and Cu-P bond lengths in the range 2.399(2)-2.413(2) Å and 2.2447(14)-2.2595(19) Å which are well within the expected range [28]. In these structures the geometry around the copper atoms is distorted tetrahedral as is evident from the angles listed in Table 2. The small S(11)-Cu(1)-S(13) bite angles observed at

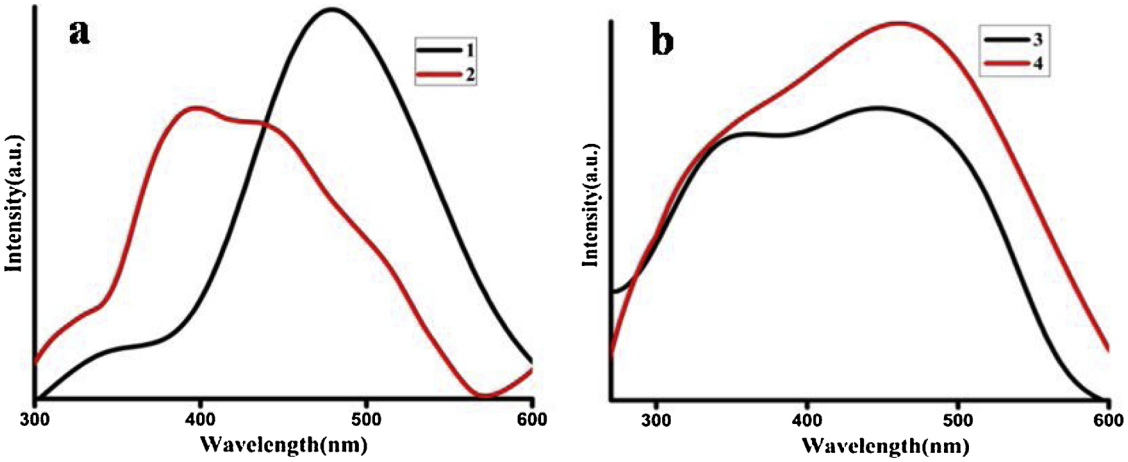


Fig. 2. Emission spectra (λ_{exc} = 300 nm) in CH_2Cl_2 solution for **1**-**2** (a) and **3**-**4** (b).

Table 1
Crystallographic data and structure refinements for complexes.

Compound	**1**.0.5CH_2Cl_2.0.5H_2O	**2**.CH_3OH.1.5H_2O	**3**.0.25CH_2Cl_2.H_2O	**4**.0.5CH_2Cl_2.2.5H_2O
Chemical formula	$C_{49.5}$ H_{44} Cl Cu $N_3O_{0.5}$ P_2 S_2	$C_{48}H_{47}CuNO_{3.98}P_2S_{2.53}$	$C_{79.25}$ $H_{65.5}$ $Cl_{1.5}$ Cu_2 N O_3 P_4 S_3	$C_{79.5}$ H_{69} Br Cl Cu_2 N $O_{4.5}$ P_4 S_3
Formula weight	913.92	907.89	1480.14	1572.85
Crystal system	Triclinic	Triclinic	Monoclinic	Monoclinic
Space group	P -1	P -1	$P2_1/c$	$P2_1/c$
a (Å)	12.4838(11)	12.4657(8)	19.9784(14)	19.817(2)
b (Å)	12.8385(10)	12.7303(9)	16.8728(9)	16.9319(13)
c (Å)	16.3550(12)	16.8683(12)	24.5716(12)	24.204(4)
α(°)	109.858(7)	101.227(6)	(90)	(90)
β(°)	91.866(7)	97.177(6)	92.488(5)	93.332(12)
γ(°)	114.915(8)	115.990(7)	(90)	(90)
V ($Å^3$)	2188.0(3)	2292.0(3)	8275.1(8)	8107.7(17)
Z	2	2	4	4
ρcalc (g cm^{-3})	1.387	1.3164	1.216	1.289
T (K)	150(2)	150(2)	295(2)	150(2)
μ (Mo Kα) (mm^{-1})	0.769	0.704	0.758	1.253
F(000)	948	946	3120	3228
Reflections collected	10687	13633	39348	38738
Independent reflns	7581	10251	14443	13602
Reflections with I > 2σ(I)	5065	7762	6044	6649
Final indices [I > 2σ(I)] R_1[a], wR_2[b]	0.0965, 0.1750	0.0860, 0.2236	0.1227, 0.3126	0.1494, 0.3567
R_1[a], wR_2[b] [all data]	0.1463, 0.1988	0.1107,0.2410	0.2314, 0.3740	0.2465, 0.4031
GOF	1.102	1.056	0.963	1.071
Residual electron density e/$Å^3$	0.858, -1.070	2.555, -0.578	1.195, -0.483	

