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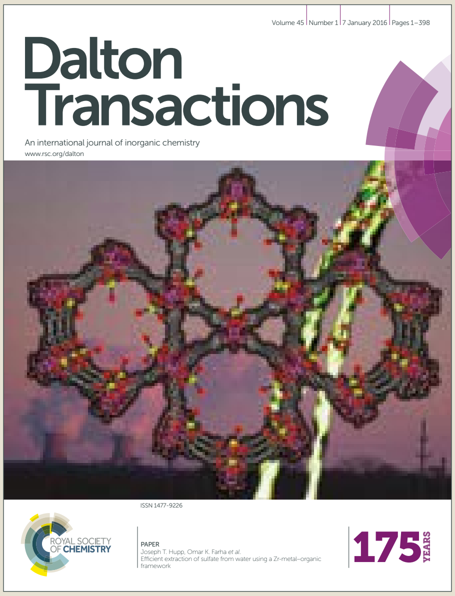

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Achieving Yellow Emission by Varying Donor/Acceptor Units in Rod-shaped Fluorenyl-alkynyl Based π-Conjugated Oligomers and Their Binuclear Gold(I) Alkynyl Complexes

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Fluorenyl-alkynyl based π-conjugated rod-shaped oligomers bearing different cetntral aromatic moieties and functionalizable di-alkynyl termini, such as H−≡−Fl−≡−Fl−≡−Fl−≡−H (**OH1**), H−≡−Fl−≡−Btz−≡−Fl−≡−H (**OH2**) and H−≡−Fl−≡−Btd−≡−Fl−≡−H (**OH3**) where Fl = 9,9-dioctylfluorene, Btz = N-hexylbenzotriazole, Btd = benzothiadiazole, were successfully synthesized by Pd(0) catalyzed Stille coupling protocol. Electron withdrawing benzothiadiazole and benzotriazole as strong to moderate acceptor, and fluorene as donor have been incorporated to adjust the Donor-Acceptor (D-A) strength for fine tuning of the bandgap (E_g) as well as the emission wavelength. The corresponding digold(I) σ-complexes, (PPh_3)Au−≡−Fl−≡−Fl−≡−Fl−≡−Au(PPh_3) (**OM1**), (PPh_3)Au−≡−Fl−≡−Btz−≡−Fl−≡−Au(PPh_3) (**OM2**) and (PPh_3)Au−≡−Fl−≡−Btd−≡−Fl−≡−Au(PPh_3) (**OM3**) have also been prepared by reaction of Au(PPh_3)Cl and methanolic NaOMe in DCM with the corresponding alkynyl functionalized oligomers, to take the advantage of heavy-atom effect on their emissive properties. The synthesized rod-shaped π-conjugated fluorene based oligomers and their binuclear Au(I) σ-complexes have been unambiguously characterized by various spectroscopic tools such as FTIR, multinuclear NMR as well as MALDI-TOF and CHN analyses. The absorption and emission spectral studies exhibited a progressive red shift with increasing electron withdrawing character of the central aromatic unit. The rod-like oligomers having alkynyl termini and the corresponding digold(I) complexes are found to be blue, cyan and yellow emissive, demonstrating fine tuning of the emission wavelength. Most importantly, the fluorene based π-conjugated yellow light emitter **OH3** and **OM3** are successfully achieved by varying donor/acceptor moiety to the fluorenyl-alkynyl backbone. The digold(I) diacetylide organometallic wires exhibit phosphorescence at 77 K in degassed CH_2Cl_2 due to the efficient intersystem crossing from the S_1 to the T_1 excited state as induced by heavy atom.

Introduction

There is a rapidly growing interest in designing and developing of rigid-rod metal-acetylide organometallic oligomers and polymers (metallopolyynes) for smart applications in optoelectronics such as in flexible organic photovoltaics (OPV), organic light emitting diodes (OLED), and field effect transistors (FET).[1] In this regard, a considerable amount of interest has been focused on developing organic light-emitting materials for OLED application.[2] Many blue, green and red light emitting organic and organometallic conjugates have been developed,[3] but highly efficient and stable yellow light emitting organic and organometallic materials are still rare.[4] The yellow emitting materials are used as a lighting source for lithography, signal lights and full-colour display.[5] In addition, yellow in combination with sky blue emission is also one of the key components for the construction of white OLEDs.[6] Handful yellow light emitting materials based on semiconducting carbon dots, quantum dots, π-conjugated organic and organometallic compounds are reported till date. Carbon dots mostly show strong emission only in the blue region exhibiting weak emission in the long-wavelength (yellow to red light), which restricts their further application.[7] Quantum dots based light emitting materials mostly contain cadmium or lead which have negative environmental and ecological impacts for its high toxicity. Consequently, it hinders their commercial application as light emitting diodes.[8] Therefore, development of highly efficient π-conjugated yellow emissive organic and organometallic congeners is essential and in high demand. Singlet-triplet intersystem crossing induced by the third row transition and late transition elements in conjunction with the π-conjugated ligands is an attractive strategy for tuning desired emission wavelength. In this regard, yellow iridium(III) cyclometalled complexes are found to be exciting materials for full-colour display and white OLEDs.[1c,5a,6a,9] Pt(II) metal complexes were explored by various groups as a promising candidate for yellow emissive materials.[10] Phosphorescent Re(I)-polypyridine complexes have been reported as a intense

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and long lived yellow emissive materials.[11] Highly luminescent Ln(III) complexes have also been utilized as a yellow light emitting materials.[12] Extended π-conjugated congeners derived from naphthalene diimide[13] and organoboron[14] based derivatives have been found to be promising yellow light emiting materials as reported. Alkyl substituted soluble fluorene based π-conjugated oligomers and polymers have emerged as a very promising candidate for OLED applications due to their high photoluminescent quantum yield, good chemical and thermal stability, excellent solubility, good film-forming property and possibility of energy level alignment by engineering the band gap through chemical functionalization. However, fluorene based oligomers and polymers exhibit emission in the blue region, allowing for using only as blue-light emitter.[15] Recently, fluorene based oligomers and polymers have attracted potential interest as yellow light emitting materials[4a,16] which are achieved by adjusting the bandgap through incorporation of electron deficient moiety to the fluorene backbone.[17] Several electron deficient monomers have been reported as the co-monomers to be incorporated into the backbone of wide bandgap oligomers and polymers. Among them, 2,1,3-benzothiadiazole (Btd) and its derivatives have great importance as building blocks for promising organic semiconducting materials due to their higher electron deficiency. For example, Jen and coworkers have demonstrated efficient green emitting copolymers of 9,9-dioctylfluorene (Fl) and Btd,[18] whereas a series of red emitting copolymers based on Fl and 4,7-di-2-thienyl-2,1,3-benzothiadiazole have been reported by Cao and coworkers.[19]

