Synthesis of benzo[b]phosphole-based alkynylgold(I) complexes with resistive memory properties modulated by donor–acceptor chromophores

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Abstract
A class of benzo[b]phosphole-based alkynylgold(I) complexes has been synthesized and characterized. These complexes share a similar benzo[b]phosphole ligand, in which the phosphole moiety is substituted with various π-conjugated units with different donor strengths, namely phenoxazinylphenyl, tris(di-tert-butylcarbazolyl)phenyl and 2,4-dimethylphenyl moieties. These phosphole-containing gold(I) complexes are found to be strongly luminescent in toluene with tunable emission maxima and possess solvatochromic behaviors, suggesting an emission of metal-perturbed intraligand charge transfer origin. Cyclic voltammetry studies reveal that the presence of gold(I) metal center strongly perturbs the electronic properties of the phosphole moiety of the resultant complexes, which can be further fine-tuned by the auxiliary ligand on the gold(I) center. In the resistive memory studies, devices based on these alkynylgold(I) complexes exhibit satisfactory binary memory behaviors, demonstrating low threshold voltages in narrow distributions, high durability and low misreading rates. Such performances are believed to be originated from a field-induced charge transfer of the alkynylgold(I) complexes, in which the electron-accepting phosphole-gold(I) unit plays a crucial role in stabilizing the charge transfer state and that led to the observed resistive switching and memory behavior.

KEYWORDS
alkynylgold(I) complexes, benzo[b]phosphole, charge transfer, donor–acceptor, resistive memories
1 | INTRODUCTION

Organometallic complexes with charge transfer moieties have gained a lot of attention in the design of functional materials and organic electronics. With a judicious structural design, the electronic properties of these molecular complexes can be readily tuned to perform different functions. Possessing various charge transfer characters including metal-to-ligand charge transfer (MLCT), ligand-to-ligand charge transfer (LLCT), and metal-perturbed intraligand charge transfer (ILCT), organometallic complexes with donor-acceptor groups have been successfully utilized as active materials of highly functional organic electronics, such as dye-sensitized solar cells (DSSCs), organic field-effect transistors (OFETs), and organic light-emitting diodes (OLEDs). Meanwhile, the growing demand for the search of high-density electronic memory materials has also led to a surge of attention in charge-neutral transition metal complexes as the active materials of resistive memories. With the early works on resistive memory devices based on coordination metal complexes, there has been a growth of interest in the design of organic and organometallic complexes with rich charge transfer characters for applications in functional resistive memory devices.

Amongst various metal complex systems, alkynylgold(I) complexes with two-coordinate linear geometry have been shown to possess rich photophysical properties and have been extensively studied. Some of these alkynylgold(I) complexes are stable in ambient conditions to serve as metal-containing functional materials for various applications, including luminescent materials, cation sensors, optical power limiting materials, and more recently, resistive memory devices.

On the other hand, phosphole, being an organic molecular compound or as a ligand for coordination to various transition metal centers, has received increasing research interests in the past decade. Desirable properties, such as tunable electrochemical characteristics, facile molecular functionalization and intermolecular packing have been observed in various classes of phosphole moieties, allowing the design of smart materials in the fields of organic electronics, photochromism, chemosensing, and supramolecular chemistry. Recent examples have also shown that the incorporation of electron-accepting phosphole oxide unit can lead to favorable effect on the resultant organic resistive memories, including the lowering of turn-on voltage ($V_{on}$), stabilization of the resistive states and generation of multilevel memory behavior. These attractive spectroscopic properties and potential functionalization by the integration of the gold(I) metal center and alkynyl moieties into the phosphole framework may warrant an exploration of this class of complexes to function as resistive memory materials, given the tunability of the phosphole acceptor ability by the Lewis acidity of Au(I) and its possible perturbation and fine-tuning via the incorporation of various auxiliary alkynyl ligands. Herein, a series of benzo[b]phosphole-containing alkynylgold(I) complexes have been designed, synthesized and characterized. The π-conjugated backbone of the phosphole ligand has been systematically varied to tune the donor–acceptor charge transfer character of the alkynylgold(I) complexes. By correlating the photophysical, electrochemical and resistive memory properties of the complexes, it is envisaged that the current work would offer insights for the investigation of resistive memory properties of organometallic complexes with donor–acceptor moieties.

