Bifunctional cross-conjugated luminescent phosphines and phosphine derivatives: *phospha*-cruciforms†

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Cross-conjugated bifunctional species including a phosphine, phosphine oxide, phosphine sulfide, phosphonium salt, phosphorus ylide and a gold(I) phosphine complex have been prepared. The photophysical characteristics of the series of compounds have been determined experimentally and are discussed/compared with simpler analogues lacking cross-conjugated branches and rationalized on the basis of DFT calculations.

Introduction

Optical properties of transition metal complexes have been of interest since the dawn of coordination chemistry, when Werner classified complexes on the basis of their color.[1,2] In more recent years, the role of chromophoric ligands in the photochemistry of transition metal complexes has been an ongoing area of interest, and chromophore-modified complexes have found use in diverse applications ranging from triplet emissive materials and light-emitting diodes (LEDs)[3-8] to nonlinear optics (NLO)[9-15] and photocatalysis.[16-20] Because of the interest in the photophysics of transition metal complexes[21] and the widespread utility of phosphine ligands in coordination chemistry,[22] it is surprising that there have been relatively few studies on transition metal complexes with visible absorbing/emitting phosphine ligands (though there are numerous phosphole complexes).[23] One reason for this may be the added synthetic challenges of phosphorus chemistry and the air sensitive, sometimes pyrophoric nature of intermediate compounds used in the preparation of phosphines. Nonetheless, significant recent progress has been made in the development of phosphorus-containing small molecule chromophores[24-27] and π-conjugated polymers[28-30] (*i.e.*, Chart 1A), and this growing field has recently been comprehensively reviewed.[25] The development of phosphorus-containing chromophores provides intriguing possibilities for their utility as ligands. Some examples of the relatively limited number of fluorescent or visible-absorbing chromophore-modified phosphine complexes that have been studied are shown in Chart 1B.[26,27,31-34] Another interesting and potentially useful aspect of phosphorus-containing systems is that a variety of phosphine derivatives can be prepared with phosphorus in +3 or +5 oxidation states, allowing access to various interchromophore geometries about the phosphorus center, as well as a range of electronic perturbations on attached π-systems.[26,35]

We recently reported luminescent metallopolymers polymerized through a chromophoric diphosphine (**LHP1**, Chart 1A) that displays visible-wavelength absorption and emission.[27] **LHP1** was readily prepared using air-stable, crystalline (4-iodophenyl)P(O)Ph_2 as a versatile precursor amenable to Pd-catalyzed coupling to various chromophores under mild conditions at room temperature. Following this work, we have become interested in visible-absorbing/emitting phosphines with a variety of absorption and emission properties for the preparation of additional organophosphorus species, photophysically interesting phosphine-metal complexes and emissive coordination polymers.

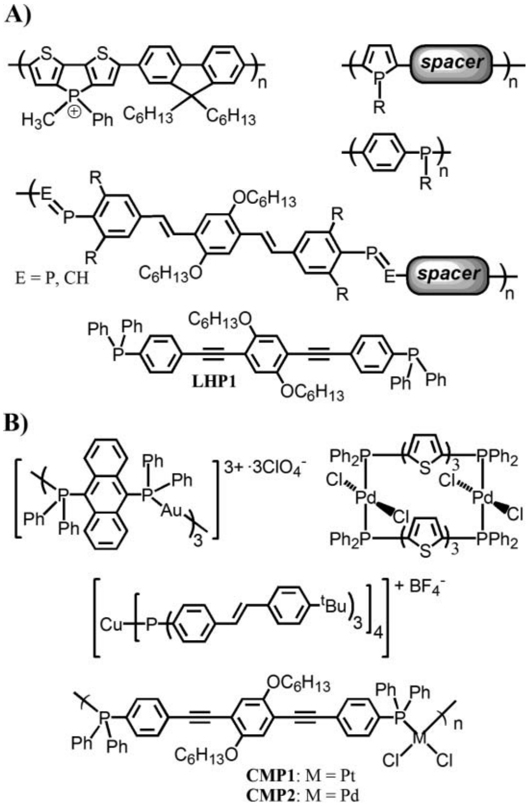

Chart 1

A relatively new class of photochemically interesting materials is comprised of materials featuring multiple π-systems that overlap at a central junction. Chromophores with such cross-conjugated

