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Research paper

Copper(I) complexes of *N*-(2-quinolynylmethylene)-1*H*-benzimidazole and triphenylphosphine: Synthesis, characterization, luminescence and catalytic properties

S.S. Devkule, S.S. Chavan *

Department of Chemistry, Shivaji University, Kolhapur, MS-416004, India

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ABSTRACT

Copper(I) complexes of the type $[Cu(\mathbf{L})(PPh_3)_2]X$ (**1**–**4**) [where **L** = *N*-(2-quinolynylmethylene)-1*H*-benzimidazole; PPh_3 = triphenylphosphine, X = NO_3(**1**), ClO_4(**2**), BF_4(**3**) and PF_6(**4**)] were prepared by the condensation of 2-aminobenzimidazole with 2-quinolinecarboxaldehyde followed by reaction with $[Cu(CH_3CN)_4]NO_3$, $[Cu(CH_3CN)_4]ClO_4$, $[Cu(CH_3CN)_4]BF_4$, $[Cu(CH_3CN)_4]PF_6$ in presence of triphenylphosphine as a coligand. The single crystal X-ray diffraction study of representative complex $[Cu(\mathbf{L})(PPh_3)_2]^+$ (**3**) reveals a distorted tetrahedral geometry around copper(I). Cyclic voltammogram of complexes **1**–**4** displayed quasireversible redox behavior corresponding to Cu(I)/Cu(II) couple. All complexes show red emission as a result of ligand to ligand charge transfer (LLCT) or intra-ligand charge transfer (ILCT) or admixture of them. The catalytic efficiency of the complexes **1**–**4** was tested and it was found that all the complexes worked as an effective catalyst for the Sonogashira coupling of phenylacetylene with different aryl halides in good yield at 90 °C.

1. Introduction

The monovalent copper(I) complexes with tetrahedral coordination geometry have received special attention due to its low toxicity, low cost advantage and relatively abundant resource compared to more precious metal systems such as Re(I) [1], Ir(III) [2], Pt(IV) [3] and Au(I) [4]. These obvious advantages make copper(I) compounds excellent candidates for their potential applications such as photosensitizers (PS) for solar energy conversion, dye-sensitized solar cells (DSSCs), organic light emitting diodes (OLEDs), light emitting electrochemical cells (LEECs), supramolecular devices, catalysis and biological relevance [5–9]. The combination of the electron rich copper(I) center, conjugated organic ligand and high degree of inherent covalence in soft acid-soft base bonding can produce low energy electronic interactions between metal center and the ligand and resulting compound possesses interesting optical and electronic properties [10,11]. Moreover, the steric, electronic and conformational effects imparted by the coordinated ligands play an essential role in stabilizing the copper(I) state and modifying the physical and chemical properties of the prepared complexes. Hence careful choice of ligand is of significant importance which will tune the properties of the resulting compound. More recently considerable interest has been paid on N-heterocyclic system especially benzimidazole and their derivatives which are reported to exhibit remarkable features like ease of preparation, electrochemical behavior, light absorption in the visible region, characteristic structural flexibility, supramolecular architecture, long-lived electronically excited states and intense luminescence [12–15]. Because of having high thermal stability, good catalytic performance and superior optical properties, metal complexes with benzimidazole ligands are important. An important feature of these system is the structural modifications which causes a large π-delocalization over the *N*-heterocyclic ligand than that of the regular complexes. The copper(I) complexes with phosphorous containing ligands are of great important to carry wide range organic transformations such as allylic amination, hydrogenation, copolymerization, cross coupling reactions etc. [16–19]. The steric crowding and π-acidic character imparted by these ligands are most important prerequisites for stabilizing the copper(I) complexes and their redox, photophysical and catalytic behavior.

In this paper we report synthesis of some mixed ligand copper(I) complexes (**1**–**4**) derived by the reaction of *N*-(2-quinolynylmethylene)-1*H*-benzimidazole (**L**) with $[Cu(CH_3CN)_4]NO_3$ $[Cu(CH_3CN)_4]ClO_4$, $[Cu(CH_3CN)_4]BF_4$ and $[Cu(CH_3CN)_4]PF_6$ in presence of triphenylphosphine as coligand. All the complexes were characterized by elemental analysis, spectroscopic techniques

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* Corresponding author.
E-mail address: sanjaycha2@rediffmail.com (S.S. Chavan).

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and representative complex **3** by X-ray crystallography analysis. The luminescent behavior and catalytic performance of all complexes for the Sonogashira coupling of phenylacetylene with aryl halides have also been reported.

2. Experimental

2.1. Materials and methods

The reagent used in synthesis of copper(I) complexes are 2-quinolinecarboxaldehyde (Alfa Aesar), 2-aminobenzimidazole (Aldrich, USA), triphenylphosphine were of reagent grade and used without further purification. Other reagents included iodobenzene, 4-iodoaniline, 1-bromo-4-iodobenzene, phenylacetylene and potassium carbonate. The copper(I) compounds $Cu(CH_3CN)_4]NO_3$ [20], $Cu(CH_3CN)_4]ClO_4$ [21], $[Cu(CH_3CN)_4]BF_4$ [21] and $[Cu(CH_3CN)_4]PF_6$ [22] were prepared according to the literature procedure.

Elemental analyses (C, H and N) of the copper(I) complexes were conducted on Thermo Finnegan FLASH EA-1112 CHNS analyzer. IR spectra were recorded on a Perkin-Elmer-100 FTIR Spectrometer, ^1H NMR and ^{13}C NMR spectra of the samples dissolved in $CDCl_3$ were measured on Bruker 300 MHz instrument using TMS $[(CH_3)_4Si]$ as an internal standard of chemical shifts (ppm). Electronic spectra were recorded in dichloromethane (10^{-5} M) Shimadzu 3600 UV–Vis-NIR spectrophotometer. Emission spectra were recorded using a Perkin-Elmer LS 55 spectrofluorometer equipped with quartz cuvette of 1 cm path length at room temperature. ESI mass spectra were recorded using a Bruker Apex3. Luminescence lifetime measurements were carried out by using time-correlated single photon counting from HORIBA JobinYvon. Cyclic voltammetry measurements were performed with a CH-400 electrochemical analyzer. Tetrabutyl ammonium perchlorate (TBAP) was used as the supporting electrolyte and ferrocene was used as an internal reference. All measurements were carried out in CH_2Cl_2 solution at room temperature with scan rate 50 mV s^{-1}

2.2. Synthesis

2.2.1. Synthesis of ligand (*L*)

N-(2-quinolynylmethylene)-1*H*-benzimidazole (**L**) was prepared by adopting and modifying the method described in the literature [23]. To a solution of 2-aminobenzimidazole (0.800 g, 6.010 mmol) in ethanol (10 ml) a solution of 2-quinolinecarboxaldehyde (0.944 g, 6.010 mmol) in EtOH (10 ml) was added drop wise with constant stirring. The resulting reaction mixture was refluxed at about 82 °C until the completion of reaction (checked by TLC). On partial removal of solvent the product obtained was filtered, washed with ethanol and dried in *vacuo*.