2 | RESULTS AND DISCUSSION

2.1 | Synthesis and characterization of the benzophosphole oxides (BPO) and alkynylgold(I) complexes

Benzophosphole oxides BPO1-3 were synthesized by standard Stille coupling of BPO–SnBu$_3$ (BPO = 1-phenyl-1H-benzo[b]phosphole-1-oxide) and the respective aryl bromides (Scheme S1). The phosphole ligand of the gold(I) complexes were generated in situ by reduction of the phosphole oxides with trichlorosilane. Metalation with [Au(th)Cl] led to the chlorogold(I) precursor complexes. The target phosphole-containing alkynylgold(I) complexes 1–5 were then successfully synthesized by reacting phenylethylene or 9-(4-((trimethylsilyl)ethynyl)phenyl)–3,6-di-tert-butyl-9H-carbazole with the corresponding chlorogold(I) precursor complexes in dichloromethane–methanol (1:1 v/v) mixture in the presence of KO'Bu (Scheme S2). All benzo[b]phosphole oxides BPO1–3 and target alkynylgold(I) complexes 1–5 (Scheme 1) are stable in ambient conditions and soluble in common organic solvents such as dichloromethane, toluene and acetone. The characterization data of the target compounds, including those from $^{1}$H and $^{31}$P($^{1}$H) NMR spectroscopy and high-resolution electrospray ionization (HR-ESI) mass spectrometry, are in good agreement with their structures.

2.2 | Photophysical studies

The electronic absorption and emission spectra of the benzo[b]phosphole oxides BPO1–3 and target complexes 1–5 are recorded in toluene solution at 298 K (Table 1). In general, the gold(I) complexes and the
benzo[b]phosphole oxides (Figures 1A and S1A) are found to absorb at ca. 315–350 nm with extinction coefficients ($\varepsilon$) in the order of $10^3$–$10^4$ dm$^3$ mol$^{-1}$ cm$^{-1}$, which can be tentatively assigned as the intraligand (IL) $\pi$–$\pi^*$ transitions of the ligands.$^{44,54,61}$ The high-energy absorption bands at ca. 290–320 nm for BPO1, BPO2, and complexes 1–3 and 5 are characteristic of the n–$\pi^*$ transitions of the corresponding N-donor moieties.$^{62,63}$ The lowest-energy electronic absorption bands of the compounds containing N-donor moiety (BPO1, BPO2, and 1–3) are found to be structureless and are shifted bathochromically with increasing electron-donating strength on going from tris(di-tert-butylcarbazolyl)phenyl to the phenoxazinylphenyl moiety. Considering the donor–acceptor (D–A) structure of these compounds, together with the absence of this low-energy band in the dimethylphenyl-substituted benzo[b]phosphole counterparts (BPO3, and complexes 4, 5), the low-energy absorption bands of BPO1, BPO2, and 1–3 are assigned to be originated from the IL $\pi$–$\pi^*$ transitions of the benzo[b]phosphole ligand with substantial mixing of intramolecular charge transfer (ICT) and metal-perturbed ILCT transitions, respectively, from the electron-donating N-donor unit to the benzophosphole oxide or the benzo[b]phosphole–gold(I) moiety. Complex 2, with the coordination of an electron-rich 4-(di-tert-carbazolyl) phenylethynyl ligand, also shows a mixing of alkynyl-to-phosphole LLCT character. The similar charge transfer absorption features of the benzo[b]phosphole oxides and the alkynylgold(I) complexes suggest that the gold(I) metal

**Scheme 1** Molecular structures of target aryl-substituted benzo[b]phosphole oxides and benzo[b]phosphole-containing alkynylgold(I) complexes
center can effectively change the electron-donating nature of the free phosphole ligand to an electron-deficient benzo-
[b]phosphole-gold(I) moiety, with electron-accepting ability comparable to that of the phosphole oxides. For complexes 4 and 5, due to the replacement of the strong N-donors on the benzo[b]phosphole ligand with the weaker electron-donating dimethylphenyl moiety, the low-energy absorption band centered at ca. 330 nm is tentatively assigned to be predominantly gold(I)-perturbed IL π-π* transitions of the benzo[b]phosphole moiety, with mixing of alkynyl-to-phosphole LLCT transitions that have been obscured by the intense IL bands.