[a] $R_1 = \Sigma||Fo| - |Fc||/\Sigma|Fo|$. [b] $R_2 = \{[\Sigma w(Fo^2 - Fc^2)/\Sigma w(Fo^2)^2]\}^{1/2}$, $w = 1/[\sigma^2(Fo^2) + (xP)^2]$, where $P = (Fo^2 + 2Fc^2)/3$.

75.09(7)°-75.36(5)° are primarily responsible for the distortion from ideal tetrahedral geometry. The P(1)-Cu(1)-P(2) angles at 124.08(8)° and 125.86(5)° are similar, whereas P-Cu(1)-S angles are observed in the range 104.88(7)°-117.38(7)° and 106.37(5)°-119.08(5)° respectively. In the complexes **1**-**2** the two planes are nearly perpendicular to each other as is evident from the angles between the two least square planes formed by Cu(1), S(11), S(13), C(12) and P(1), Cu(1), P(2) which are 83.97(8)°, 82.26(6)° respectively. The r.m.s. deviations from planarity of the atoms Cu(1), S(11), S(13) and C(12), defining the chelate rings, are 0.030 and 0.008 Å respectively. In the structure of **2**, one five membered ring is identified as furan with the oxygen disordered between two positions while the other five-membered ring is disordered between furan and thiophene.

In the structure of **3** [$Cu_2(PPh_3)_4(L^3)$] the p-chlorobenzenesulphonyl dithiocarbimate ligand is bonded in S,S –chelating mode to one of the Cu(1)$(PPh_3)_2$ units and simultaneously bridges the other Cu(2)$(PPh_3)_2$ through the N,S- donor atoms. Both Cu(1) and Cu(2) atoms have distorted tetrahedral geometries with CuP_2S_2 and CuP_2NS cores respectively. The Cu(1)- Cu(2) distance at 4.850(2) Å is large enough to rule out any metal-metal bonding. The dimer contains a central planar core containing Cu(1), Cu(2), S(11), C(12), S(13), N(14) and S(15) with an r.m.s deviation of 0.046 Å. The two PPh_3 ligands attached to Cu(1) and Cu(2) atoms complete the tetrahedral coordination of each metal with Cu-P distances in the range 2.241(3) Å -2.262(3) Å. The bridging Cu-S (13) distance at 2.464(3) Å is longer than that to the chelating Cu-S(11) at 2.415(3) Å. The Cu(2)-N(14) bond length at 2.153(7) Å is well within the expected values for a Cu(2)-N bond [18a].

As expected the C(12)-N(14) bond distances at 1.35(1) Å in (**1**,**2**) are intermediate between the single C–N (1.47 Å) and double C = N (1.27(1)Å) bond lengths and are significantly longer than that observed for **3** at 1.293(11) Å, a difference which is associated to the contribution of resonating structures (Scheme S2). The C–S bond lengths at 1.700(6) Å -1.744(9) Å in **1**-**3** are significantly smaller than the C–S single bond (ca. 1.81 Å) which indicate the delocalization of the π electrons over NCS_2 unit.

The important role of C—H···π(MCS_2, chelate) interactions in metal bis(1,1-dithioligand) complexes have been described in the formation of supramolecular assembly of varying dimensionality [29]. It was suggested that for homoleptic bis-dithio complexes the values of α < 20, β ranging from 110-180° and d between 2.4 and 3.6 Å were crucial to assesses the interactions where α is the angle between the perpendicular to the ring and the CG···H vector, β, the CG…H-C angle

Table 3
Selected bond lengths(Å) and bond angles(°) for dithiocarbimate complex **3.**