Yield: 89% (1.560 g, 3.107 mmol); Elemental analyses (C, H and N, wt%) Anal. Calc. for $C_{17}H_{12}N_4$: C, 78.98; H, 4.44; N, 20.58; found: C, 78.89; H, 4.40; N, 20.67%; IR (KBr; cm^{-1}); 3365, υ(NH), 1618, υ (HC=N); 1381, υ(C–N); 3056, υ(Ar–CH); ^1H NMR ($CDCl_3$; 300 MHz): δ 10.26 (s, 1H, NH), δ 9.31 (s, 1H, HC=N), δ 7.29–8.35 (m, 10H, Ar–H); ^{13}C NMR ($CDCl_3$); 300 MHz: δ 161.4 (N=CN), 152.9 (quin-C), 146.9 (HC=N), 139.9 (benzi-C), 132.6 (quin-C), 131.6 (quin-C), 129.9 (quin-C), 129.7 (quin-C), 128.8 (quin-C), 127.1 (quin-C), 126.9 (quin-C), 123.8 (quin-C), 120.9 (benzi-C), 113.7 (benzi-C); ESI (MS): 272 $[M]^+$.

2.2.2. Synthesis of $[Cu(\mathbf{L})(PPh_3)_2]NO_3$ (*1*)

To a 10 ml acetonitrile solution of $[Cu(CH_3CN)_4]NO_3$ (0.266 g, 0.918 mmol), 2 equivalent of triphenylphosphine (0.481 g, 1.836 mmol) were added and the solution was stirred for 30 min. The crystalline product $[Cu(CH_3CN)_2(PPh_3)_2]NO_3$ obtained was added to a stirring solution of ligand **L** (0.250 m, 0.918 mmol) in 10 ml of dichloromethane and stirred for 2 h at room temperature. The volume of solvent reduced under vacuum and the solid product was produced by diffusion of diethyl ether into the filtrate.

Yield: 82% (0.642 g, 0.701 mmol); Elemental analyses (C, H, N, wt%) Anal. Calc. for $C_{53}H_{42}N_5O_3P_2Cu$: C, 69.01; H, 4.59, N, 7.59; found: C, 68.96; H, 4.49, N, 7.68%; IR (KBr; cm^{-1}); 3362, υ(NH), 1587, υ(HC=N), 1384, υ(C–N); 3066, (Ar–CH); 488 υ(Cu–N); 1482, 1436, 695, 518, υ(PPh_3); 1375, 821, υ(NO_3): UV–Vis (CH_2Cl_2) λ_{max} (nm) ($\varepsilon/M^{-1}\ cm^{-1}$): 294 (75,000), 352 (35,000), 458 (7000); ^1H NMR ($CDCl_3$; 300 MHz); δ 11.03 (s, 1H, NH), δ 9.48 (s, 1H, HC=N), δ 7.12–8.46 (m, 10*H*, Ar–H); ^{13}C NMR ($CDCl_3$; 300 MHz) δ 160.3 (N=CN), 150.7 (quin-C), 146.1 (HC=N), 138.9 (benzi-C), 133.4 (ph-C), 132.1 (quin-C), 130.3 (ph-C), 130.2 (ph-C), 129.5 (quin-C), 128.5 (ph-C), 128.1 (ph-C), 127.9 (quin-C), 126.5 (quin-C), 125.7 (quin-C), 125.1 (quin-C), 122.5 (quin-C), 119.4 (benzi-C), 112.5 (benzi-C); ESI (MS): 859 $[M-NO_3]^+$.

2.2.3. Synthesis of $[Cu(\mathbf{L})(PPh_3)_2]ClO_4$ (*2*)

Complex **2** was prepared by a procedure similar to that used for the preparation of **1** except that, $[Cu(CH_3CN)_4]NO_3$ was replaced by $[Cu(CH_3CN)_4]ClO_4$ (0.300 g, 0.918 mmol).

Yield: 87% (0.717 g); Elemental analyses (C, H, N, wt%) Anal. Calc. for $C_{53}H_{42}N_4P_2O_4ClCu$: C, 66.32; H, 4.41, N, 5.84; found: C, 66.21; H, 4.33, N, 5.95%; IR (KBr; cm^{-1}); 3362, υ(NH), 1588, υ (HC=N), 1384, υ(C–N); 3065, (Ar–CH); 488 υ(Cu–N); 1482, 1436, 695, 518, υ(PPh_3); 1097, 622, υ(ClO_4); UV–Vis (CH_2Cl_2) λ_{max} (nm) ($\varepsilon/M^{-1}\ cm^{-1}$): 292 (71,000), 349 (33,000), 451 (8000); ^1H NMR ($CDCl_3$; 300 MHz): δ 11.04 (s, 1H, NH), δ 9.47 (s, 1H, HC=N), δ 7.11–8.49; ^{13}C NMR ($CDCl_3$; 300 MHz): δ 160.2 (N=CN), 150.7 (quin-C), 145.9 (HC=N), 139.0 (benzi-C), 133.4 (ph-C), 132.2 (quin-C), 130.3 (ph-C), 130.2 (ph-C), 129.5 (quin-C), 128.5 (ph-C), 128.1 (ph-C), 127.7 (quin-C), 126.9 (quin-C), 125.6 (quin-C), 125.2 (quin-C), 122.6 (quin-C), 119.5 (benzi-C), 112.4 (benzi-C); ESI (MS): 859 $[M-ClO_4]^+$.

2.2.4. Synthesis of $[Cu(\mathbf{L})(PPh_3)_2]BF_4$ (*3*)

Complex **3** was prepared by a procedure similar to that used for the preparation of **1** except that, $[Cu(CH_3CN)_4]NO_3$ was replaced by $[Cu(CH_3CN)_4]$ BF_4 (0.289 g, 0.918 mmol).