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branches,[36-40] sometimes called cruciforms,[41-45] are a class of molecules that can exhibit the unusual feature of having HOMOs and LUMOs that are geometrically separate. Some examples pertinent to the current study are shown in Chart 2. Certain conjugated polymers have also shown geometrically separate HOMO and LUMO levels.[46,47] By appending stimuli-responsive functionalities to cross-conjugated constructs, the energy of one frontier orbital may be perturbed while that of the other remains fairly constant. Researchers have taken advantage of this property to rationally design sensors with anticipated responses characterized by a larger signal transduction relative to that observed from traditional π-conjugated chromophores.[44,48-51]

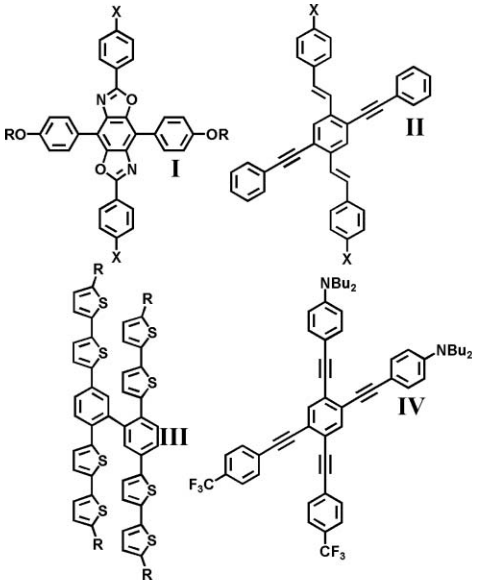


Chart 2

The particularly impressive success of cruciform-type molecules for metal-ion detection, coupled with our ongoing interest in unique chromophoric ligands for coordination control and materials assembly[52-54] have lead us to explore cross-conjugated diphosphines. Herein, we describe the preparation of phosphorus(III) and (V)-bearing cruciforms and a gold complex (Schemes 1 and 2), with accompanying photophysical characterization and density functional theory calculations.

Table 1 Select properties of **8-13** and model **M1**

	$\lambda_{\pi-\pi^*}$	log ε	$\lambda_{\text{emit}'}$/nm	Φ	^{31}P NMR (ppm)
8	325.0	5.19	418.5	0.415	29.3
9	330.0	5.27	419.4	0.049	–4.3
10	330.0	5.12	449.4	0.217	22.6
11	330.0	5.33	423.3	0.294	33.7
12	325.0	4.99	422.5	0.405	43.7
13	320.0	—	406.0	—[a]	20.5
M1	322.4	5.50	394.4	0.773	none

[a] Quantum yield too low to accurately measure.