The recent development of π-conjugated rigid-rod metal-acetylide organometallic wires has attracted great interest as smart materials for its emerging optoelectronic application.[20] Efficiency of organic light emitting diodes is typically controlled by the presence of triplet state emission, which can be achieved by the incorporation of heavy metals to the π-conjugated organic backbone. The strong spin-orbit coupling, induced by the heavy metals, mixes the singlet and triplet excited states through efficient intersystem crossing (ISC), which allows to measure the spin-forbidden triplet emission (phosphorescence) experimentally. In this regard, the photophysical properties of gold(I/III)–σ-acetylide complexes have received much current attention due to their rich photophysical properties.[21] The presence of gold(I) with tertiary phosphine ligands constituting a linear geometry through σ-alkynyl unit of the π-conjugated alkynyl termini, makes it most attractive and promising candidate for the construction of linear organometallic molecular wires, which may possess unique properties such as long-lived phosphorescence,[22] liquid-crystallinity,[23] and nonlinear optical behaviour[24] allowing its applications in electronic devices.[25] Furthermore, Au(I)···Au(I) interaction plays an important role resulting strong luminescence properties in many Au(I) complexes of wide range of molecular structures.[26]

With these ideas in mind, we aim to develop yellow light emitting D-π-A-π-D type of fluorenyl-alkynyl based oligomers with alkynyl spacers and termini by varying donor/acceptor moieties through stepwise synthetic protocol. Electron withdrawing benzothiadiazole and benzotriazole as strong to moderate acceptor, and fluorene as a weak donor have been incorporated to adjust the D-A strength to tune the bandgap (E_g) and hence the emission wavelength. The alkynyls termini in the rod-like oligomers offer the opportunity to introduce Au(I) fragments to achieve phosphorescent organometallic molecular wires with the consequence of triplet state emission.

Results and discussion

Synthesis and characterization

A stepwise synthetic protocol has been followed to develop yellow light emitting fluorene based emitter. A series of fluorene based π-conjugated D-π-A-π-D rod-shaped oligomers were synthesized by varying the π-conjugated organic spacers in between two fluorenyl-alkynyl units, following Stille coupling protocol as shown in Scheme 1. Incorporation of alkyl group is necessary to improve the solubility and solution processability of the fluorene based rigid oligomers. Hence 2-bromo-7-((trimethylsilyl)ethynyl)-9,9-dioctylfluorene (4) was selected as a key starting material for the alkynyl appended precursor, which was synthesized by adaptation of the literature procedure starting from fluorene.[27] The desired rod-like π-conjugated fluorene based trimer with alkynyl termini (O1) was obtained by Stille coupling between 4 and the stanylated derivative (**9**) which was generated *in-situ* by treating LDA and tributylstannylchloride on diethynyl-functionalized fluorene (**8**). To tune the emission to a longer wavelength, electron withdrawing benzotriazole (Btz) group was intended to incorporate in between the two fluorene moieties connected through –C≡C– units. Thus the rod-like π-conjugated fluorene-benzotriazole based D-π-A-π-D oligomer (**O2**) conjugated with alkynyl spacers was synthesized by Stille coupling between 15 and 4. After successful inclusion of benzotriazole in fluorene moieties, stronger acceptor unit such as benzothiadiazole (Btd) was also incorporated to the fluorenyl-alkynyl backbone to further modulate its photophysical properties, specially the emission wavelength. Therefore Pd(0)-catalyzed Stille coupling between 4 and **20** was accomplished to afford the desired rod-like π-conjugated benzothiadiazole-fluorene hybrid with alkynyl termini and spacers (**O3**) exhibiting yellow emission as desired. Column chromatography (silica gel) using EtOAc/hexanes as eluent afforded analytically pure **O1-O3** in 61-64% yield, which were characterized by ^{1}H, ^{13}C and DEPT-135 NMR studies confirming its chemical structures.† Formation of the oligomers were further confirmed by MALDI-TOF study, exhibiting the molecular ion peaks at 1407.088, 1219.905 and 1152.766 ($[M+H]^+$) respectively. After several attempts by varying crystallization techniques and conditions, the orange needle-like single crystals suitable for X-ray crystallography were successfully harvested by layering MeOH on DCM

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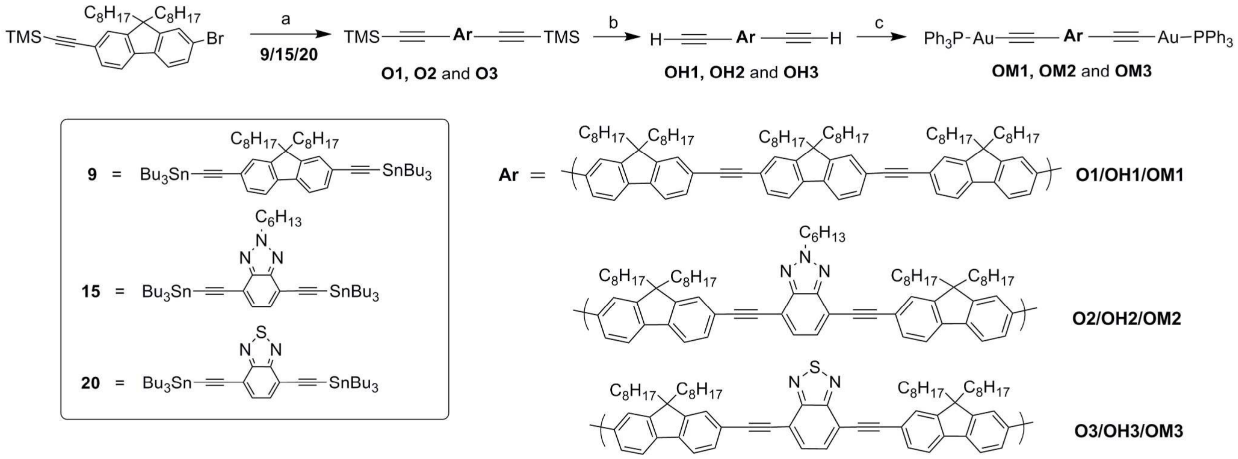

Scheme 1 Synthesis of the binuclear gold(I) σ-complexes
Reagents and conditions: a) 3 mol% $Pd(PPh_3)_4$, THF, reflux, 24 h; b) K_2CO_3, DCM, MeOH, 28 °C, 4 h; c) 2.1 eqv. of $Au(PPh_3)Cl$, NaOMe, MeOH, DCM, 28 °C, 12 h.

solution of **O3.** It crystallized in P-1 space group having two independent molecules in the asymmetric unit. Disorder and higher thermal vibration which are very common for the long chain octyl and terminal trimethylsilyl groups respectively resulted relatively higher R_1 and wR_2 values calculated from data with $I>2\sigma(I)$.[28] However, the rigid rod skeleton of the polyyne, **O3** has been confirmed unambiguously from the single crystal X-ray structural determination as depicted in Fig. S108†.