Yield: 88% (0.902 g); Elemental analyses (C, H, N, wt%) Anal. Calc. for $C_{53}H_{42}N_4P_2F_4BCu$: C, 67.20; H, 4.47, N, 5.91; found: C, 67.11; H, 4.38, N, 5.99%; IR (KBr; cm^{-1}); 3363, υ(NH), 1585, υ (HC=N), 1384, υ(C–N); 3066, (Ar–CH); 488 υ(Cu–N); 1482, 1436, 695, 518, υ(PPh_3); 1058 υ(BF_4); UV–Vis (CH_2Cl_2) λ_{max} (nm) ($\varepsilon/M^{-1}\ cm^{-1}$): 291(69,000), 346 (33,000), 454 (9000); ^1H NMR ($CDCl_3$; 300 MHz): δ 11.03 (s, 1H, NH), δ 9.48 (s, 1H, HC=N), δ 7.12–8.46; ^{13}C NMR ($CDCl_3$; 300 MHz): δ 160.2 (N=CN), 150.7 (quin-C), 146.2 (HC=N), 138.9 (benzi-C), 133.4 (ph-C), 132.1 (quin-C), 130.3 (ph-C), 130.2 (ph-C), 129.6 (quin-C), 128.5 (ph-C), 128.4 (ph-C), 127.9 (quin-C), 126.4 (quin-C), 125.8 (quin-C), 125.2 (quin-C), 122.5 (quin-C), 119.4 (benzi-C), 112.1 (benzi-C); ESI (MS): 859 $[M-BF_4]^+$.

2.2.5. Synthesis of $[Cu(\mathbf{L})(PPh_3)_2]PF_6$ (*4*)

Complex **4** was prepared by a procedure similar to that used for the preparation of **1** except that, $[Cu(CH_3CN)_4]NO_3$ was replaced by $[Cu(CH_3CN)_4]PF_6$ (0.342 g, 0.918 mmol).

Yield: 84% (0.911 g); Elemental analyses (C, H, N, wt%) Anal. Calc. for $C_{53}H_{42}N_4P_3F_6Cu$: C, 63.32; H, 4.21, N, 5.57; found: C, 63.22; H, 4.13, N, 5.69%; IR (KBr; cm^{-1}); 3362, υ(NH), 1589, υ (HC=N), 1384, υ(C–N); 3066, (Ar–CH); 488 υ(Cu–N); 1482, 1436, 695, 518, υ(PPh_3); 842,562 υ(PF_6) UV–Vis (CH_2Cl_2) λ_{max} (nm) ($\varepsilon/M^{-1}\ cm^{-1}$): 292 (62,000), 351 (29,000), 456 (11,000): ^1H NMR ($CDCl_3$; 300 MHz): δ 11.04 (s, 1H, NH), δ 9.48 (s, 1H, HC=N), δ 7.12–8.46; ^{13}C NMR ($CDCl_3$; 300 MHz): δ 160.3 (N=CN), 150.7 (quin-C), 146.1 (HC=N), 139.0 (benzi-C), 133.5 (ph-C), 132.2

(quin-C), 130.3 (ph-C), 130.2 (ph-C), 129.5 (quin-C), 128.5 (ph-C), 128.1 (ph-C), 127.8 (quin-C), 126.9 (quin-C), 125.7 (quin-C), 125.1 (quin-C), 122.6 (quin-C), 119.5 (benzi-C), 112.5 (benzi-C); ESI (MS): 859 $[M-PF_6]^+$.

2.3. X-ray crystallography

A single crystal of $[(Cu(\mathbf{L})(PPh_3)_2]BF_4{\cdot}CH_2Cl_2$ (**3**) suitable for X-ray analysis was obtained by slow diffusion of diethyl ether in dichloromethane solution. X-ray study performed on a Bruker KAPPA Apex-II diffractometer. Data were collected in omega and phi scan modes, MoKα = 0.71073 Å at room temperature with scan width of 0.3° at θ (0°, 90° and 180°) by keeping distance at 40 mm between sample and fixed detector at 24°. The X-ray generator was operated at 50 kV and 30 mA. The details of crystal data, data collection and the refinement are given in Table 1. The X-ray data collection was monitored by SMART program (Bruker, 2003). All the data were collected using SAINT and SADABS programs (Bruker, 2003). SHELXL-2014 was used for the solution of the structure and full matrix least-squares refinement on F2 [24]. Molecular and packing diagrams were generated using ORTEP-3 [25] and Mercury-3 [26].

2.4. Catalytic activity for the Sonogashira coupling of phenylacetylene with aryl halides

The Sonogashira coupling reaction of phenylacetylene with different aryl halides catalyzed by copper(I) complexes was carried out according to the procedure: 10 mol% of copper(I) catalyst was added to 2 mmol of respective aryl halide, 2.5 mmol of phenylacetylene, 2 mmol of K_2CO_3 in toluene and the reaction mixture was stirred for 16 h at 90° under nitrogen. The reaction mixture was then cooled to room temperature and the solution was filtered to remove the precipitated base. The filtrate was concentrated and crude product was purified by column chromatography using ether:chloroform (9:1). The purified product obtained was characterized by elemental analyses, IR, ^{1}H NMR and mass spectral studies.

Table 1
Crystal data and structure refinements details for$[(Cu(\mathbf{L})(PPh_3)_2]BF_4{\cdot}CH_2Cl_2$ (**3**).