Bond lengths(Å)	**3**	Bond angles(°)	**3**
Cu(1)-P(2)	2.262(3)	P(1)-Cu(1)-P(2)	120.52(10)
Cu(1)-P(1)	2.252(3)	P(2)-Cu(1)-S(11)	119.49(10)
Cu(1)-S(11)	2.415(3)	P(1)-Cu(1)-S(11)	112.02(11)
Cu(1)-S(13)	2.436(3)	P(2)-Cu(1)-S(13)	106.05(9)
Cu(2)-N(14)	2.153(7)	P(1)-Cu(1)-S(13)	115.04(10)
Cu(2)-P(3)	2.241(3)	S(11)-Cu(1)-S(13)	74.22(9)
Cu(2)-P(4)	2.254(3)	P(3)-Cu(2)-N(14)	112.9(2)
Cu(2)-S(13)	2.464(3)	P(4)-Cu(2)-N(14)	118.4(2)
C(12)-S(11)	1.706(9)	P(3)-Cu(2)-P(4)	123.91(11)
C(12)-S(13)	1.744(9)	S(13)-Cu(2)-N(14)	65.9(2)
C(12)-N(14)	1.293(11)	P(3)-Cu(2)-S(13)	115.24(10)
Cu(1)-Cu(2)	4.850(2)	P(4)-Cu(2)-S(13)	105.22(11)

Table 2
Selected bond lengths (Å) and bond angles(°) for dithiocarbamate complexes **1**-**2.**

Bond lengths(Å)	**1**	**2**	Bond angles(°)	**1**	**2**
Cu(1)-P(2)	2.248(2)	2.2447(14)	P(1)-Cu(1)-P(2)	124.08(8)	125.86(5)
Cu(1)-P(1)	2.260(2)	2.2481(14)	P(2)-Cu(1)-S(11)	112.44(7)	119.08(5)
Cu(1)-S(11)	2.413(2)	2.4008(14)	P(1)-Cu(1)-S(11)	104.88(7)	106.37(5)
Cu(1)-S(13)	2.399(2)	2.4112(14)	P(2)-Cu(1)-S(13)	111.60(7)	106.41(5)
C(12)-S(11)	1.721(7)	1.700 (6)	P(1)-Cu(1)-S(13)	117.38(7)	112.46(5)
C(12)-S(13)	1.709(7)	1.718(5)	S(11)-Cu(1)-S(13)	75.09(7)	75.36 (5)
C(12)-N(14)	1.355(9)	1.352(7)			

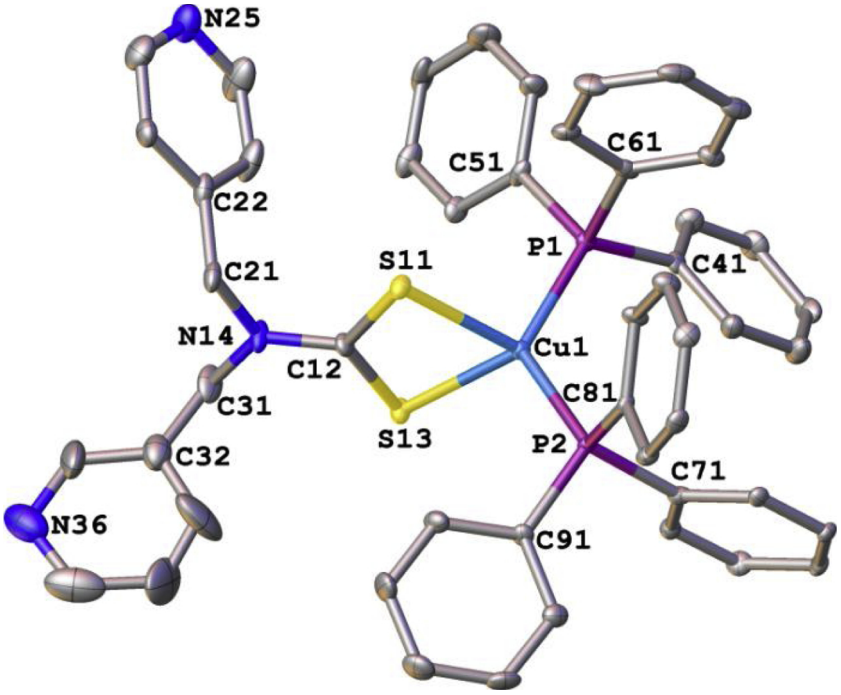


Fig. 3. ORTEP diagram of **1** with thermal ellipsoids set to 30% probability level. Solvent molecules and hydrogen atoms are omitted for clarity.