Synthesis of Binuclear Au(I) Alkynyl σ-Complexes. After successful synthesis of blue, cyan and yellow luminescent fluorenyl-alkynyl based π-conjugated rod-like oligomers, Au(I) was incorporated into the π-conjugated organic backbone to take the advantage of heavy atom effect in their photophysical properties, aiming for spin forbidden triplet yellow emission (phosphorescence) induced by strong spin-orbit coupling. One of the elegant strategies to construct linear main-chain metallopolyyne with extensive electronic conjugation is through the formation of linear two-coordinate gold(I)–acetylide (Au–C≡C-) bond. All the π-conjugated oligomers **O1**, **O2** and **O3** having trimethylsilylalkynyl termini at the both ends were desilylated by a base-promoted deprotection using K_2CO_3 as base in DCM/MeOH to obtain **OH1**, **OH2** and **OH3** respectively with alkynyl (-C≡C-H) termini. The corresponding digold(I) diacetylide complexes (**OM1**, **OM2** and **OM3**) were synthesized by treating with 2.1 eqv. of $Au(PPh_3)Cl$ in presence of NaOMe in MeOH as outlined in Scheme 1. The binuclear Au(I) σ-complexes were purified by precipitating their concentrated CH_2Cl_2 solution in anhydrous MeOH, followed by a short column chromatography (neutral alumina) using dry EtOAc/hexanes (1:20) as eluent in inert atmosphere to achieve analytically pure organometallic molecular wires **OM1-OM3** in 88-92% yield respectively. $^{31}P\{^1H\}$ NMR spectra of the analytically pure Au(I) organometallic complexes, exhibiting singlet resonance at 42.7 (**OM1** and **OM2**) and 42.9 ppm (**OM3**) attributed to the Au(I)-coordinated PPh_3, suggests the formation of digold(I) diacetylide organometallic wires having symmetrical -C≡C-$Au(PPh_3)$ terminal groups in solution (Fig. S25, S41 and S56†). The organometallic wires were further characterized by multinuclear NMR and IR spectra, mass spectrometry as well as by elemental analysis. The comparison of the ^1H NMR spectra with the integration value of selected proton signals of **OM1**-**OM3** is depicted in Fig. 1. The multiplicity of the proton signals and the associated relative intensities unambiguously confirm the proposed structures. In $^{13}C\{^1H\}$ NMR the characteristic signal at 105.4 ppm (for **OM1** and **OM2**) and at 105.5 ppm (**OM3**) indicate the presence of carbon attached to gold(I) (Au-$\underline{C}$≡C), which are further confirmed by the disappearance of the resonance at 105.4 ppm (for **OM1** and **OM2**) and at 105.5 ppm (**OM3**) in DEPT-135 NMR.[21n,29] The characteristic $\bar{\upsilon}_{C\equiv C}$ (C≡C attached to Au(I)) stretching frequency for all the organometallic complexes (**OM1**-**OM3**) appears at 2200-2204 cm^{-1} which are subsequently higher than their parent analogues (**OH1**-**OH3**) by ca. 100 cm^{-1}.[30] Finally, the organometallic wires (**OM1**-**OM3**) were characterized by MALDI-TOF, revealing the molecular ion peaks, ($[M+H]^+$) at 2180.158, 1992.790 and 1925.690 respectively. The isotopic distribution pattern for the molecular ion peak obtained from the experimental data is in perfect agreement with the simulated data for all the digold(I) diacetylide complexes as shown in Fig. 2.

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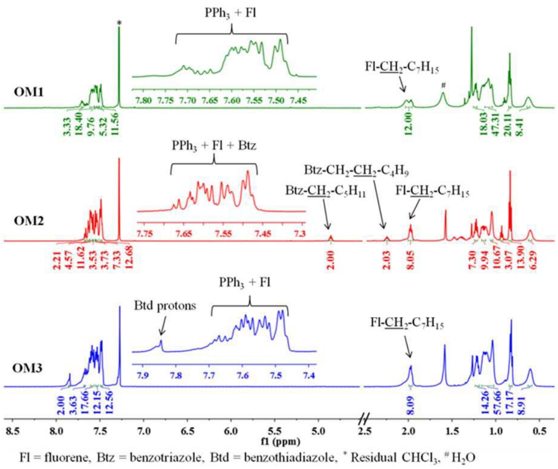

Fig. 1 ^{1}H NMR (600 MHz, CDCl$_3$) spectra with the integral ratio of the protons in **OM1-OM3**.

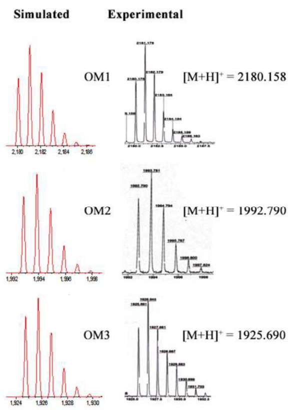

Fig. 2 Experimental and simulated isotopic distribution pattern for the molecular ion peaks ([M+H]$^+$) of **OM1-OM3** respectively, obtained from MALDI-TOF MS.

Electrochemical properties. To understand the influence of the acceptor properties of Btz and Btd units on the HOMO-LUMO energy levels, the cyclic voltammetric experiments of the rigid rod-like π-conjugated oligomers and their corresponding digold(I) diacetylide complexes were conducted (Fig. S92†). For this purpose, film of the synthesized π-conjugated oligomers and their binuclear Au(I) complexes were prepared by drop casting the corresponding DCM solution on GC-disc electrode. The measurement was carried out in CH$_3$CN using n-Bu$_4$NPF$_6$ (0.1 M) as supporting electrolytes, Pt wire counter electrode and Ag/AgCl reference electrode. The electrochemical data are summarized in Table 1. HOMO energy levels were calculated from the onset oxidation potentials considering E_{HOMO} (eV) = -(E_{ox}^{onset} + 4.71).[31] The E_{HOMO} energy levels of **OH1** to **OH3** are calculated as -5.87, -5.85, and -5.90 eV based on their onset oxidation potential. Similarly the calculated E_{HOMO} energy levels of **OM1** to **OM3** are -5.80, -5.79, and -5.88 eV. **OH3** exhibits a reversible redox wave at $E_{1/2}$ = -1.17(80) V corresponding to the Btd acceptor unit. However, the reduction process becomes quasi-reversible for the corresponding Au(I) complex, **OM3**. As there is no prominent reduction process for **OH1-OH2** and **OM1-OM2**, we have calculated the E_{LUMO} levels from the values of E_{HOMO} and its optical band gaps (E_{LUMO} = E_{HOMO} + E_g^{opt}).[6d,15g,17a] The E_{LUMO} energy levels of **OH1**-**OH3** are calculated as -3.05, -3.17, and -3.53 eV. The E_{LUMO} energy levels of **OM1- OM3** are -3.04, -3.18, and -3.57 eV. Incorporation of electron withdrawing aromatic units into the π-conjugated backbone lowers down the E_{LUMO} energy, which is reflected in the energy levels of **OH1** to **OH3**, consequently **OM1** to **OM3**.