Empirical formula	$C_{53}H_{42}CuN_4P_2$, BF_4, CH_2Cl_2
Formula weight	1032.12
Crystal system	Triclinic
Space group	*P*-1
a (Å)	10.8832(6)
b (Å)	12.7145(8)
c (Å)	18.0915(11)
α (°)	85.378(3)
β (°)	81.531(3)
γ (°)	86.740(3)
V (A^3)	2465.5(3)
Z	2
Density (mg/m^3)	1.390
μ ($M_oK_α$) (mm^{-1})	0.673
F (000)	1060
Data collection	
Temperature (K)	296(2)
θ mini.-maxi.(deg)	2.28–24.11
Data set [*h, k, l*]	−12/12, −15/15, −21/21
Total, unique data, R_{int}	[R(int) = 0.0656]
Observed data	>2[*spsbackslash*]s(I)
Refinement	Full-matrix least-squares on F^2
Data/restraints/parameters	8664/42/636
Final R indices [I > 2sigma(I)]	*R*1 = 0.0703, w*R*2 = 0.1813
R indices (all data)	*R*1 = 0.1208, w*R*2 = 0.2256
Goodness-of-fit	1.047

3. Result and discussion

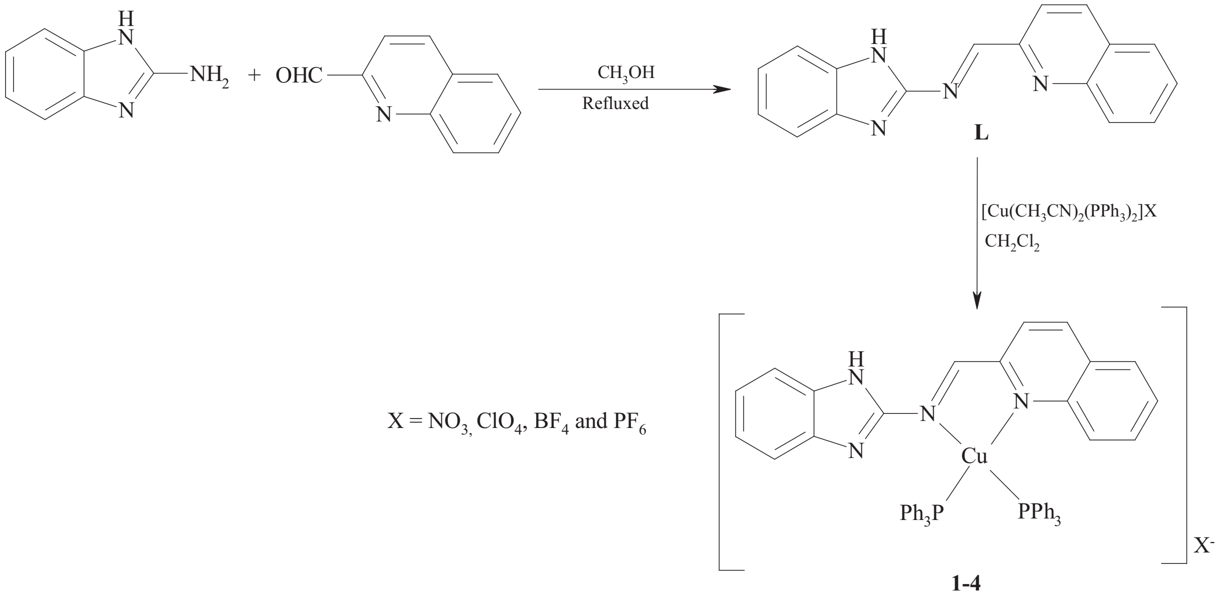
N-(2-quinolynylmethylene)-1*H*-bezimidazole (**L**) was synthesized by the reaction of 2-amino benzimidazole with 2-quinolinecarboxaldehyde. The obtained spectral data, elemental analysis and mass spectra confirm the formation of **L**. The mononuclear copper(I) complexes **1**–**4** possessing **L** and phosphine ligands were prepared (Scheme 1) *via* two simple steps. The complexes $[Cu(\mathbf{L})(PPh_3)_2]X$ (X = NO_3, ClO_4, BF_4 and PF_6) were firstly afforded by the treatment of $[Cu(CH_3CN)_4]X$ (X = NO_3, ClO_4, BF_4 and PF_6) with two equivalent of PPh_3 then one equivalent of **L** was slowly added. The complexes prepared show a good thermal stability and are soluble in common organic solvents such as dichloromethane, chloroform, acetonitrile, THF, methanol, ethanol etc. Composition and identity of all the complexes were deduced from the satisfactory elemental analysis, FTIR, UV–Visible, ^{1}H NMR and ^{13}C NMR spectra and complex **3** by a single crystal X-ray diffraction study. Molar conductivity values of all the complexes in 10^{-3} M solution of CH_2Cl_2 suggest that, they are 1:1 electrolytes indicating anions are not coordinated to the central copper(I) atom. At room temperature all the complexes are diamagnetic which is characteristic of presence of copper(I) (d^{10}).

3.1. Spectral characterization

The IR spectra of free ligand **L** exhibit a band at 3365 cm^{-1} is due to υ(N–H). No significant shift in υ(NH) stretching were observed in the infrared spectra of **1**–**4** in comparison with the free ligand **L** feature non-involvement of the benzimidazole N–H in a possible complexation to the metal ion [27]. On the other hand, the band at 1618 cm^{-1} in the spectrum of **L** which is characteristic of υ(HC=N) vibration shifted to lower frequency by 29–33 cm^{-1} in **1**–**4** indicative of π-back bonding from the electron rich copper(I) ion to vacant π*-orbital of the ligand [28]. The IR spectra of all copper(I) complexes **1**–**4** exhibit an expected band due to the PPh_3 ligand at 1482,1436,695 and 518 cm^{-1}. The strong band at 1375 cm^{-1} and medium intensity band at 821 cm^{-1} in the spectrum of **1** assigned for presence of ionic nitrate in the complexes. The perchlorate complex **2** exhibit a broad band at 1097 ($υ_3$) and strong band at 622 ($υ_4$) suggesting stretching vibration of non-coordinated ClO_4 ion in the complex [29]. A broad band at 1058 cm^{-1} in **3** corresponds to presence of antisymmetric υ(B-F) stretching mode [30]. However, the strong band at 842 cm^{-1} and 562 cm^{-1} in **4** are consistent with presence of PF_6^- anion in the complex [31].

The UV–Vis absorption spectra of the complexes were recorded in CH_2Cl_2 solution (10^{-5} M) at room temperature and are shown in Fig. 1. The free ligand **L** exhibit high energy bands at λ_{max} 282 and 336 nm assigned to π-π* transitions inside **L**. While the copper(I) complexes **1**–**4** exhibited intense high energy absorption bands at 291–294 and 346–352 nm are likely arise due to π-π* (benzimidazoline) and π-π*(phosphine) intra-ligand (IL) transitions. The red shift of π-π* transitions in **1**–**4** compare to free ligand **L** indicating involvement of imine and quinolynyl nitrogen in coordination with copper(I) ion. In addition to these bands, the low energy broad absorption bands observed in all copper(I) complexes at 451–458. This band remain absent in **L** and is assigned to the metal to ligand charge transfer(MLCT) transition from dπ orbital of the copper(I) to the unoccupied π* orbitals of ligand **L** [32]. The complexes **1**–**4** are diamagnetic and hence provide no optical absorption band; no d-d transition is encountered for copper(I) with d^{10} configuration.