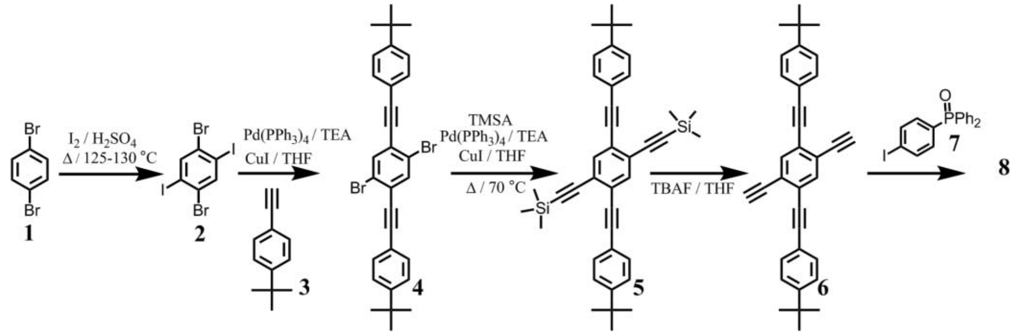
Results and discussion

Synthesis

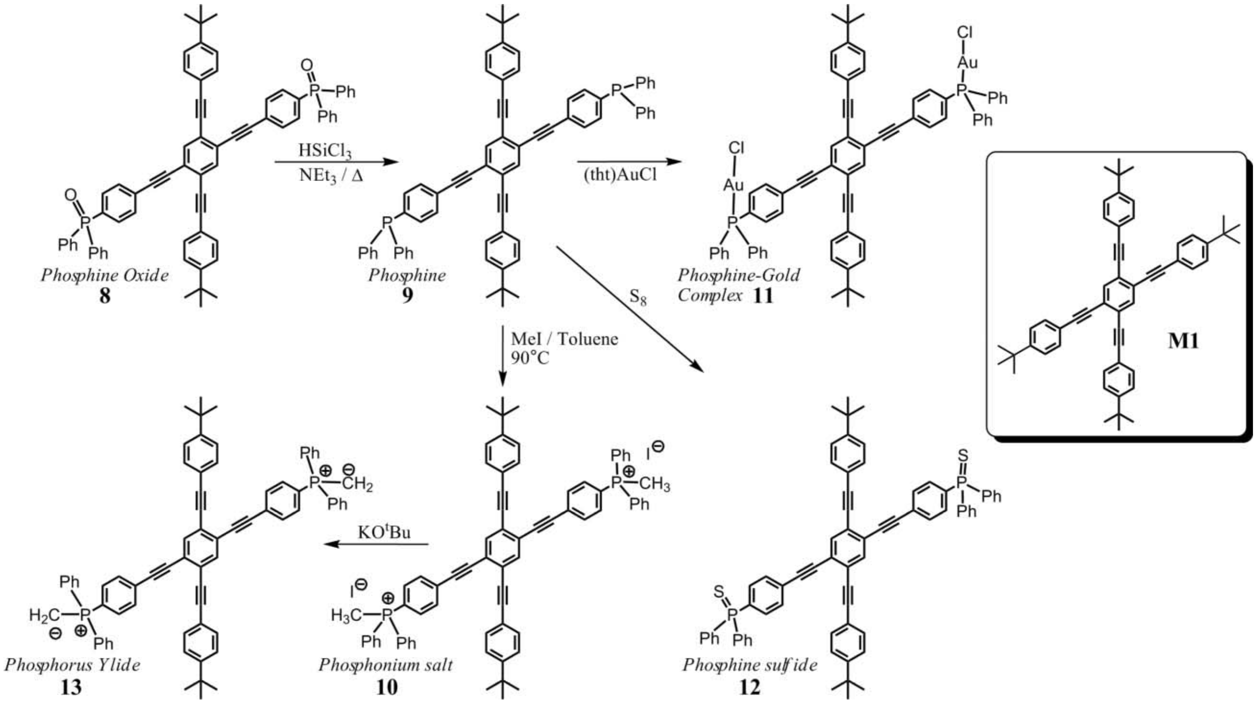
The first *phospha*-cruciform, phosphine oxide **8** (46%), was prepared from **7**[27] and commercial precursors *via* the procedure outlined in Scheme 1, culminating in Sonogashira-Miyaura type coupling of **6** and **7** to create the cross-conjugated cruciform architecture and install the phosphorus center. With **8** in hand, transformation to other phosphorus-bearing species proceeded smoothly by classic methods (Scheme 2). Reduction of **8** to phosphine **9** was affected by the action of $HSiCl_3$ in toluene in 52% yield. Compound **9** was readily converted to phosphonium salt **10** (62%) by reaction with methyl iodide, to the gold complex **11** (89%) by reaction with (tht)AuCl (tht = tetrahydrothiophene), and to phosphine sulfide **12** (69%) *via* reaction with S_8. All of these compounds were found to have good air stability in the solid state, though samples of phosphine **9** in solution were observed to slowly transform to oxide at rates comparable to PPh_3 (as gauged by ^{31}P NMR spectroscopy). We attempted to convert phosphonium salt **10** to the phosphorus ylide by deprotonation with KO^{t}Bu in THF. Although we were unable to isolate **13** in pure form due to its instability compared to the other *phospha*-cruciforms, the conversion of **12** to **13** was reasonably clean by ^{31}P NMR spectroscopy, with the resonance at 20.5 ppm attributed to the bis(ylide). The ^{31}P NMR resonances are summarized in Table 1.

Density-functional theory calculations

Because many of the stimuli-responsive properties of a cruciform derive from the geometric distribution of its HOMO and LUMO, materials **8**, **9** and **10** were examined by Density Functional Theory (DFT) calculations at the B3LYP/6-31G(d) level.[51] The calculated



Scheme 1 Synthesis of phosphine oxide **8** (structure provided in Scheme 2).