Table 1 Electrochemical data and HOMO-LUMO energy levels.

Compound	E_{ox}^{onset}, V	E_{HOMO}, eV^a	E_{LUMO}, eV^b
OH1	1.16	-5.87	-3.05
OH2	1.14	-5.85	-3.17
OH3	1.19	-5.90	-3.53
OM1	1.09	-5.80	-3.04
OM2	1.08	-5.79	-3.18
OM3	1.17	-5.88	-3.57

^{a}E_{HOMO} (eV) = -(E_{ox}^{onset} + 4.71). ^{b}(E_{LUMO} = E_{HOMO} + E_g^{opt}). E_g^{opt} values are estimated from solid state absorption spectra (*vide infra*).

Thermal analysis. Thermal properties of these fluorenyl-alkynyl based π-conjugated oligomers and the Au(I) complexes were examined by thermogravimetric analyses (TGA) and differential scanning calorimetry (DSC). TGA study clearly indicates that all the fluorene based π-conjugated oligomers and their Au(I) complexes have good thermal stability. The decomposition temperatures for **OH1** to **OH3** are found to be 380, 151 and 154 °C respectively with ca. 2% weight loss as observed for the similar rod-shaped oligomers.[22h] The decomposition temperatures for **OM1**-**OM3** were observed at 208, 191 and 187 °C respectively. In case of the π-conjugated oligomers, weight loss of 44-48% was observed at 486, 508 and 498 °C due to removal of alkyl groups, whereas for the digold(I) diacetylide complexes, the weight loss of 24-50% can be ascribed to the removal of PPh$_3$ and alkyl groups at 454, 459 and 455 °C. While recording DSC, the glass-transition temperatures (T_g) for **O1** to **O3** with trimethylsilylalkynyl termini were observed at 57, 49 and 47 °C. For the corresponding digold(I) σ-complexes (**OM1**-**OM3**), T_gs were determined as 46, 42 and 38 °C. With increasing the substituents on π-conjugated backbone, the mobility of the molecule decreases leading to increase in chain rigidity and T_g.[32] Hence, T_g decreases from **OM1** to **OM3** with decreasing the numbers of alkyl substituents and consequent reduction in rigidity in the molecular chain.

Absorption and photoluminescence studies. All the new π-conjugated rod-shaped oligomers are air stable and highly soluble in common organic solvents even in hexanes. The good solubility of the π-conjugated oligomers and their

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corresponding rigid-rod organometallic wires allowed us to explore the photophysical properties in solution. The electronic absorption of the compounds **OH1-OH3** and their corresponding digold(I) diacetylide complexes (**OM1-OM3**) was studied in distilled and degassed 1,2-DCE at 298 K. The absorption maxima (λ_{max}) associated with the π-π* transition of the π-conjugated oligomers **OH1** and **OH2** were 384 nm (ε= 9.25 × 10^4 M^{-1} cm^{-1}) and 401 nm (ε= 5.57 × 10^4 M^{-1} cm^{-1}) whereas the absorption maxima for their corresponding Au(I) organometallic wires were slightly red shifted by 7-9 nm (Fig. 3) with similar ε values. Interestingly, **OH3** and **OM3** show two distinct absorption bands. The absorption band with shorter wavelength at 332 nm (ε= 4.32 × 10^4 M^{-1} cm^{-1}) and 350 nm (ε= 6.53 × 10^4 M^{-1} cm^{-1}) for **OH3** and **OM3** respectively are assigned as π-π* transition. The absorption bands of low energy at 445 nm (ε= 2.60 × 10^4 M^{-1} cm^{-1}) and 453 nm (ε= 3.32 × 10^4 M^{-1} cm^{-1}) are attributed to intramolecular charge transfer (ICT) between electron-rich fluorene and electron-deficient benzothiadiazole moiety.[17a] The solid state absorption spectra for **OH1**-**OH3** and the digold(I) diacetylide complexes were recorded as thin films spin coated on quartz substrates. The maximum red shift in absorption maxima were observed for **OH3** (8 nm) and **OM3** (13 nm) in solid state. The insignificant bathochromic shift in solid state absorption spectra for all the oligomeric and organometallic wires suggests the rigid-rod structure having extensive π-conjugation even in solution ensured by acetynyl bridges in between the aromatic units. The optical bandgap (E_g^{opt}) for **OH1**-**OH3** and **OM1-OM3** are 2.82, 2.68, 2.37, 2.76, 2.61, and 2.31 eV respectively as calculated from the onset of solid state absorption by using the equation E_g^{opt}(eV) = 1240/$\lambda_{cut\ off}$. The bandgap of the binuclear Au(I) σ-complexes are lower than their corresponding oligomers, suggesting enhanced π-conjugation of the ligands through the metal orbitals. Most importantly, the absorption studies suggest that the bandgap can be tuned successfully by varying the electron withdrawing property of the π-conjugated aromatic spacers in between the two fluorene moieties connected through acetynyl groups. Thus bandgap decreases significantly in case of benzothiadiazole (**OH3**) than the benzotriazole (**OH2**) as the acceptor unit in this series of D-π-A-π-D based oligomer, as the acceptor property of the former is relatively higher. The absorbance data of **OH1** to **OH3** and their corresponding digold(I) σ-complexes are tabulated in Table 2. The absorption spectra of **O1**-**O3** were also studied showing similar photophysical properties to the alkynyl substituted analogues (Fig. S82 and Table S1†).

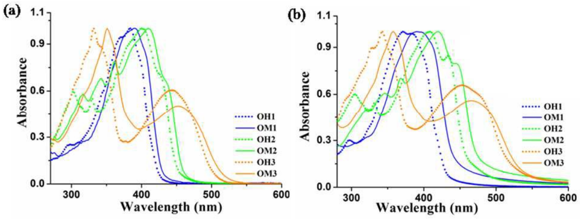

Fig. 3 Normalized absorption spectra of **OH1-OH3** and **OM1-OM3** recorded as (a) ~1x10^{-5} M solution in degassed 1,2-DCE (b) thin film (spin coated on quartz plate).