In toluene solution at 298 K, all phosphole oxides BPO1–3 and alkynylgold(I) complexes 1–5 are found to be emissive upon excitation at λ ≥ 350 nm (Table 1). All the compounds display structureless emission bands with emission maxima spanning from 414 to 576 nm with emission lifetimes in the nanosecond regime, suggesting the singlet origin of the excited state. The variation of the aryl substituent at the α-position of the phosphorus atom on the phosphole moiety has been shown to affect the emission maxima (Figures 1B and S1B) and the photoluminescence quantum yields (PLQY) of the compounds significantly (Table 1). Similar to the observations in the absorption spectra, the more electron-donating phenoxazinylphenyl moiety would lower the energies of the emission band. Thus, the emissions of the compounds are assigned as originated from the 1IL π-π* (phosphole) excited state with mixing of 1ILCT character from the N-donor moiety to the electron-deficient phosphole-gold(I) moiety.

| Compound | Absorption λmax (nm) (ε [dm³ mol⁻¹ cm⁻¹]) | Emission λmax (nm)ᵇ | τ [ns] | Φlumᶜ |
|----------|-----------------|------------------|------|-----|
| PHEN–OXZ–C₆H₄–BPO (BPO1) | 321 (54,900), 335 (58,630), 423 (11,110) | 574 (0.8) | 0.09 |
| (1Bu₂CBZ₃)C₆H₂–BPO (BPO2) | 299 (73,540), 326 (40,850), 341 (39,870), 405 (21,240) | 513 (3.1) | 0.39 |
| Me₂C₆H₄–BPO (BPO3) | 316 (7,940), 335 (8,810) | 414 (4.8) | 0.71 |
| [Au(C≡C-Ph)(PHEN–OXZ–C₆H₄–BP)] (1) | 337 (64,440), 405 (10,840) | 557 (0.5) | 0.02 |
| [Au(C≡C–C₆H₄–1Bu₂CBZ) (PHEN–OXZ–C₆H₄–BP)] (2) | 300 (74,850), 325 (79,420), 429 (10,900) | 576 (0.4) | 0.02 |
| [Au(C≡C–Ph)[(1Bu₂CBZ₃)C₆H₂–BP]] (3) | 297 (90,240), 328 (42,840), 342 (40,270), 392 (20,480) | 506 (2.1) | 0.21 |
| [Au(C≡C–Ph)(Me₂C₆H₃–BP)] (4) | 329 (12,390) | 417 (2.4) | 0.51 |
| [Au(C≡C–C₆H₄–1Bu₂CBZ)(Me₂C₆H₃–BP)] (5) | 297 (28,100), 314 (16,400), 334 (12,100) | 417 (2.2) | 0.49 |

ᵃMeasured in toluene solution at 298 K.
ᵇExcited at ≥350 nm.
ᶜRelative PLQY, measured at 298 K using a solution of quinine sulfate in 0.5 M H₂SO₄ as a standard.

![Figure 1](image-url)
The solvatochromic properties of BPO2 and complex 3 have been investigated as representative examples to elucidate the charge transfer properties of this series of compounds (Table S1). Upon increasing solvent polarities, the low-energy absorption band of the complex 3 is found to be slightly blue-shifted with increasing solvent polarities (Figure S2), while the emission profiles are found to display a pronounced bathochromic shift (Figure 2). Their emission energies in wavenumber (cm\(^{-1}\)) in various solvents are plotted against the Dimroth’s solvent parameters,\(^{64}\) and the Stokes shifts derived from the spectra in various solvents are also plotted against the orientation polarization (\(f\)) according to the Lippert-Mataga\(^{65,66}\) model (Figures S3 and S4).