and d, the CG···H distance where CG is the centre of gravity of the chelate ring. For **1** the C—H···π(CuCS$_2$, chelate) interaction involving H (96) of the PPh$_3$ group to CG of the CuCS$_2$ ring is found with α 0, β 136° and d 2.707 Å (Fig. S3a). On the other side of the chelate ring H(52) shows values of 7, 121°, 3.055 Å. Also, in **2** two C—H···π(Cu1-CS$_2$, chelate) interactions are found between hydrogen atoms of PPh$_3$ moieties H(42) and H(92) on opposite sides of the ring with parameters, 4, 133°, 2.798 Å and 1, 121°, 2.872 Å respectively (Fig. S3b). In **3** similar interactions with the Cu(1)CS$_2$, chelate are found for H(56) and H(76) with parameters 9, 113°, 3.319 Å and 11, 144°, 3.136 Å respectively (Fig. S3c).

Complex **3** also contains a C–H···π(Cu(2)CNS, chelate) ring which forms similar interactions with H(92), H(136) of the two PPh$_3$ moieties with α, β and d values of 6, 114°, 3.165 Å and 7, 144°, 2.956 Å in **3** (Fig. S3c).

The weak inter molecular H···H interactions are found in complexes **1** and **3** with an H (31B)···H(54) distance of 2.37 Å in **1** (Fig. S4a) and an H(134)···H(135) distance of 2.37 Å in **3** (Fig. S4b). The intermolecular C–H···π interactions sustain the supramolecular structures of **1** and **3**.

3.5. Catalytic activity of the pre-formed Cu(I) complexes in click chemistry: synthesis of diverse glycoconjugates triazoles

We investigated the developed mono-/ dinuclear Cu(I) dithiocarbamate / dithiocarbimate- PPh$_3$ complexes **1**-**4** for azide-alkyne cycloaddition reaction of diverse sugar azides (**5a-m**) with the vaniline

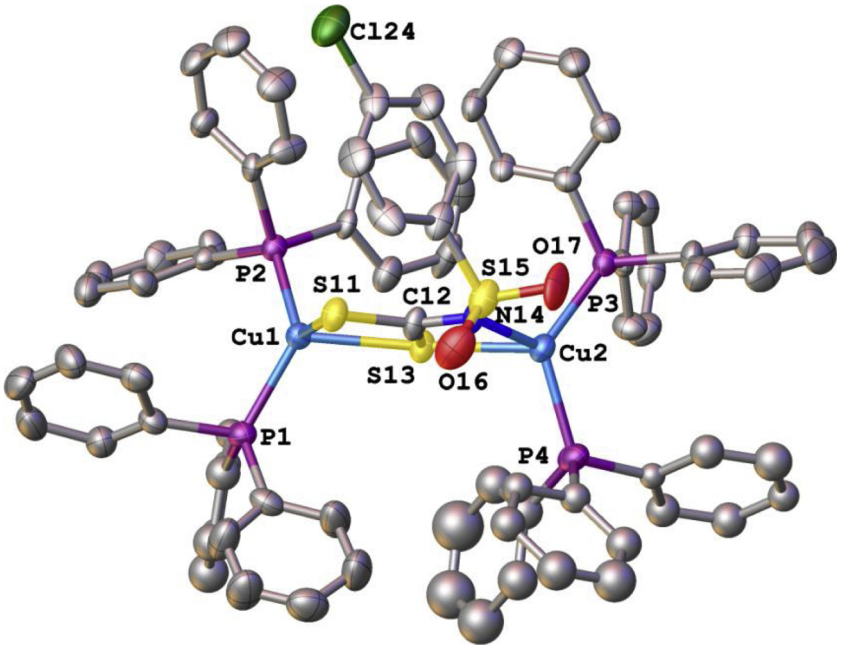
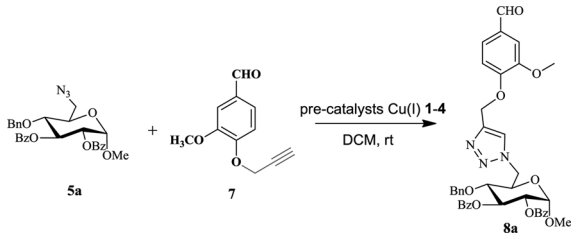


Fig. 4. ORTEP diagram of **3** with thermal ellipsoids set to 30% probability level. Solvent molecules and hydrogen atoms are omitted for clarity.