The ^{1}H NMR spectra of copper(I) complexes **1**–**4** were recorded in $CDCl_3$ and analyzed on comparing with free ligand value. The free ligand **L** displayed a singlet at δ 9.31 ppm assigned to imine



Scheme 1. Synthetic route of **L** and its copper(I) complexes (**1**–**4**).

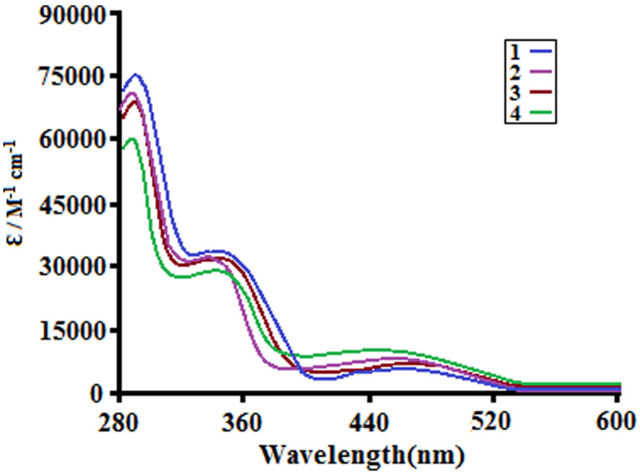


Fig. 1. UV–Visible absorption spectra of **1**–**4**.

(HC=N) proton. In the spectra of **1**–**4**, the signal of imine proton is considerably deshielded and appears as a singlet at around δ 9.48 ppm due to positive charge delocalization on the corresponding C-atom through resonance resulting from the coordination of ligand [33]. Benzimidazole N–H appears as a singlet at 10.26 ppm in **L** is significantly shifted to downfield side at ~11.03 ppm in all copper(I) complexes. However, the broad multiplet appeared in the range δ 7.11–8.49 ppm for **1**–**4** assigned to the PPh_3 protons together with ring protons of ligand **L**.

*3.2. X-ray structure of [(Cu(**L**)(PPh$_3$)$_2$]BF$_4$·CH$_2$Cl$_2$ (**3**)*

The crystals of [(Cu(**L**)(PPh$_3$)$_2$]BF$_4$·CH$_2$Cl$_2$ (**3**) were grown by slow diffusion of diethyl ether into the solution of complex in dichloromethane and its structure was determined by X-ray crystallography. The molecular structure of **3** along with atom numbering scheme is illustrated in Fig. 2 and selected bond lengths and bond angles are collected in Table 2. X-ray analysis reveals that complex **3** crystallizes in triclinic space group with discrete [Cu(**L**)(PPh$_3$)$_2$]$^+$ cation and tetrafluroborate as counter anion with one CH_2Cl_2 molecule, and exhibit a highly distorted tetrahedral geometry around the copper(I) with P_2CuN_2 coordination The dis-

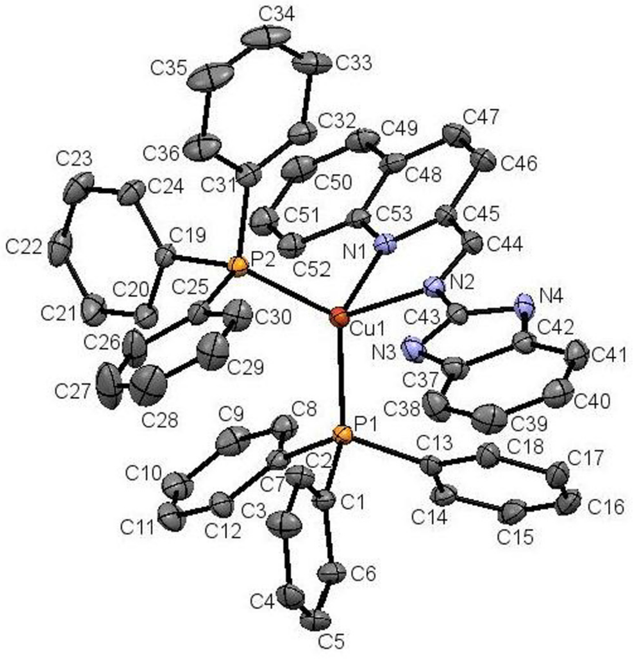


Fig. 2. Molecular structure of [Cu(**L**)(PPh$_3$)$_2$]BF$_4$.CH$_2$Cl$_2$(**3**) showing 50% probability ellipsoids. The hydrogen atoms, counter anion and solvent molecules have been removed for clarity.

Table 2
Selected bond lengths (Å) and bond angles (°) for **3**.

Bond lengths		Bond Angles	
Cu(1)–N(1)	2.121(5)	N(2)–Cu(1)–N(1)	78.19(18)
Cu(1)–N(2)	2.105(5)	N(2)–Cu(1)–P(2)	113.41(14)
Cu(1)–P(1)	2.2707(15)	N(1)–Cu(1)–P(2)	108.04(13)
Cu(1)–P(2)	2.2659(16)	N(2)–Cu(1)–P(1)	110.95(13)
		N(1)–Cu(1)–P(1)	116.16(13)
		P(2)–Cu(1)–P(1)	121.95(6)

torted tetrahedral coordination geometry of copper(I) is completed by imine nitrogen, quinolynyl nitrogen and two phosphorous atoms from two PPh_3 ligands. The largest deviation from the ideal tetrahedral geometry is arises from the restricted bite angle of the chelating ligand. The intra-ligand chelate angles N(2)–Cu(1)–N(1) is much less than 109.4°, being 78.19(18)°. However, the P(2)–Cu (1)–P(1) 121.95 (6) Å angle have open up due to the steric effects from bulky PPh_3 ligands. The average Cu–N and Cu–P bond lengths are 2.113 and 2.2683 Å, respectively and are comparable to those reported for $[Cu(\mathbf{L})(PPh_3)_2]BF_4{\cdot}2CH_2Cl_2$ complexes [2.076 and 2.2591 Å] [34]. The Cu(1)–N(1) (Pyridyl bond length, 2.121(5)° is longer than Cu(1)–N(2) (imine bond length, 2.105(5)°), which means that the intermolecular attraction between Cu(I) center and N(imine) is stronger than that between Cu(I) center and N(quinolynyl) [35]. Torsion angles in the chelating ring are given in Table 3. The chelating ring Cu(1)–N(1)–C(45)–C(44) and Cu(1)–N (2)–C(44)–C(45) are 3.5(6)° and 2.0(7)°. The significant strain in the chelate ring is observed by the deviations from 120° for the angles about the N atom; Cu(1)–N(1)–C(45), Cu(1)–N(1)–C(53), Cu(1)–N(2)–C(44) and Cu(1)–N(2)–C(43) are 112.7(4)°, 129.8(4)°, 113.6(4)° and 125.2(4)°.