Scheme 2 Synthesis of compounds **9-13** and structure of phosphorus-free model **M1**.

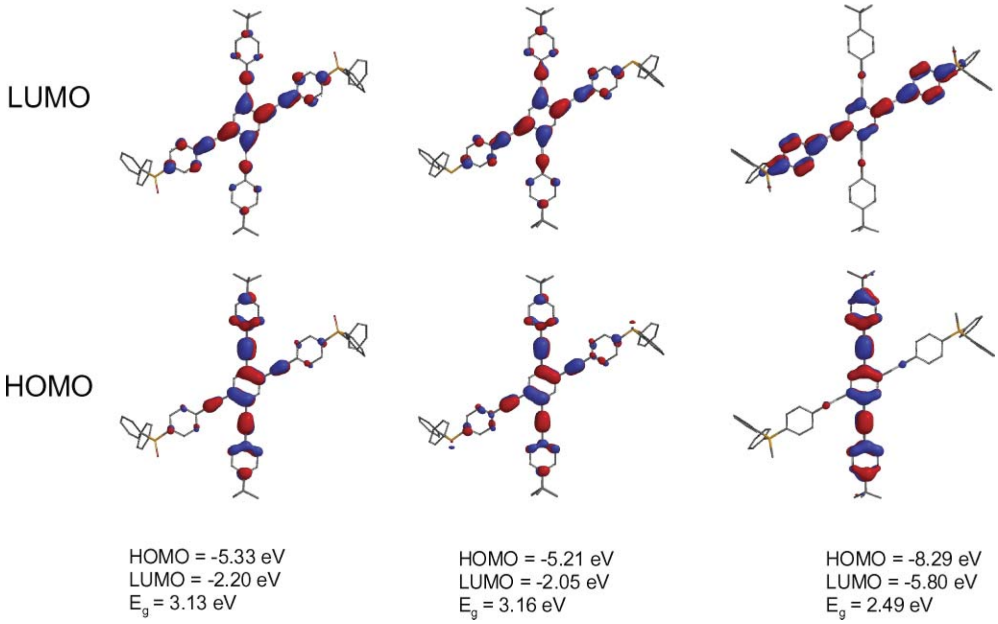


Fig. 1 HOMO, LUMO and band gap (E_g) parameters from DFT calculations (B3LYP-6-31G* level) for compounds **8** (left), **9** (center) and **10** (right).

HOMOs and LUMOs for **8**, **9**, and **10** are provided in Fig. 1. The calculated HOMO–LUMO gaps (E_g) are in good agreement with the optical bandgap estimated by the red edge absorption onset in absorption spectra for **8** and **9**, though for phosphonium salt **10** the calculated bandgap (2.49 eV) was somewhat lower than the experimental optical bandgap (2.81 eV). This is probably due to the fact that calculations do not account for counterion effects or solvent effects, both of which are expected to be much more influential in the ionic **10** *versus* neutral compounds **8** and **9**. The HOMO and LUMO become significantly more geometrically distinct as the electron-withdrawing nature of the phosphorus functionality are increased from phosphine **9** and phosphine oxide **8** to cationic phosphonium **10**. The lack of significant HOMO–LUMO geometric separation in **9** is rather expected because the electronegativity of P and C are quite similar, such that the phosphine-bearing and *t*-butyl bearing arms will have similar electronic and energetic profiles. Furthermore, the orbital size/energy mismatch between P and C leads to only limited n-π interaction.[28-30] This is in contrast to nitrogen containing systems, such as polyaniline or amino-derivatised cruciforms, in which the lone pair can engage in delocalization with an appended π-system.[55,56] Because of the cationic nature of the substituents in **10**, however, the significant inductive withdrawing effect leads to predictably notable perturbation of orbital energies. The phosphorus-centered lone pair in **9** shows the greatest contribution to the HOMO-1 orbital (not shown in Fig. 1), and plays a limited role in the photophysical properties as discussed below.