Table 4
Optimization of catalytic efficiency of developed Cu(I) pre-catalyst **1–4** in the synthesis of vanillin glycoconjugates **8a.**



Entry	Catalyst	Solvent	Base (1 equiv)	Time (h)	Yield (%)[d]
1[a]	**1** (5 mol%)	DCM	Et_3N	4	89
2[a]	**2** (5 mol%)	DCM	Et_3N	4	91
3[a]	**3** (5 mol%)	DCM	Et_3N	4	25
4[a]	**4** (5 mol%)	DCM	Et_3N	4	55
5[b]	**1** (5 mol%)	DCM	Et_3N	4	87
6[b]	**2** (5 mol%)	DCM	Et_3N	4	90
7[b]	**1** (10 mol%)	DCM	Et_3N	2	94
8[b]	**2** (10 mol%)	DCM	Et_3N	2	92
9[c]	**1** (10 mol%)	DCM	–	2	93
10[c]	**2** (10 mol%)	DCM	–	2	Nd
11[c]	**1** (10 mol%)	MeOH	–	2	28
12[c]	**1** (10 mol%)	EtOH	–	2	32
13[c]	**1** (10 mol%)	CH_3CN	–	2	45
14[c]	**1** (10 mol%)	THF	–	2	70
15	CuI(10 mol%)	DCM	Et_3N	2	48
16	$CuSO_4$/NaAsc	THF/H_2O	–	2	43

[a] Reaction proceeded with **5** (1 equiv), **7** (1 equiv) and Et_3N (1 equiv) in dry DCM under argon atmosphere.
[b] Reaction proceeded with **5** (1 equiv), **7** (1 equiv) and Et_3N (1 equiv) in normal DCM in air.
[c] Reaction proceeded with **5** (1 equiv) and **7** (1 equiv) in air.
[d] Yield after purification (SiO_2).

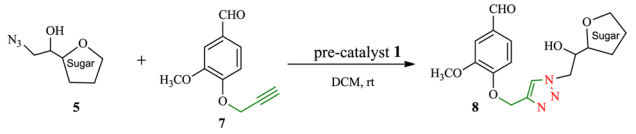
based alkyne **7** to synthesis of relatively rare biologically relevant vanillin-glycoconjugates (**8a-m).** We also investigated the efficiency and recyclability of homo-dinuclear **3**-**4** complexes in click protocol with **5n** and phenylacetylene **9** for synthesis of triazolyl glycoconjugate.