Highly emissive nature of all the compounds both in solution and solid state prompted us to study the emission properties systematically to understand the structure-property relationship. The emission of the rod-shaped alkynyl functionalized fluorophores (**OH1**-**OH3**) and their corresponding digold(I) diacetylide complexes was studied in degassed 1,2-DCE in the order of 10^{-5} M concentration at 298 K. The emission data is tabulated in Table 3. The intense emission with λ_{max} in the rage of 412-564 nm is assigned as intraligand π-π* transition (i.e., $S_1 \rightarrow S_0$).[33] **OH1** and **OH2** exhibit structured emission with major emission centered at 412 and 433 nm. Interestingly, **OH3** having benzothiadiazolyl-alkynyl moiety in between the fluorenyl-alkynyl units shows relatively broad emission centered at 542 nm, with a remarkable bathochromic shift compared to the other rigid-rod π-conjugated oligomers. The similar emission behavior was observed for the trimethylsilyl protected oligomers with alkynyl termini, **O1**-**O3** (Fig. S83 and Table S2†). The emission maxima for their corresponding digold(I) diacetylide complexes were red shifted

Table 2 Absorbance data of **OH1-OH3** and their Au(I) σ-complexes (**OM1-OM3**)

Compound	Absorption			
	Solution[a]	Thin flim[b]		
	λ_{max}, nm (ε×10^4 $M^{-1}cm^{-1}$)	λ_{max}, nm	$\lambda_{max,}$ cut off	E_g, eV (optical)
OH1	294 (sh), 370 (sh), 384 (9.25)	297, 371, 385	439	2.82
OH2	302 (3.34), 329 (3.06), 401 (5.57), 426 (sh)	304, 331, 408, 434	463	2.68
OH3	332 (4.32), 344 (sh), 445 (2.60)	327, 342, 453	523	2.37
OM1	378 (sh), 391 (10.39)	396	449	2.76
OM2	315 (3.54), 342 (4.21), 360 (4.87), 410 (6.64), 435 (sh)	322, 346, 368, 421, 446 (sh)	473	2.61
OM3	350 (6.53), 453 (3.32)	357, 466	535	2.31

[a] ~1 × 10^{-5} M 1,2-DCE solution at 298 K. [b]Measured as thin films on quartz substrates.

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Table 3 Emission data of **OH1-OH3** and their Au(I) σ-complexes (**OM1-OM3**)

Compound	Emission			
	Solution^{a}			Thin flim^{b}
	λ_{em} (λ_{ex}), nm	Quantum Yield (Φ)	Stokes Shift, cm^{-1}	λ_{em} (λ_{ex}), nm
OH1	412, 433 (384)	0.42	1769	472, 499 (385)
OH2	449, 474 (401)	0.39	2665	509 (408)
OH3	542 (445)	0.26	4021	551 (453)
OM1	426, 443 (sh) (391)	0.27	2101	474 , 504 (396)
OM2	462, 485 (410)	0.21	2745	519 (421)
OM3	564 (453)	0.13	4344	566 (466)

^{a} ~1 × 10^{-5} M in 1,2-DCE solution at 298 K. ^{b}Measured as thin films on quartz substrates.

by 14-22 nm compared to that of the parent analogues with alkynyl termini. The photoluminescence spectra of **OH1**-**OH3** and the corresponding binuclear Au(I) σ-complexes (**OM1**-**OM3**) suggests that they are blue, cyan and yellow emitters respectively (Fig. 4). The modulation of the π-acceptor groups by increasing the strength of acceptor units in between two fluorene moieties results in significant perturbation in the photonic properties, demonstrating tuning of the PL wavelength. Most importantly, the strategy to incorporate benzothiadiazole in between the two fluorene units attached through alkynyl spacers has successfully renders yellow emission. Thus, the desired yellow emissive material was successfully achieved by fine tuning of the acceptor unit in the D-π-A-π-D molecular systems. These yellow emissive fluorenyl-alkynyl based π-conjugated molecular wires are of interest for potential application as yellow light emitters. The PL quantum yields were calculated by using the absolutely measured quantum yield of quinine sulphate in degassed 0.1 M H_2SO_4 solution as reference. Quantum yield decreases from 0.42 to 0.26 on moving from **OH1** to **OH3**, suggesting strong donor-acceptor interaction leading to quenching in fluorescence.[34] Incorporation of heavy metal species, Au(I) further causes decrease in quantum yield because of strong spin-orbit coupling. No change in emission intensity of the organometallic wires was observed while studying in oxygen saturated solvent suggesting that the origin of the emission is presumably due to singlet state. The absorption and the emission spectra of **OH1**-**OH3** and **OM1**-**OM3** were also measured in different solvents to demonstrate the dependence of photophysical properties on polarity of the medium. The absorption spectra of **OH1**-**OH3** and **OM1**-**OM3** were not sensitive to the solvent polarity. The emission spectra of **OH1**-**OH2** and **OM1**-**OM2** were also insensitive with different solvent polarity. However, for **OH3** and **OM3**, a remarkable bathochromic shift in λ_{em} was observed with increasing solvent polarity (Fig. 5 and S85†). The emission maxima is shifted by 40 nm and 53 nm with increasing polarity from hexanes (0.0) to acetone (5.1) for **OH3** and **OM3** respectively. Maximum bathochromic shifts were observed in polar chlorinated solvents (CH_2Cl_2, $C_2H_4Cl_2$, $CHCl_3$) showing emission maxima at 545-551 nm (**OH3**) and 562-568 nm (**OM3**) with the Stokes shift of *ca.* 4123-4372 cm^{-1} (Table S3 and S4†). The bathochromic shift in the emission wavelength with increasing solvent polarity for **OH3** and **OM3**, having benzothiadiazole as acceptor unit suggests that the first excited state has higher dipole moment compared to its ground state.[35]

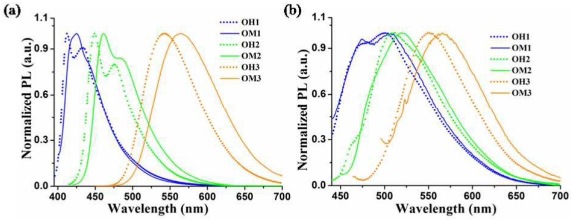

Fig. 4 Normalized PL spectra of **OH1-OH3** and **OM1-OM3** recorded as (a) ~1x10^{-5} M solution in degassed 1,2-DCE (b) thin film (spin coated on quartz plate).