### 2.3 | Electrochemical studies

The electrochemical properties of the phosphole oxides and the gold(I) complexes have been studied by cyclic voltammetry (CV) in dichloromethane solution with 0.1 M \(\text{^nBu}_4\text{NPF}_6\) as the supporting electrolyte at room temperature.

The gold(I) complexes are found to display one irreversible reduction wave at \(-1.67\) to \(-1.78\) V (vs. standard calomel electrode, SCE). Similar to the behavior of other reported benzo[b]phosphole-gold(I) complexes, this reduction process is assigned as the one-electron reduction of the benzo[b]phosphole ligand.\(^{41}\) Results from the CV measurements are tabulated in Table 2. The cyclic voltammograms have been depicted in Figures 3 and S5. Interestingly, the phosphole ligands of the gold(I) complexes are reduced at similar potentials as the corresponding phosphole oxides BPO1–3. Such observation suggests that the benzo[b]phosphole–gold(I) and benzo[b]phosphole oxide moieties possess similar electron-acceptor properties, which corroborates with the results of the photophysical studies.

In the oxidative scan, only BPO3 does not show oxidation waves within the solvent window of dichloromethane, which is ascribed to the lack of strong electron-donating moiety in the molecular structure. On the other hand, the other compounds display irreversible oxidation waves. Straight lines with good correlations are obtained in all the plots, supporting the charge transfer nature of the excited states.

### Table 2 | Electrochemical data of phosphole oxides BPO1–BPO3 and alkynylgold(I) complexes 1–5

| Compound | Oxidation \(E_{1/2} \ [\text{V}^0 \text{ vs. SCE}] (\Delta E_p \ [\text{mV}]) \) | Reduction \(E_{1/2} \ [\text{V}^0 \text{ vs. SCE}] (\Delta E_p \ [\text{mV}]) \) |
|---|---|---|
| PHEN–OXZ–C\(_6\)H\(_4\)–BPO (BPO1) | +0.74 (63) | −1.66 (71) |
| (\(\text{^tBu}_2\text{CBZ}_3\))C\(_6\)H\(_2\)–BPO (BPO2) | +1.18 (70), [+1.43], [+1.77] | −1.58 (67) |
| Me\(_2\)C\(_6\)H\(_3\)–BPO (BPO3) | \(\text{e}\) | −1.72 |
| [Au(C≡C–Ph)(PHEN–OXZ–C\(_6\)H\(_4\)–BP)] (1) | +0.78 (72), [+1.89] | −1.74 |
| [Au(C≡C–C\(_6\)H\(_4\)–^tBu\(_2\)CBZ)] (PHEN–OXZ–C\(_6\)H\(_4\)–BP)] (2) | +0.79 (66), +1.26 (89) | −1.67 |
| [Au(C≡C–Ph)(\(\text{^tBu}_2\text{CBZ}_3\))C\(_6\)H\(_2\)–BP)] (3) | +1.21 (77), [+1.50], [+1.89] | −1.71 |
| [Au(C≡C–Ph)(Me\(_2\)C\(_6\)H\(_3\)–BP)] (4) | [+1.92] | −1.77 |
| [Au(C≡C–C\(_6\)H\(_3\)–^tBu\(_2\)CBZ)(Me\(_2\)C\(_6\)H\(_3\)–BP)] (5) | +1.21 (62) | −1.78 |

*a in dichloromethane solution with 0.1 M \(^nBu\_4\text{NPF}_6\) as supporting electrolyte at room temperature; scan rate = 100 mV s\(^{-1}\).

\(E_{1/2} = (E_{pa} + E_{pc})/2; E_{pa}\) and \(E_{pc}\) are peak anodic and peak cathodic potentials, respectively; \(\Delta E_p = |E_{pa} − E_{pc}|\).

\(\text{Irreversible oxidation wave; } E_{pa}\) refers to anodic peak potential.