In the heteroatomic part of benzimidazoline, the angles N(4)–C (43)–N(2), 126.1(6)°, N(3)–C(43)–N(2), 120.8(5)° and N(3)–C(43)–N(4), 113.1(6)° indicate the sp^3 hybridize state of the carbon atom and the geometry around C(43) can be viewed in terms of a distorted tetrahedral geometry. The two N–C(sp^2) bond distances [N (2)–C(44), 1.267(8)° and N(3)–C(43), 1.301(8)°] show double bond character, while one N(4)–C(43), 1.359(7)° show single bond character. The bond angles around N(3) and N(4) are C(43)–N(3)–C(37), 104.7(5)° and C(43)–N(4)–C(42), 107.1(6)° respectivaly. Further, the tortional angle of N(2)–C(43)–N(3)–C(37) is 179.1(5° indicating an periplanar arrangement.

The crystal packing structure of $[Cu(\mathbf{L})(PPh_3)_2]BF_4$. CH_2Cl_2 (**3)** was given in Fig. 3. In the space packing of **3** there exist plenty of weak H–F bonding between the F(1) atoms of BF_4^- anion and the hydrogen atoms of the phenyl rings of PPh_3 to form supramolecular structure.

3.3. Photoluminescence

The photoluminescence property of ligand **L** and its copper(I) complexes **1**–**4** were studied at room temperature in CH_2Cl_2 solution (10^{-5} M). The emission spectra of **1**–**4** are shown in Fig. 4 and the data are summarized in Table 4. Free ligand **L** emits a green colour centered at λ_{max} = 532 nm with an excitation at 280 nm attributed to fluorescent emission from a ligand centered π-π^* transition. Upon excitation at ~295 nm, complexes **1**–**4** show steady state marked differences in emission behavior at λ_{max} 706, 704, 702 and 711 nm with lifetime of 2.48, 2.51 2.54 and 2.60 ns, respectively. The complexes do not show significant emission when they are excited at their MLCT band maxima, hence the emission band in **1**–**4** may be assigned to the ligand to ligand charge transfer (LLCT) or intra-ligand charge transfer (ILCT) or admixture of them. The enhancement of fluorescence efficiency observed in **1**–**4** may be due to coordination of **L** and PPh_3 ligands to copper(I) ion, which effectively increases the rigidity to the structure of the complexes that restricts vibrational relaxation. Moreover, intermolecular and intramolecular $\pi\cdots\pi^*$ interactions in **1**–**4** along with a large P–Cu–P bite angle may also play a key

Table 3
Torsion angles for chelating ring.

Cu(1)–N(1)–C(45)–C(44)	3.5(6)
Cu(1)–N(2)–C(44)–C(45)	2.0(7)
Cu(1)–N(1)–C(53)–C(52)	−6.0(8)
Cu(1)–N(1)–C(53)–C(48)	172.9(4)
Cu(1)–N(2)–C(43)–N(3)	−14.5(8)
Cu(1)–N(2)–C(43)–N(4)	164.8(5)

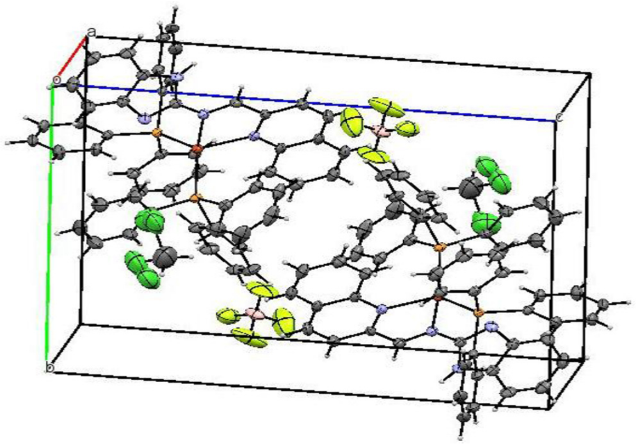


Fig. 3. Perspective view of cell packing in the complex $[Cu(\mathbf{L})(PPh_3)_2]BF_4.CH_2Cl_2$(**3**).

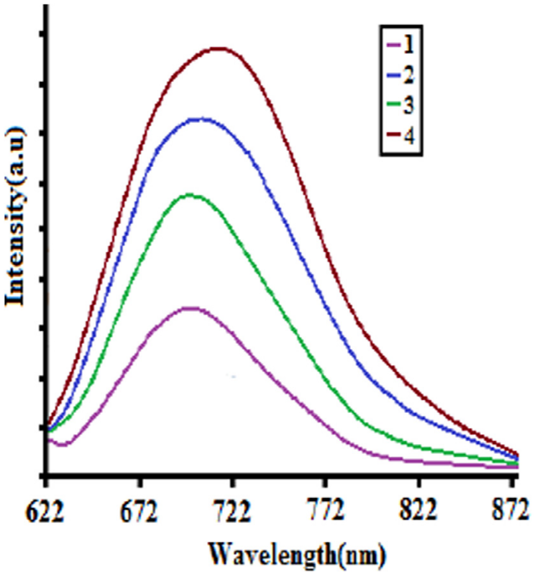


Fig. 4. Emission spectra of **1**–**4**.

Table 4
Emission data of copper(I) complexes in CH_2Cl_2(10^{-5} M) (**1**–**4**).

Complex	λ_{em} (nm)	ϕ	τ (ns)	K_r ($s^{-1}/10^7$)	K_{nr} ($s^{-1}/10^9$)
L	632	0.075	2.12	3.537	0.436
1	706	0.084	2.48	3.387	0.369
2	704	0.092	2.51	3.665	0.360
3	702	0.088	2.54	3.464	0.359
4	711	0.096	2.60	3.692	0.347

Table 5
Electrochemical data for copper(I) complexes (**1**–**4**).