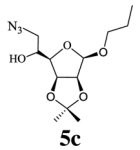
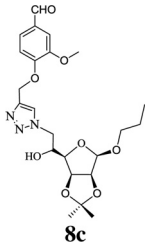
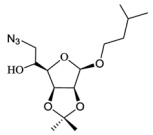
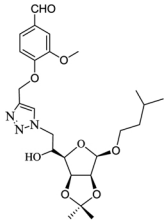
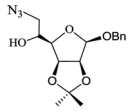
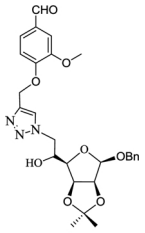
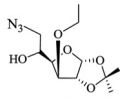
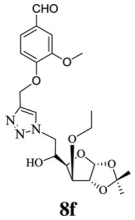
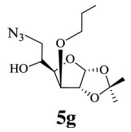
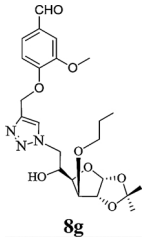
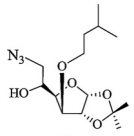
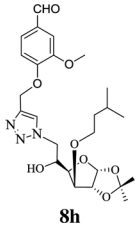
The synthetic work began with the synthesis of diverse sugar azides **5a-m** from readily available monosaccharides using various high yielding steps of protections and modifications [30]. The synthesis of vanillin based terminal alkynes **7**/**9** was accomplished through the substitution reaction at the free hydroxyl position of *p*-vanillin with propargyl bromide and potassium carbonate. Initially, the catalytic activity of pre-catalyst **1–4** in the azide-alkyne cycloaddition reaction with the vanillin based terminal alkyne **7** and sugar azide **5a** was investigated. In the preliminary examination, we treated **7** (1 equiv) with **5a** (1 equiv) in dry dichloromethane under inert atmosphere in the presence of triethylamine (1 equiv) with a set up of four separate reactions for each catalytic system in which the initial loading of catalysts was 5 mol%. Consumption of starting material was observed after four hours. These results all showed the catalytic efficiency of complexes **1–4.** In particular the mono nuclear Cu(I) complexes (**1**,**2**) exhibited virtually similar efficacy (Table 4, entries 1,2) thus yielding product **8a** in 89% and 91% respectively. By contrast the di-nuclear Cu(I) complexes **3** and **4** showed sluggish reaction and yielded **8a** in 25% and 55% respectively (Table 4, entries 3,4), albeit they completed the reaction in good yield within 8–10 hours. Furthermore, the eco-friendly character of pre-catalysts was checked by performing the reactions in air and in simple dichloromethane (non dried DCM) but oxidation of copper (I) complexes to copper (II) during the course of reaction was not observed as evident by the fact that no perceptible change in color, i.e. blue to – green, appeared in solution and thus the product was isolated with similar efficiency (Table 4, entries 5, 6). Out of the four Cu (I) complexes the mononuclear complexes (**1**, **2**) were found to provide excellent results, therefore, they were investigated further. The effect of the amount of catalyst used on reactivity was also observed and it was found that the loading of catalyst with double quantities (10 mol %), reduced the reaction time, with completion within two hours (Table 4, entries 7, 8). Next, to make the catalytic system more precise and economic for the synthesis of medicinal valued triazolyl glycoconjugates, the reactions were performed in the absence of base. Surprisingly the reaction proceeded well in the presence of catalyst **1** and afforded excellent yield (Table 4, entry-9) but by contrast complex **2** did not react and no product was formed. Presumably this may be ascribed to the presence of two pyridine moieties in complex **1** thereby enhancing the basicity of the reaction medium that was needed to initiate the reaction. Finally, it was established that complex **1** behaves as a highly efficient catalyst that enables the reaction to proceed smoothly in air without a base, with no need of dry solvent so that the reaction was completed within two hours. Indeed, pre-catalyst **1** showed high activity in different reaction media such as methanol, ethanol, acetonitrile and tetrahydrofuran. However because of the low solubility of **1** in methanol and ethanol, the reactions proceeded sluggishly. Although, reactions performed in tetrahydrofuran displayed better results than in acetonitrile but poorer results than in dichloromethane (Table 4, entries 13–14). The performance of **1** was also compared with at traditional Cu (I) source using CuI (10 mol%) in dichloromethane and also by using a combination of $CuSO_4.5H_2O$(5 mol %)/sodium ascorbate (10 mol%) in THF/H_2O for the synthesis of vanillin-glycoconjugate derivatives (Table 4, entries 1516).

Further synthesis were explored by applying these optimized reaction conditions for clicking the vanillin derived alkynes with diverse sugar azides and azido alcohols (Table 5). The reactions of **5c-k** with **7** in presence of pre-catalyst **1** (10 mol%) in dichloromethane in air were also studied with appropriate reaction conditions. This afforded a library of biological relevant vanillin glycoconjugates. The catalytic system was found suitable for all reactions and exhibited wide functional group tolerance. All synthesized compounds were characterized by NMR spectroscopy (Table S2).

The recyclability of catalysts **1**-**4** was investigated. All complexes were recovered from the crude reaction product via different

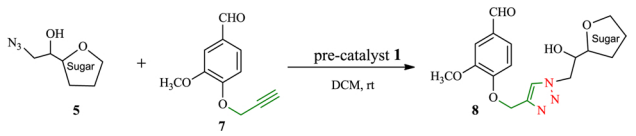
Table 5
Synthesis of triazole-linked *p*-vanillin glycoconjugates **8c-k** using pre-catalyst **1**.