\(\text{Irreversible reduction wave; } E_{pc}\) refers to cathodic peak potential.

*No observable oxidation waves.
or quasi-reversible oxidation waves characteristic of the phenoazine, di-tert-butylcarbazole and phenylethynyl moieties. In particular, 1, 2 and BPO1 display a quasi-reversible oxidation wave at +0.73 to +0.79 V versus SCE, corresponding to the one-electron oxidation of the phenylphenoazine moiety. 3 and BPO2 display a quasi-reversible first oxidation couple (at +1.17 to +1.21 V vs. SCE) and consecutive irreversible oxidation waves (at +1.43 to +1.77 V vs. SCE), which can be assigned to the oxidation processes of the tris(di-tert-butylcarbazolyl)phenyl moiety. For complexes with the (di-tert-butylcarbazolyl)phenylethynyl ligand (2 and 5), they are found to display a quasi-reversible oxidation couple at +1.21 to +1.26 V versus SCE, which is attributed to the one-electron oxidation of the di-tert-butylcarbazole moiety. On the other hand, for the complexes possessing a phenylethynyl as the alkynyl ligand, the irreversible oxidation at +1.81 to +1.92 V versus SCE of complexes 1, 3, and 4 is attributed to the phenylethynyl-based ligand-centered oxidation. These potentials also reflect the stronger electron-donating strength of the phenoazine moiety than that of the di-tert-butylcarbazole moiety, which agrees with the photophysical studies where a bathochromic shift of the absorption and emission profiles are observed on going from complexes 3 to complexes 1 and 2.

In addition, it is found that the optical and the electrochemical bandgaps of complexes 1–3 are in good agreement (Table S2), while the bandgaps estimated from the photophysical and electrochemical data of dimethylphenylbenzo[b]phosphole-based complexes 4 and 5 are less comparable. To investigate the difference between these complexes, density functional theory (DFT) and time-dependent DFT (TDDFT) calculations have been performed on complexes 1–5. In particular, the lowest-energy absorption bands of complexes 1–3 are found to correspond to the HOMO → LUMO transitions (Table S3, Figures S6–S9), which are originated from the intramolecular charge transfer transition from the N-donor to benzo[b]phosphole-gold(I) moiety (Figures 4–6). On the contrary, the lowest-energy absorption bands of complexes 4 and 5 are found to correspond to the transitions involving molecular orbitals mainly localized on the phosphole-gold(I) units (Figures S10–S13). Furthermore, the HOMOs of 4 and 5 are found to be localized on the alkynylgold(I) moiety. Thus, the discrepancy of the optical and electrochemical band gap of 4 and 5 can be attributed to the fact that the HOMO and LUMO of these complexes are centered on the alkynyl and phosphole ligand respectively, while the optical transitions of the complexes are dominated by the metal-perturbed IL(phosphole) transition that obscures the alkynyl-to-benzo[b]phosphole LLCT transition.

2.4 Resistive memory studies

All the complexes 1–5 have been employed as active materials of resistive memory devices. For the construction of the device, the complex is first spin-coated on an indium–tin oxide (ITO) glass, followed by sequential vacuum-deposition of a thin layer (ca. 5 nm) of LiF and aluminum top electrode. The corresponding layer thicknesses of the device based on 3 are determined by scanning electron microscopy (SEM). From the SEM image (Figure S14), the device is found to have uniform active layer and thermally deposited Al electrode of ca. 120 and 100 nm, respectively.