Complex	E_{pa} (V)	E_{pc} (V)	ΔE_p (mV)	$E_{1/2}$ (V)
1	0.741	0.621	120	0.681
2	0.743	0.624	119	0.683
3	0.745	0.629	116	0.687
4	0.751	0.632	120	0.691

Supporting electrolyte: n-Bu_4NClO_4 (0.05 M); complex: 0.01 M; solvent: CH_2Cl_2; $E_{1/2} = 1/2(E_{pa} + E_{pc})$; Scan rate: 50 mV s^{-1}.

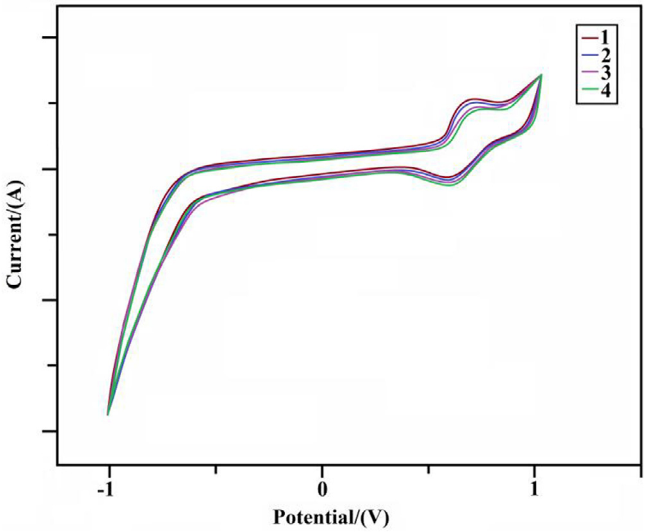
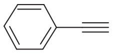
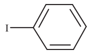
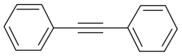
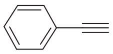
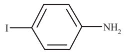
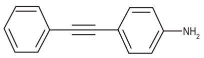
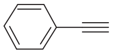
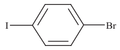
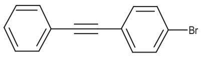


Fig. 5. Cyclic voltammogram of **1**–**4**.

Table 6
Sonogashira coupling reaction of phenylacetylene with aryl halides.

Entry	Phenylacetylene	Aryl halide	Product	Complex	% yield
1.				1	71
2.				2	80
3.				3	76
4.				4	83
5.				1	77
6.				2	84
7.				3	80
8.				4	91
9.				1	66
10.				2	74
11.				3	70
12.				4	79

Reaction conditions: phenylacetylene, 2.5 mmol; aryl halide, 2 mmol; copper(I) catalyst (10 mol%); K_2CO_3 (2 mmol); Toluene, 20 ml; temperature 90 °C; reaction time 16 h.

role for the enhancement of the luminescence behavior of the complexes [36]. It is to be noted that the emission energies of all the complexes (**1–4**) are sensitive to the size of the counter ion, following the sequence $PF_6 > ClO_4 > BF_4 > NO_3$ [37]. These results could be attributed to coordinating ability of the counterion as well as differences in solubility of the complexes in CH_2Cl_2.

The experimental measured τ and ϕ values are used to calculate the radiative k_r and nonradiative k_{nr} rate constants. The k_{nr} values of **1**–**4** show the marked decrease displaying that the rigidity and the size of the counterion play a dominant role in CH_2Cl_2 solution.

3.4. Cyclic voltammetry

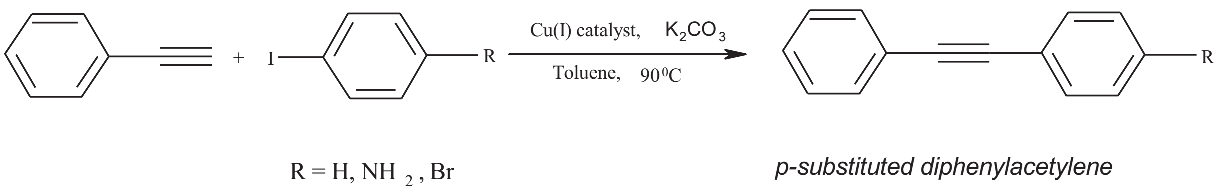
The electrochemical behavior of the copper(I) complexes **1**–**4** was examined cyclic voltammetrically in 0.01 M CH_2Cl_2 solution and the results are displayed in Table 5. The cyclic voltammogram of **1**–**4** are shown in Fig. 5. All copper(I) complexes **1**–**4** displayed oxidative response at 0.741–0.751 V (E_{pa}) corresponding to Cu(I)/Cu(II) oxidation, whilst the potential appeared in the reverse scan at 0.621–0.632 V (E_{pc}) is associated with reduction of Cu(II) to Cu(I). The Cu(I)/Cu(II) redox couple at $E_{1/2} = 0.685$ V for **1**–**4** is also supported by a comparison between cyclic voltammetry experiments of ferrocene which involve Fe (II)/Fe(III) couple occurs in very similar potential range at same scan rate. The ratio of peak current (*Ipc*/*Ipa*) for complexes **1**–**4** is not equal to 1, the values of ΔE_p ($\Delta E_p = E_{pa} - E_{pc}$) ranging from 116 to 120 mV. These results confirm the quasireversible redox behavior of these complexes and are in good agreement with the similar copper(I) complexes reported in the literature [38].