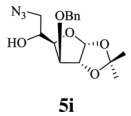
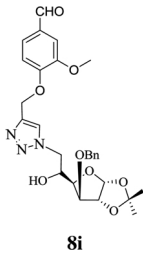
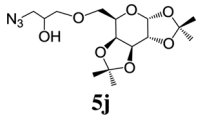
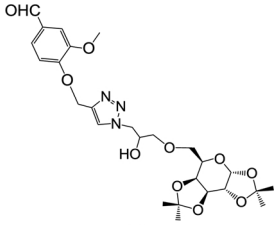
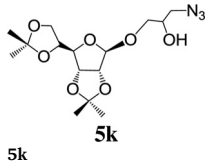
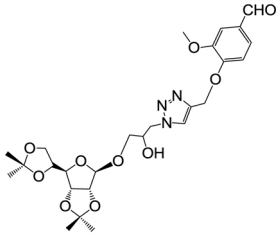


Entry[a]	Azide[b] (**5**)	Product[c] (**8**)	Time (h)	Yield[d] (%)
1	 **5c**	 **8c**	2.5	88
2	 **5d**	 **8d**	3	87
3	 **5e**	 **8e**	2	84
4	 **5f**	 **8f**	2	85
5	 **5g**	 **8g**	3	89
6	 **5h**	 **8h**	3	86

(*continued on next page*)

Table 5 (*continued*)



Entry[a]	Azide[b] (**5**)	Product[c] (**8**)	Time (h)	Yield[d] (%)
7	 **5i**	 **8i**	2	90
8	 **5j**	 **8j**	2.5	85
9	 **5k**	 **8k**	2.5	82

[a] Molar ratio of reagents Azide (1.0 equiv), Alkyne (1.2 equiv) and pre-catalyst (10 mol%).
[b] developed glycosyl azides.
[c] developed triazolyl glycoconjugates.
[d] isolated yield of product after purification (SiO_2).

techniques. Thus the recyclability of complex **1** by clicking azide **5a** and alkyne **7** was evaluated under optimized reaction conditions. We set up three reactions sequentially, in which each reaction was initiated with the catalyst recovered from the former reaction and the reaction crude was extracted with 2 ml of methanol three times where the product was soluble in methanol and decayed in another pot. The remaining solid was identified as the catalyst which was reused in the next reaction for azide-alkyne cycloaddition.

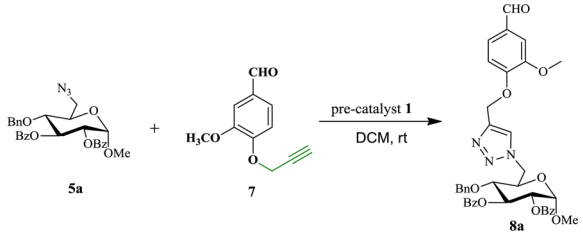
Recyclability of complex **2** was also observed and recovered in slightly less amount than used initially in the first reaction using column chromatography during purification of the product. For this, we proceeded three different reactions sequentially, in which each reaction was catalyzed with recovered catalyst **2** from the former reaction mixture (Table 6). First, the reaction was catalyzed with 10 mol% of catalyst in the presence of base Et_3N (1 equiv) which completed the reaction within 2 h. Likewise, the other reactions were performed with similar equivalents of reactants and recovered quantity of the catalyst (Table 7).

Further, we explored the scope of catalysts **3** and **4** with anomeric azides **5m-n** and alkyne **7**, **9** (Table 8, entries 1, 6–7). We observed that both catalysts were found efficient for the synthesis of glycoconjugates **8n-p;** though, they required slightly longer reaction times 6–8 h than necessary in the case of 6-azido sugar **5a** (Table 1). Both the dinuclear complexes **3** and **4** were also observed to be reusable catalysts (Table 8) and recovered using column chromatography during purification of the product. Catalyst loading of 10 mol% for these complexes was found sufficient for catalyzing the reaction and obtaining recyclability (Table 8, entries 1–5).

4. Conclusions

New mono- and homo-dinuclear Cu(I) dithiocarbamates (**1**,**2**) and dithiocarbimates (**3**,**4**) complexes bearing PPh_3 ligands were synthesized, structurally characterized and their catalytic activities under the Click protocol for the transformation of azides and alkynes into glycoconjugate triazoles have been investigated. Among these pre-catalysts the mono-nuclear Cu(I) dithiocarbamate complexes (**1**,**2**) are highly efficient and reusable; in particular **1** is equally efficient under base free conditions due to the presence of the pyridyl group which provides the basicity in the reaction medium. By comparison under similar mild reaction conditions and low catalytic loadings, the observed activity of dinuclear dithiocarbimate complexes (**3**,**4**) is rather sluggish; their weaker efficiency may be attributed to the varied environment about the two copper(I) centres, which provide electronic characteristics that