Photophysical properties

Normalised absorption (Fig. 2A) and emission spectra (Fig. 2B) for the series of compounds **8-12** are shown in Fig. 2 along with those for the benchmark compound 1,2,4,5-tetrakis(2-(4-*tert*-butylphenyl)ethynyl)benzene (**M1**) for comparison. **M1** was selected for comparison because it features the same π-system as phosphine **9**, but lacks the phosphorus substituents, and the substitution of phosphino substituents with *tert*-butyl groups meant that the electronegativity of atom directly attached to the π-system remained relatively constant. As noted previously, the spectral data are in line with the properties anticipated from DFT calculations, though caution must be exercised in comparing ground state calculations with photophysical data that are impacted by expected changes in excited state geometries relative to the ground state. Molar absorptivities of **8-12** are on the order of 10^5–10^6, consistent with the anticipated π–π* transitions. Absorption spectra for **8-12** each feature a $\lambda_{\pi-\pi^*}$ band at around 330 nm in addition to a shoulder to the red at around 350–400 nm. The shoulder is attributed to a charge transfer band between the π orbital on one of the cross-conjugated segments and the π* of the other π-conjugated segment, a feature observed in many tetraethynylbenzene derivatives.[57] The absorption maxima of the higher energy band for phosphine-containing **8-12** are slightly red-shifted compared to that of **M1** because of the small extension of conjugation through the phosphorus centres[30] and the electron-withdrawing nature of many of the phosphorus derivatives.

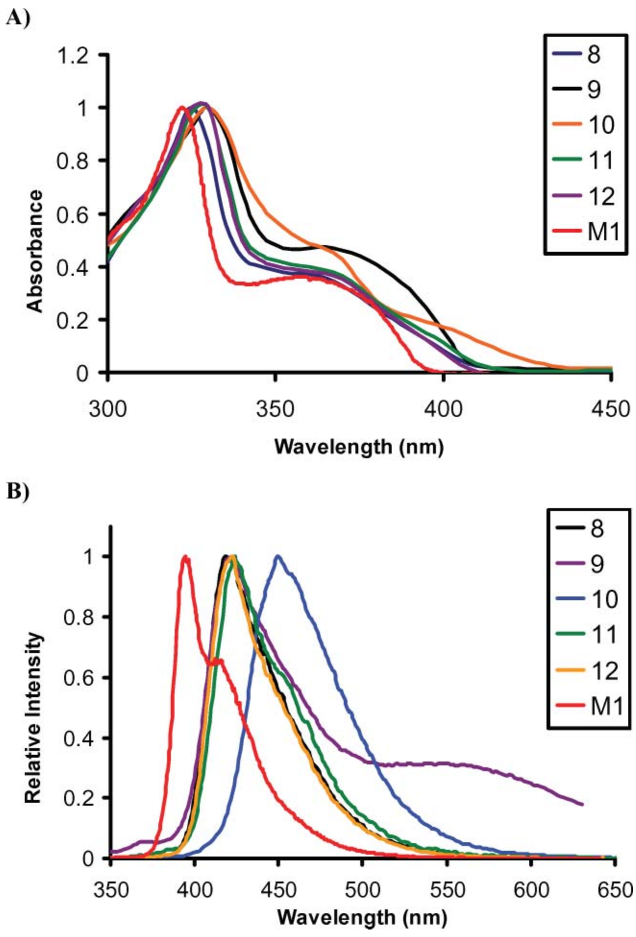


Fig. 2 Absorption (A) and photoluminescence (B) spectra for compounds **8-12** and **M1** in dichloromethane. The trace for **9** is cut off before reaching baseline resolution because it overlaps the expected overtone peak at double the excitation wavelength at 660 nm (λ_{ex} = 330 nm).

Although the ylide **13** was not isolable in the solid state, the reaction solutions were examined by absorption spectroscopy and the data are summarized in Table 1. The ylide-containing solution did not exhibit appreciable fluorescence, but does exhibit a violet color. Although the ylide can be drawn in a resonance structure wherein there is a P–C double bond, the orbital makeup of phosphorus ylides suggests that this will not lead to any appreciable extension of p-π type conjugation.[58-61] The change in the absorption features are likely promulgated through n-π interactions.

The fluorescence emission spectra of the series show a single band regardless of whether excitation is provided into the p-p* band at *ca.* 330 nm or into the charge transfer band. All of the phosphorus-containing species **8-12** have emission maxima that are bathochromically shifted *versus* **M1** despite very similar absorption maxima. The larger Stokes shift in **8-12** *versus* **M1** reflects the polarizability and electron withdrawing nature of the phosphorus centers, as most dramatically illustrated by the considerably larger shift for cationic **10** (λ_{em} = 449 nm), with its large Stokes shift of 119 nm.