3.5. Catalytic properties

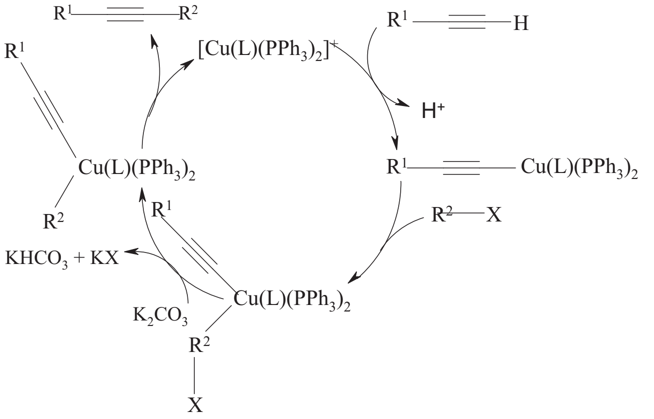
The Pd-catalyzed Sonogashira cross-coupling reaction of terminal alkyne with aryl halides is one of the most powerful and reliable tool for the synthesis of polyfunctional alkyne, which finds extensive applications in pharmaceuticals, dyes, sensors, electronics, polymers, guest-host constructs, natural products and heterocycle synthesis [39–42]. Traditionally, such coupling reaction have been performed with palladium complex catalyst such as $PdCl_2(PPh_3)_2$ or $Pd(PPh_3)_4$ [43]. However, the cost of reagents, removal of trace palladium from late stage synthetic intermediate, and difficulties in coupling of electron-rich or *ortho*-substituted aryl halides are the drawbacks of this method. Copper-catalyzed Sonogahira cross-coupling reaction is another choice of the reaction for the production of alkyne due to their low cost advantage, low toxicity and environmentally benign character. However, most of the copper-catalyzed couplings reported so far are not well defined [44], as they are generated in situ based on copper salt, ligands and additives. Only few papers have been reported to use

Table 7
Microanalytical and spectral data of coupling product.

Compound	C, H, N found (calculated)			IR (cm^{-1})	Mass	^1H NMR (δ ppm)
	C	H	N			
Diphenylacetylene	94.24 (94.34)	5.53 (5.66)	– –	2156	m/z 178 $[C_6H_5C{\equiv}CC_6H_5]^+$, 77 $[C_6H_5]^+$	δ 7.43–7.56, (m, Ar-H)
4-Amino-diphenylacetylene	86.86 (87.01)	5.68 (5.74)	7.34 (7.22)	3413, 3295, 2153	m/z 193 $[C_6H_5C{\equiv}CC_6H_4NH_2]^+$, 178 $[C_6H_5C{\equiv}CC_6H_5]^+$, 77 $[C_6H_5]^+$	δ 7.42–7.68, (m, Ar-H) δ 3.83, (s, 2 H, NH_2)
4-Bromo-diphenylacetylene	65.29 (65.40)	3.48 (3.53)	– –	2156	m/z 257 $[C_6H_5C{\equiv}CC_6H_4Br]^+$, 178 $[C_6H_5C{\equiv}CC_6H_5]^+$, 77 $[C_6H_5]^+$	δ 7.43–7.56, (m, Ar-H)



Scheme 2. Sonogashira coupling of phenylacetylene with aryl halides catalyzed by **1**–**4**.



Scheme 3. Probable mechanistic route for Sonogashira coupling of phenylacetylene with aryl halides using **1**–**4**.

copper complex catalyst for this C–C bond formation process [45,46]. In order to check the catalytic efficiency of copper(I) complexes **1–4**, the Sonogashira coupling reaction of phenylacetylene with aryl halide was carried out using K_2CO_3 as a base and solvent toluene at 90 °C (Scheme 2). Under these reaction conditions, coupling reactions of phenylacetylene with aryl halides proceeded very smoothly by attaining the desired diphenylacetylene product in high yields. The isolated product was characterized by elemental analysis, IR, ^1H NMR and mass spectral studies (Table 7). When no catalyst was added, the blank reaction in solvent toluene and K_2CO_3 as base exhibited extremely low reactivity results into decrease in yield of diphenylacetylene with many byproducts. The catalytic efficiency of **1**–**4** was compared with the previously reported [47] similar type of copper(I) complexes and it was found that all reactions proceeded at relatively low temperature and reached the yield of diphenylacetylene up to 66–91% (Table 6). With iodobenzene the coupling yield reached up to 71–83% (Table 6, entries 1–4). With 1-bromo-4-iodoaniline containing electron withdrawing group at *para* position, the coupling yield was observed up to 66–79% (Table 6, entries 9–12). However, with 4-iodoaniline containing electron donating NH_2 group at para position, the coupling reaction proceeds with considerable increase in the yield up to 77–91% (Table 6, entries 5–8). These results confirmed that the variety of functional groups such as bromo and amino tolerated on aryl halide component and significant electronic effect was observed for substituted aryl halide containing electron donating group at *para*-position. It was also observed that the copper(I) complexes with different counter anions exhibit different activities. It is evident that the copper(I) complex with PF_6^- ion exhibit higher catalytic activities than the complexes with ClO_4^-· BF_4^- and NO_3^- as their counter anions and follow the sequence $PF_6^- > ClO_4^- > BF_4^- > NO_3^-$. These results could be attributed to difference in coordinating ability of counterion with metal ion as well as difference in solubility of the complexes in solvent during the reaction.

The probable mechanism for the coupling of phenylacetylene with aryl halides using present complexes **1**–**4** is illustrated in Scheme 3. At first copper(I) complex activates C–H bond of the terminal alkyne to form a copper-acetylide intermediate (species I), which on oxidative addition of aryl halide leads to formation of species II. The species II again activated in presence of base to give species III which undergoes reductive elimination to give diphenylacetylene and regenerate corresponding copper(I) catalyst.

4. Conclusion

In conclusion, a series of mixed ligand copper(I) complexes have been prepared by the reaction of *N*-(2-quinolynylmethylene)-1*H*-benzimidazole with $[Cu(MeCN)_2(PPh_3)_2]NO_3$, $[Cu(MeCN)_2(PPh_3)_2]ClO_4$, $[Cu(MeCN)_2(PPh_3)_2]BF_4$, $[Cu(MeCN)_2(PPh_3)_2]PF_6$ and characterized. Complex $[Cu(\mathbf{L})(PPh_3)_2]BF_{4.}$ CH_2Cl_2 (**3**) crystallizes in a triclinic space group *P*-1 and show a distorted tetrahedral geometry around copper(I). The quasireversible redox process ($E_{1/2}$ = 0.685 V versus $Fc^{0/+)}$ attributed to Cu(I)/Cu(II) couple. The complexes exhibit red emission, and complex **4** shows highest emission intensity in CH_2Cl_2 solition. The emission observed in all complexes primarily related to ligand charge transfer (LLCT) or intra-ligand charge transfer (ILCT) or mixture of them. These complexes have been successfully employed as a catalyst for the sonogashira coupling of phenylacetylene with aryl halides at low temperature. The differences in size of the counterions in the complexes have a marked effect on catalytic properties of the complexes.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.ica.2017.05.076.

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