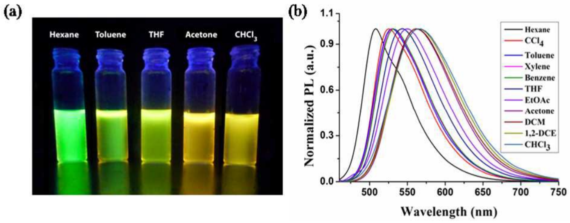

Fig. 5 (a) Visual appearance of **OM3** in different solvents under UV illumination at 365 nm. (b) Normalized PL spectra of **OM3** in solvent with different polarity.

Solid state emissive organic chromophores are of considerable interest for practical thin-film device applications, such as organic light emitting diodes, organic solid state lasers, organic field-effect transistors, nonlinear optics, organic photovoltaics (OPV).[36] In general, the luminescence of π-conjugated oligomeric compounds is quenched in the solid state due to the enhanced nonradiative deactivation *via* intermolecular interaction.[37] Interestingly, in our case an appreciable amount of emission in the solid state was observed for rigid-rod like π-conjugated oligomers, **OH1**-**OH3** and also for the digold(I) diacetylide complexes, **OM1**-**OM3** as shown in Fig. 6. The solid state PL spectra for all the

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compounds were recorded as thin films spin coated on quartz substrates, with a maximum red shift by 66 and 78 nm for **OH1** and **OM1** compared to its solution state (in 1,2-DCE) emission. For **OH3** and **OM3**, solution and solid state emission was similar with negligible red shift. Interestingly, the PL spectra of thin films of **OH1** and its corresponding binuclear Au(I) σ-complex are extremely broad, suggesting the possibility of coexistence of multiple degrees of aggregations.[17a] It is well documented in the literature that planar polyaromatic compounds form aggregates in solution through π-π interaction. The concentration dependent fluorescence analysis of **OH1**-**OH3** were studied in 1,2-DCE at 298 K to explore self-association behaviour of the wire-like fluorophores. At higher concentration (~10^{-3} M), a broad band was observed centered at 504, 521 and 580 nm respectively with relatively lower intensity. Upon gradual dilution emission wavelength was blue shifted (Fig. S88†). Upon dilution beyond 10^{-5} M, the aggregates dissociate to form monomers exhibiting emission at lower wavelength. The broad band at higher concentration (10^{-3} M) was attributed to the self-assembled aggregates formed through π-π interaction which becomes predominant with increase in concentration. Being emissive as thin film, these newly synthesized fluorenyl-alkynyl based rod-shaped π-conjugated oligomers and their binuclear Au(I) acetylide complexes may find application in optoelectronic devices as the efficiency of the optoelectronic devices depends on the solid state emission.

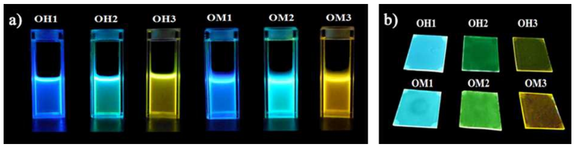

Fig. 6 Visual appearance of **OH1-OH3** and **OM1-OM3** demonstrating tuning of emission wavelength; (a) in 1,2-DCE (b) in Thin film (spin-coated on quartz plate) showing appreciable amount of emission even in solid state (under UV illumination at 365 nm).

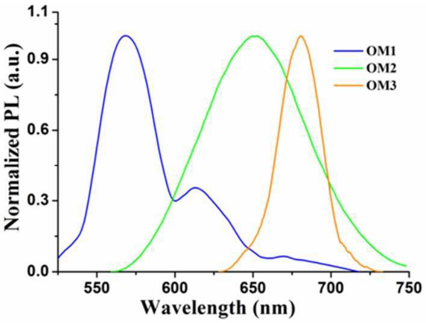

Fig. 7 Normalized phosphorescence spectra of **OM1-OM3** recorded in degassed CH_2Cl_2 at 77 K.

Phosphorescence. Triplet state emission (phosphorescence) plays an important role in optoelectronics in the π-conjugated oligomers and polymers, which is generally achieved by incorporation of heavy metal into the π-conjugated backbone.[22f-g,29,33] The PL spectra of the synthesized digold(I) diacetylide organometallic complexes were measured in degassed CH_2Cl_2 at 77 K (Fig. 7). We observed virtually no fluorescence band but only the spin-forbidden triplet emission (phosphorescence) for all the organometallic wires. **OM1** exhibits emission at 569 nm along with a low intense band at 614 nm, whereas **OM2** exhibits broad emission centered at 653 nm. Interestingly, **OM3** reveals comparatively narrow emission band centered at 683 nm with FWHM (full width at half maxima) of 31 nm. The role of Au(I) on inducing phosphorescence was further confirmed by studying the phosphorescence spectra of the parent oligomers with -C≡C-H termini (**OH1**-**OH3**) in similar condition, exhibiting no phosphorescence. The difference of the emission maximum in PL spectra of binuclear Au(I) complexes in 298 K and 77 K are 143, 191 and 119 nm respectively, which are in accordance with the previously reported literature.[22f-g] The phosphorescence quantum yields of **OM1**-**OM3** are 0.30, 0.23 and 0.19, which were calculated by using the absolutely measured quantum yield of 9,10-diphenylanthracene in degassed CH_2Cl_2 at 77 K.[22f] The emission intensity of the organometallic wires was completely quenched while using oxygen saturated solvent, and the phosphorescence was reappeared by deoxygenating the solution by saturation with argon gas, confirming that the origin of the emission is due to triplet state (Fig. S90†). Thus, our investigation indicates that the organic triplet emissions can be harvested by the incorporation of Au(I) to the π-conjugated oligomers, which enables efficient intersystem crossing from the S_1 singlet to the T_1 triplet excited state. In principle, the phosphorescent materials are superior to the fluorescent substrates for small-molecule OLED applications as the efficiency of organic light emitting diodes is typically controlled by the presence of triplet state emission.