The quantum yields are highest (40% and 41%, respectively) for the phosphine oxide (**8**) and phosphine sulfide (**12**). The trend in photoluminescent quantum yields (Φ) for other phosphorus species mirror those reported for tris(stilbenyl)phosphine[26] and **LHP1**[24] (Chart 1A) derivatives. Just as was observed for tris(stilbenyl) phosphorus species, the phosphine exhibits significantly lower Φ than the phosphonium, phosphine oxide or d^{10} metal complex. This is attributable to the ability of the polarizable phosphorus lone pair to facilitate nonradiative decay processes. The exceptionally low Φ of **9** allows the observation of a very weak ($\Phi < 0.01$) red-shifted emission feature in Fig. 2B that may be attributable to some very weak triplet emission or emission from aggregates in solution. The later would not be unexpected due to the limited solubility of the compounds, and it should be stressed that this emission band accounts for < 1% of absorbed photons.

Conclusions

In summary, we have successfully synthesized and characterized six novel phosphorus-containing cross-conjugated cruciform systems and examined their photophysical properties. The presence of phosphorus centers on the tetraethynylbenzene core lead to a decrease in the bandgap and increased Stokes shifts *versus* the hydrocarbon model compound. DFT calculations and optical bandgap estimates indicate that band gap energies (E_g) for these materials are within the range of other materials that have found utility in organic optoelectronic applications. Extensions of these molecules to the preparation of various luminescent charge-transfer polymers, polyelectrolytes and metallopolymers are currently being carried out in our lab.

Experimental

Reagents and general methods

Reagents were obtained form Acros, Aldrich Chemical Co., TCI America, or Alfa Aesar and used as received from the suppliers without further purification. Solvents were purified by passage through alumina column under a N_2 atmosphere employing an MBraun solvent purification system. All the air sensitive manipulations were performed in an MBraun dry box or using standard Schlenk techniques under N_2 atmosphere. 1,4-dibromo-2,5-diiodobenzene (**2**),[62] 1,4-dibromo-2,5-bis(2-(4-*tert*-butylphenyl)ethynyl)benzene (**4**),[63] and 1,4-bis(2-(4-*tert*-butylphenyl)ethynyl)-2,5-diethynylbenzene (**6**)[64] were synthesized by modification of reported methods. Compounds were characterized by ^{1}H, ^{13}C, and ^{31}P NMR spectra using a Bruker Avance 300 spectrometer operating at 300 MHz for ^{1}H, 75.4 MHz for ^{13}C, and 121.5 MHz for ^{31}P nuclei. All the spectra were collected at 25 °C and referenced to TMS or residual solvent peak for ^{1}H and ^{13}C and to 85% phosphoric acid for ^{31}P. Absorption spectra were recorded using Varian Cary 50 spectrophotometer and photoluminescence (PL) data were recorded using Varian Eclipse spectrofluorimeter in quartz cuvettes with a pathlength of 1 cm in DCM. Quantum yield (Φ) for all compounds were calculated relative to quinine bisulfate in 0.1 M H_2SO_4 (aq) (Φ = 0.546).[27]

Synthesis of 1,4-bis(2-(4-*tert*-butylphenyl)ethynyl)-2,5-bis(2-(4-(diphenylphosphoryl) phenyl)ethynyl)benzene (8). In a round bottom flas, 1,4-bis(2-(4-*tert*-butylphenyl)ethynyl)-2,5-diethynyl benzene **6** (0.34 g, 0.78 mmol) and (4-iodophenyl)-diphenylphosphineoxide) **7** (0.85 g, 2.1 mmol) were degassed and taken into the dry box. Compound **7** was dissolved in THF (100 mL) followed by the addition of tetrakis(triphenylphosphine) palladium(0) (250 mg, 0.24 mmol) and copper iodide (45 mg, 0.24 mmol). In a vial, 1,4-bis(2-(4-*tert*-butylphenyl)ethynyl)-2,5-diethynylbenzene **6** was dissolved in diisopropyl amine (20 mL) and added into the reaction mixture drop wise. The reaction mixture was stirred for 48 h at room temperature. Dichloromethane (100 mL) was added into the reaction mixture, which was then extracted with saturated sodium bicarbonate solution (4 × 100 mL). The combined organics were collected, dried over sodium sulfate and all volatiles were removed under reduced pressure. The residue was washed recursively with acetonitrile to afford a yellow solid (0.35 g, 46%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.34 (s, 18H, 6 × CH_3), 7.40 (d, 4H, J = 6.8 Hz, Aromatic), 7.54–7.48 (m, 12H, Aromatic), 7.60–7.57 (m, 4H, Aromatic), 7.74–7.66 (m, 16H, Aromatic), 7.78 (s, 2H, Aromatic). ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 31.1, 34.9, 86.6, 90.0, 94.3, 96.1, 119.6, 125.0, 125.5, 125.6, 126.7, 126.7, 128.5, 128.7, 131.4, 131.5, 131.6, 132.0, 132.1, 132.1, 132.8, 133.5, 135.0, 152.3. ^{31}P NMR (121.4 MHz, $CDCl_3$): δ = 29.3. HRMS $(M+H)^+$: calc. for $C_{70}H_{57}O_2P_2$: 991.3834; found, 991.3837. UV-vis: λ_{max} 325 nm (ε = 160,000 M^{-1} cm^{-1}).