The memory performances of all the devices are summarized in Table 3. Representative current–voltage (I–V) characteristics, retention times of the high-conductivity (ON) and low-conductivity (OFF) states, and bar charts of the distribution of the turn-on voltages (V_{TH}) of binary memory devices fabricated with complex 3 have been depicted in Figures 7–9. As shown in Figure 7, when the...
applied voltage is swept from 0 to 5 V (Sweep 1), the device based on 3 is found to display a sharp increase in current from $10^{-7}$ A to $10^{-3}$ A at a switching threshold voltage ($V_{\text{Th}}$) of ca. 2.8 V. This switching process represents the "writing" process of the memory device from the OFF state to the ON state. The device is found to remain in the ON state during the second sweep (Sweep 2) from 0 to 5 V and a reverse sweep from 0 to −5 V (Sweep 3). After turning off the power supply for several hours, the ON state of the devices can be relaxed to the OFF state, and the binary memory behavior can be repeated. In addition, with a constant voltage stress of 0.9 V as the "read" voltage for over 15,000 s, a high ON/OFF current ratio of $10^4$ is retained with no observable degradation (Figure 8), suggesting the durability of the memory device and a low misreading rate. By studying the cell-to-cell performance on 15 individual devices fabricated with 3, the corresponding $V_{\text{Th}}$ values are distributed narrowly in the range
of 2.4–3.0 V (Figure 9). Similar $I-V$ performances, stabilities of the different conductivity states and distributions of the cell-to-cell performance have also been observed in the as-fabricated devices using 1 and 2 as the active components. Based on these observations, the resistive memory devices fabricated from these complexes can be regarded as static random access memory (SRAM), similar to the assignment in some previously reported devices.\textsuperscript{14,67} On the other hand, the devices based on 4 and 5, where the phosphole ligand of the gold(I) complexes is substituted with 2,5-dimethylphenyl moiety, no resistive memory effect has been observed (Figure S15). Based on these observations and given 5 nm of LiF has been applied as an interlayer to avoid the migration of Al$^{3+}$ ions from the cathode to the active layer, the origin of the resistive memory effect should arise from the donor–acceptor charge transfer character of the phosphole-containing gold(I) complexes.

To correlate the memory performances with the electrochemical properties of the complexes, the energy levels of the HOMO and LUMO of the complexes are estimated from the electrochemical data obtained in Section 2.3 and are summarized in Table S9. With respect
to the energy level distributions of 1–3 (Figure S16), the energy differences between the work function of ITO electrode and the HOMOs are smaller than the differences between the LUMOs and the work function of aluminum electrode, suggesting that the hole injections from the ITO electrode to the active layers have probably dominated the conduction processes of the memory devices. It is believed that the resistive switching of these memory devices is based on a field-induced charge transfer (CT) process.67,68 Judging from the molecular structures of 1–3, the charge transfer character of these complexes is likely to be originated from the electron-donating N-donor unit to the phosphole-gold(I) electron acceptor moiety. The formation of the stable and highly conductive CT states of molecules in the active layer can account for the low resistance of the ON state. Also, the switching threshold voltages of the resistive memory devices are found to be following the same trend as the corresponding electrochemical bandgaps of 1–3 (Table S9), supporting that the electrochemical properties of the complexes could play an important role in perturbing the parameters of the devices. On the contrary, the less electron-donating dimethylphenyl unit would remove the resistive memory property of complexes of 4 and 5 due to the reduced charge transfer character, which corroborates with the lack of ILCT characters observed in the photophysical studies.

Comparing the resistive memory devices from 1–3 with the previously reported devices based on trinuclear triindole-containing alkynylgold(I) complexes,15 the current devices, despite having larger switching voltages, display comparable ON/OFF current ratios, and potentially slightly longer retention times from >10,000 s of the trinuclear alkynylgold(I)-based devices to >15,000 s of the current phosphole-Au(I)-based devices. In addition, while both sets of devices display SRAM behavior, the time for the retention of the ON state after removing the power supply has been improved (from ca. 30 min to at least several hours). The differences in the origin of the electrical bistability of these devices, namely the field-induced CT origin of the phosphole-Au(I) complex-based devices versus the charge-trapping origin of the triindole moiety of the trinuclear alkynylgold(I) complexes,15 have led to their differences in switching voltages, retention times, relaxation times and the stability of the devices.

3 CONCLUSION

A series of benzo[b]phosphole-based alkynylgold(I) complexes have been synthesized and characterized. These complexes share a similar benzo[b]phosphole ligand, in which the phosphole moiety are tethered to π-conjugated
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CONFLICT OF INTERESTS

The authors declare no conflict of interest.

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