Lifetime. To study the dynamics of the emissive species, the fluorescence lifetime of **OH1**-**OH3** and their Au(I) σ-complexes was measured in deoxygenated 1,2-DCE in the order of 10^{-5} M concentration at 298 K using Time Correlated Single Photon Counting (TCSPC) instrument. The samples were excited with pulse laser at 408 nm. The results obtained for the π-conjugated oligomers and the respective organometallic wires are shown in Fig. S89† and Fig. 8 and tabulated in Table 4. A mono-exponential decay curve was observed for the oligomers, whereas bi-exponential decay curve was observed for their binuclear Au(I) organometallics complexes. The average lifetime (τ_{av}) increases on going from **OH1** to **OH3** (0.51, 0.98, and 3.18 ns respectively) and the similar trend is observed for the Au(I) σ-complexes, as a result of gradual decrease in bandgap.[38] Incorporation of heavy metal caused decrease in the fluorescence lifetime values, because of spin-orbit coupling induced by the heavy atom resulting the mixing of the singlet and the triplet excited states through the efficient intersystem crossing (ISC). The phosphorescence life time of the binuclear gold(I) complexes, measured in degassed CH_2Cl_2 at 77 K, were found to be 766, 1211 and 1931 µs for

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OM1-**OM3** respectively which are consistent with the reported Au(I) organometallic congeners.[22f,38]

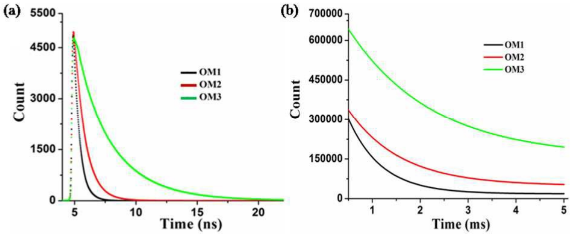

Fig. 8 Time resolved (a) fluorescence (298 K) and (b) phosphorescence (77 K) spectra of **OM1**-**OM3.**

Table 4 Lifetime values for **OM1**-**OM3**.

Compound	Fluorescence lifetime, ns			Phosphorescence lifetime, µs
	τ_1 (A_1)	τ_2 (A_2)	τ_{av}[a]	
OM1	0.42 (98%)	0.99 (2%)	0.43	766
OM2	0.73 (70%)	1.05 (30%)	0.83	1211
OM3	0.85 (19%)	3.12 (81%)	2.69	1931

[a]The average lifetime (τ_{av}) was calculated using the equation, $\tau_{av} = (A_1/(A_1 + A_2))\tau_1 + (A_2/(A_1 + A_2))\tau_2$, where A_1 and A_2 are the contribution from each components.

Conclusions

In summary, we have successfully synthesized and characterized a series of fluorenyl-alkynyl based D-π-A-π-D rod-shaped oligomers with alkynyl termini and their corresponding digold(I) diacetylide organometallic wires. Judicious incorporation of different donor and acceptor aromatic moieties through alkynyl spacers in between two fluorenyl-alkynyl units allowed fine tuning of the electronic properties. The effect of modulation of the π-conjugated spacers was clearly revealed in their photophysical studies. The fluorenyl-alkynyl oligomers with –C≡CH termini and their corresponding binuclear Au(I) complexes (**OM1**-**OM3**) are blue, cyan and yellow emitter respectively. Thus the bandgap and emission wavelength were finely tuned by increasing electron deficient character of the central π-conjugated aromatic unit (Fl, Btz and Btd) to the fluorenyl-alkynyl backbone. Consequently, the fluorene based π-conjugated yellow emitter was successfully achieved as targeted. The binuclear Au(I)-alkynyl σ-complexes exhibited phosphorescence at 77 K due to heavy atom effect by gold, enhancing efficient intersystem crossing leading to triplet emission, as manifested by the life time values in the range of millisecond. These phosphorescent digold(I) diacetylide organometallic wires, specially the yellow emissive, **OH3** and **OM3** are attractive building blocks for application in OLEDs and other optoelectronic devices. In addition, yellow phosphorescence in combination with sky blue phosphorescence is also one of the key components for the construction of white OLEDs. Further studies for searching yellow light emitting materials for developing yellow and white OLED devices is underway.

Experimental section

Materials and methods

All moisture sensitive reactions and manipulations were carried out under an atmosphere of pre-purified argon or nitrogen using dual manifold standard Schlenk techniques. The glasswares were oven-dried (at 180 °C) and cooled under vacuum. Tetrahydrofuran and toluene were dried over Na/benzophenone. Dry DCM and 1,2-DCE were obtained by distillation over CaH_2 whereas MeOH and EtOH were dried by Mg cake and stored on 3 Å molecular sieves.[39] Unless otherwise mentioned all the chemicals were of analytical grade, obtained from Aldrich, and used without further purification. $HAuCl_4$ was acquired from Alfa Aesar. Triphenylphosphine was purchased from Spectrochem and purified by recrystallization from EtOH. Silica gel (60-120 mesh) and alumina, used for column chromatography were purchased from Merck. Eluting systems for column chromatography purifications were determined by thin layer chromatography (TLC) analysis. TLC plates were visualized under UV light (254 nm) or in iodine chamber. $PdCl_2$ was purchased from Arora Matthey Ltd., India. Compounds 2,7-dibromo-9,9-dioctylfluorene (**3**),[40] 2,7-diiodo-9,9-dioctylfluorene (**6**),[41] 2,7-Bis((trimethylsilyl)ethynyl)-9,9-dioctylfluorene (**7**),[41] 2,7-diethynyl-9,9-dioctylfluorene (**8**),[41] 4,7-diethynyl-2-hexylbenzotriazole (**14**)[42] and 4,7-diethynylbenzothiadiazole (**19**)[43] were prepared as previously reported literature procedure (see supporting information for detailed synthesis). $Pd(PPh_3)_4$,[44] $Pd(PPh_3)_2Cl_2$,[45] and $Au(PPh_3)Cl$[46] were synthesized following the procedures described in the literature.

^{1}H (600 MHz, 400 MHz, 200 MHz), ^{13}C{^{1}H} (150 MHz, 100 MHz, 50 MHz) and ^{31}P{^{1}H} (162 MHz) NMR spectra were obtained from Bruker Lambda spectrometer using $CDCl_3$ unless otherwise mentioned. Spectra were internally referenced to residual solvent peaks (δ = 7.26 ppm for proton and δ = 77.23 for carbon (middle peak) in $CDCl_3$ or an externally capillary of 85% H_3PO_4 for ^{31}P). All coupling constants (*J*) are given in Hz. MALDI-TOF MS study was performed with DHB (2,5-dihydroxy benzoic acid) matrix by using Bruker UltrafleXtreme instrument. The absorption and fluorescence spectra were collected using a Shimadzu (Model UV-2450) spectrophotometer and a Hitachi (Model F-7000) spectrofluorimeter respectively. The phosphorescence spectra were recorded on a Jobin Yvon-Spex Fluorolog-3 spectrofluorimeter equipped with temperature-controlled sample holder at 77 K in CH_2Cl_2. The time-resolved emission decays were recorded using a time correlated single photon