Synthesis of 1,4-bis(2-(4-*tert*-butylphenyl)ethynyl)-2,5-bis(2-(4-(diphenylphosphino) phenyl)ethynyl)benzene (9). Under an atmosphere of dry nitrogen, 1,4-bis(2-(4-*tert*-butylphenyl)ethynyl)-2,5-bis(2-(4-(diphenylphosphoryl)phenyl)ethynyl)benzene **8** (0.1 g, 0.1 mmol) was dissolved in 1 : 1 mixture of THF and toluene (30 mL) followed by addition of triethylamine (1 mL). Trichlorosilane (1.34 mL, 3.00 mmol) was added and the mixture was refluxed overnight. After cooling to room temperature, degassed saturated aqueous sodium bicarbonate (10 mL) was slowly added. A yellow precipitate was filtered off and the organic layer was further extracted with saturated aqueous sodium bicarbonate (3 × 50 mL). The organic layer was collected, dried over sodium sulfate and all volatiles were removed under reduced pressure. The residue was dissolved in minimal dichloromethane, followed by slow addition of pentane (20 mL) to yield the product as a yellow crystalline solid upon cooling, filtering and drying *in vacuo* (50 mg, 52%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.34 (s, 18H, 6 × CH_3), 7.39 - 7.27 (m, 28H, Aromatic), 7.56–7.49 (m, 8H, Aromatic), 7.76 (s, 2H, Aromatic). ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 31.1, 34.8, 86.8, 88.7, 95.1, 95.7, 119.8, 123.2, 125.1, 125.4, 125.4, 128.5, 128.6, 128.9, 131.4, 131.5, 131.6, 133.3, 133.5, 133.7, 134.0, 134.9, 136.5, 136.6, 138.5, 138.6, 152.3. ^{31}P NMR (121.4 MHz, $CDCl_3$): δ = –4.3. HRMS $(M+H)^+$: calc. for $C_{70}H_{57}P_2$, 959.3936; found, 959.3957. UV-vis: λ_{max} 330 nm (ε = 190,000 M^{-1} cm^{-1}).

Synthesis of phosphonium salt (10). Under a nitrogen atmosphere, **9** (25.0 mg, 0.026 mmol) was dissolved in toluene (20 mL) followed by addition of methyl iodide (16.0 mg, 0.100 mmol). The reaction mixture was refluxed for 16 h. All the volatiles were removed under reduced pressure and the residue was triturated with pentane (10 mL) to yield the yellow solid (20.0 mg, 62.5%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.33 (s, 18H, 6 × CH_3), 3.35 (d, 6H, J_{HP} = 12.0 Hz), 7.43 (d, 4H, J = 9.0 Hz, Aromatic), 7.52 (d, 4H, J = 9.0 Hz, Aromatic), 7.67–7.84 (m, 30H, Aromatic). ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 31.1, 34.9, 86.2, 92.7, 93.2, 96.6, 118.2, 119.4, 124.7, 125.7, 125.8, 128.5, 128.7, 130.2, 130.5, 130.7, 131.4, 132.0, 132.1, 133.1, 133.3, 133.3, 133.4, 133.5, 135.3, 135.6, 152.6. ^{31}P NMR (121.4 MHz, $CDCl_3$): δ = 22.6. MS $(M-2I^-)^{2+}$: calc. for $C_{72}H_{62}P_2$, 988.4; found, 988.4. UV-vis: λ_{max} 330 nm (ε = 130,000 M^{-1} cm^{-1}).