Table 6
Recyclability of pre-catalyst **1** in the synthesis of triazole-linked *p*-vanillin glycoconjugates **8a.**



Entry[a]	Catalyst	Temp	Time (h)	Yield (%)[b]
1	10 mol%	Rt	2	94%
2	- [c]	Rt	2	89%
3	- [d]	Rt	2	86%

[a] Molar ratio: **5a** (1 equiv.) and **7** (1.2 equiv.) in DCM (2 mL).
[b] Yields reported after purification by column chromatography (SiO_2).
[c] Pre-catalyst recovered from entry 1.
[d] Pre-catalyst recovered from entry 2.

might be affect their activity. The development of Cu(I) dithiocarbamate based complexes bearing phosphine ligands may show wider and efficient utility in Click chemistry under eco-friendly conditions. The synthesis of these catalysts is easy and the chemicals involved are rather cost effective. **1**-**4** emits green luminescence in solution at room temperature.

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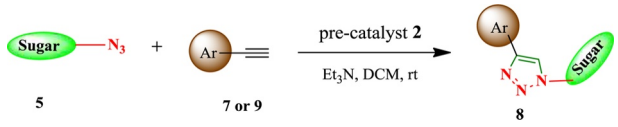
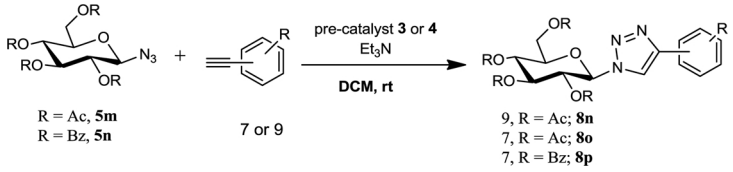
Table 7
Synthesis of triazole-linked *p*-vanillin glycoconjugates **8** using pre-catalyst **2.**



Entry	Azide (**5**)		Product (**8**)	Time (h)	Yield[d](%)
1[b]	**5b**	**7**	**8b**	2	92
2[b]	**5l**	**7**	**8l**	2.5	87
3[c]	**5l**	**9**	**8m**	2.5	83

[a] Reaction proceeded with 5 (1 equiv), 7 (1 equiv), Et_3N and pre-catalyst **2** (10 mol%).
[b] Reaction proceeded with recovered pre-catalyst **2** from entry 1.
[c] Reaction proceeded with recovered pre-catalyst **2** from entry 2.
[d] Isolated yield after purification.

Table 8
Synthesis of *N*-glycosides through triazole formation using pre-catalyst **3** and **4**.



R = Ac, **5m**
R = Bz, **5n**

7 or 9

9, R = Ac; **8n**
7, R = Ac; **8o**
7, R = Bz; **8p**

Entry[a]	Azide	Alkyne	Product	Catalyst (10 mol%)	Time (h)	Yield[f] (%) Y1 and Y2
1	**5m**	**9**	**8n**	**3**	8	Y1 = 75
2[b]	**5m**	9	**8n**	–	8	Y1 = 69
3[c]	**5m**	**9**	**8n**	**4**	6	Y2 = 92
4[d]	**5m**	9	**8n**	–	6	Y2 = 87
5[e]	**5m**	9	**8n**	–	6	Y2 = 82
6	**5m**	7	**8o**	**3 or 4**	8	Y1 = 76 Y2 = 88
7	**5n**	7	**8p**	**3 or 4**	8	Y1 = 72 Y2 = 85

[a] Reaction proceeded with alkyne (1.0 equiv), azide (1.0 equiv), Et_3N (1 equiv) and pre-catalyst **3**.
[b] Reaction proceeded with recovered pre-catalyst **3** from entry 1.
[c] Reaction proceeded with alkyne (1 equiv), azide (1 equiv), Et_3N (1 equiv) and pre-catalyst **4**.
[d] Reaction proceeded with recovered pre-catalyst **4** from entry 3.
[e] Reaction proceeded with recovered pre-catalyst **4** from entry 4.
[f] Y1 represented yield for catalyst **3** and Y2 for catalyst **4**.

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Appendix A. Supplementary data

Supplementary material related to this article can be found, in the online version, at doi:https://doi.org/10.1016/j.mcat.2019.03.009.

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