Synthesis of phosphine gold complex (11). Under a nitrogen atmosphere, **9** (20.0 mg, 0.021 mmol) was dissolved in dichloromethane (15 mL) followed by addition of (tht)AuCl (14.0 mg, 0.044 mmol, tht = tetrahydrothiophene). The reaction mixture was stirred for 16 h. All the volatile was removed under reduced pressure and the residue was triturated with pentane (5 mL) and dried *in vacuo* to yield **11** as a yellow solid (26 mg, 89%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.35 (s, 18H, 6 × CH_3), 7.42 (d, 4H, J = 6.0 Hz, Aromatic), 7.49–7.67 (m, 32H, Aromatic), 7.80 (s, 2H, Aromatic). ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 31.1, 34.9, 86.5, 90.6, 93.9, 96.2, 119.6, 124.9, 125.6, 125.6, 126.8, 126.9, 127.9, 128.6, 128.7, 129.3, 129.4, 131.4, 132.1, 132.1, 132.2, 132.2, 133.9, 134.1, 134.1, 134.2, 135.2, 152.5. ^{31}P NMR (121.4 MHz, $CDCl_3$): δ = 33.7. MALDI: calc. for $C_{70}H_{56}Au_2Cl_2P_2$ $(M+H)^+$, 1423.3; found, 1423.1. UV-vis: λ_{max} 330 nm (ε = 210,000 M^{-1} cm^{-1}).

Synthesis of 1,4-bis(2-(4-*tert*-butylphenyl)ethynyl)2,5-bis(2-(4-diphenylphosphorothioyl)phenyl)ethynyl)benzene (12). Under nitrogen atmosphere, compound **9** (15 mg, 0.016 mmol) was dissolved in dry THF (5 mL) followed by addition of S_8 (1.6 mg, 0.048 mmol). The reaction mixture was stirred for 16 h, after which all the volatiles were removed under reduced pressure. The residue was further purified by dissolution in $CHCl_3$ and filtering through a 0.4 mm PTFE syringe filter to remove excess sulfur. $CHCl_3$ was removed under pressure, and the solid was rinsed with pentane and dried *in vacuo* to yield the product as a yellow solid (11 mg, 69%). ^1H NMR (300 MHz, $CDCl_3$): $\delta = 1.34$ (s, 18H, 6 × CH_3), 7.41 - 7.38 (m, 4H, Aromatic), 7.57–7.46 (m, 16H, Aromatic), 7.66–7.62 (m, 4H, Aromatic), 7.80–7.71 (m, 13H, Aromatic). ^{13}C NMR (75.4 MHz, $CDCl_3$): $\delta = 31.2$, 35.0, 86.6, 90.2, 94.4, 96.2, 119.7, 125.0, 125.6, 126.4, 128.6, 128.8, 131.5, 131.6, 131.7, 131.8, 132.0, 132.2, 132.4, 132.7, 133.1, 133.8, 135.1, 152.4. ^{31}P NMR (121.4 MHz, $CDCl_3$): $\delta = 43.7$. HRMS $(M+H)^+$: calc. for $C_{70}H_{57}Au_2Cl_2P_2$, 1023.3377; found, 1023.3417. UV-vis: λ_{max} 330 nm ($\varepsilon = 100{,}000$ M^{-1} cm^{-1}).

Synthesis of phosphorus ylide (13). Under a nitrogen atmosphere, compound **10** (19.0 mg, 0.015 mmol) was dissolved in THF-d_8 (1 mL) followed by addition of potassium *tert*-butoxide until compound **10** completely dissolved. Upon addition of the first portion of the base, an immediate color change from pale yellow to a light violet-brown color was observed. Consumption of **10** was completed within 30 min as determined by NMR spectroscopy. ^{31}P NMR (121.4 MHz, $CDCl_3$): $\delta = 20.5$ (attributed to **13**); smaller resonances were present at $\delta = 25.0$, 23.9, 13.6 and 11.2. The spectrum is shown in the ESI.

Acknowledgements

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