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counting (TCSPC) picoseconds spectrophotometer (IBH). FTIR spectroscopy was recorded in Spectrum-BX (Perkin Elmer). Cyclic Voltammetry (CV) and Differntial Pulse Voltammetry (DPV) analyses were performed on a BASi Epsilon electrochemical workstation. Solid state electrochemical analyses in CH_3CN medium were performed on film made by drop casting of the sample on a BASi glassy carbon (GC) disk electrode. For solution electrochemical studies, DCM was used as solvent. The electrochemical study was conducted using 0.1 M *tetra*-n-butylammonium hexafluorophosphate ($TBAPF_6$) as supporting electrolyte. The reference electrode was Ag/AgCl and the auxiliary electrode was a Pt wire. The ferrocene/ferrocenium couple occurs at $E_{1/2}$ = +0.51 (70) V versus Ag/AgCl under the same experimental conditions. Thermogravimetric analysis (TGA) was carried out using a Perkin Elmer Pyris Diamond TG/DTA instrument. The thermal stabilities of the samples under nitrogen were determined by measuring their weight losses while heating at a rate of 5 ^{o}C/min. Differential scanning calorimetry (DSC) was performed on a TA DSC Q20 unit operated at a heating and cooling rates of 10 ^{o}C/min. Elemental analysis was carried out in Perkin Elmer Series II CHN 2400 analyzer.

Pertinent crystallographic data (Table S8†) for **O3** including X-ray data collection and refinement detail have been summarized in SI. The orange needle-like single crystals of **O3** suitable for X-ray crystallography, were obtained by layering MeOH on DCM solution of **O3**. The title compound crystallizes in the triclinic space group, P-1. Two independent molecules of **O3** were located in the asymmetric unit with negligible differences in their metrical parameters.[47] CCDC 1512387 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Synthesis and characterization

Synthesis and characterization of the key precursors and oligomers having -C≡C-TMS (**O1-O3**) and -C≡C-H termini (**OH1-OH3**) are included in supporting information.†

Synthesis of OM1. OH1 (124 mg, 0.098 mmol) and $Au(PPh_3)Cl$ (102 mg, 0.21 mmol) were dissolved in 10 mL of dry DCM in a 100 mL Schlenk flask under argon atmosphere. To that NaOMe (26 mg, 0.49 mmol in 5 mL of dry MeOH) was added through a syringe. The reaction flask was covered with aluminium foil to protect it from light. The reaction mixture was stirred for overnight at 28 ^{o}C under argon atmosphere. It was filtered through celite bed (2 cm height and 18 mm diameter) by using a Schlenk frit under argon atmosphere to remove NaCl. The solvent was evaporated under reduced pressure and dissolved in minimum amount of dry DCM (2 mL). The compound was precipitated from its concentrated CH_2Cl_2 solution by adding dry MeOH (20 mL) under stirring. A bright yellow precipitate was obtained, which was separated by filtration through a filter-paper-stripped cannula. Finally, the precipitate was purified by a short (column height 6 cm and diameter 18 mm) alumina column using degassed and distilled EtOAc/ hexanes as eluent under inert atmosphere to afford an analytically pure yellow solid of **OM1**. Yield: 0.188 g (88%). ^{1}H NMR ($CDCl_3$, 600 MHz): δ (ppm) 7.69-7.46 (m, 48H, $H_{Fl,Ph}$), 2.00-1.93 (m, 12H, octyl CH_2 attached to fluorene), 1.25-1.03 (m, 60H, H_{octyl}), 0.85-0.76 (m, 18H, H_{octyl}), 0.67-0.54 (m, 12H, H_{octyl}); $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 150 MHz): 151.1, 150.7, 141.2, 140.7, 139.3, 134.4, 134.3, 134.2, 132.2, 132.1, 131.6, 129.3, 129.2, 129.1, 119.7, 119.6, 114.1 (aromatic carbons), 105.4 (-Fl-C≡$\underline{C}$-Au), 90.9 (-Fl-C≡$\underline{C}$-Fl-$\underline{C}$≡C-Fl-), 90.5 (-Fl-$\underline{C}$≡C-Fl-C≡$\underline{C}$-Fl-), 83.2 (-Fl-$\underline{C}$≡C-Au), 55.4 (carbon at 9-position of Fl), 40.3, 31.5, 30.1, 29.4, 23.8, 22.6, 14.1 (alkyl carbons); $^{31}P\{^{1}H\}$ ($CDCl_3$, 162 MHz): 42.7 ppm; FTIR (KBr, cm^{-1}): 2204 ($\upsilon_{C\equiv C\ stretching}$); MALDI-TOF MS (m/z): $C_{131}H_{150}Au_2P_2$; Calculated 2180.062 ($[M+H]^{+}$); Experimental 2180.158 ($[M+H]^{+}$); Anal. Calc. for $C_{131}H_{150}Au_2P_2$: C, 72.16; H, 6.93. Found: C, 65.24, H, 7.24. UV-Vis λ_{max}: 391 nm ($\varepsilon = 10.39\times10^{4}\ M^{-1}cm^{-1}$); $\lambda_{em}(\lambda_{ex})$: 426 (391) nm. In elemental analysis of **OM1**, even after repeated attempt, identical result was observed with 6.9 % less in 'C' (See SI). This is presumably due to the formation of Au particles embedded in the carbon matrix (generated from fluorenyl-alkynyl moieties).

Synthesis of OM2. OM2 was prepared using a similar procedure as that for **OM1** using **OH2** (125 mg, 0.12 mmol), $Au(PPh_3)Cl$ (119 mg, 0.24 mmol) and NaOMe (31 mg, 0.58 mmol in 5 mL of dry MeOH). It was purified by a short (column height 5 cm and diameter 18 mm) alumina column using degassed and distilled EtOAc/ hexanes as eluent under inert atmosphere to get analytically pure dark yellow solid of **OM2**. Yield: 0.212 g (92%). ^{1}H NMR ($CDCl_3$, 600 MHz): δ (ppm) 7.65-7.47 (m, 44H, $H_{Btz,\ Fl,\ Ph}$), 4.85-4.83 (t, *J*= 6 Hz, 2H, (Btz)N-$\underline{CH_2}$-C_5H_{11}), 2.23-2.21 (m, 2H, (Btz)-N-CH_2-$\underline{CH_2}$-C_4H_9) 1.96-1.93 (m, 8H, octyl CH_2 attached to fluorene), 1.25-1.02 (m, 46H, $H_{hexyl,\ octyl}$), 0.82-0.80 (m, 15H, $H_{hexyl,\ octyl}$), 0.61-0.56 (m, 8H, H_{octyl}); $^{13}C\{^{1}H\}$ ($CDCl_3$, 150 MHz): 151.1, 150.8, 144.3, 141.7, 139.2, 134.4, 131.6, 131.3, 130.1, 129.1, 127.1, 126.2, 123.8, 120.9, 119.7, 113.8 (aromatic carbons), 105.4 (-Fl-C≡$\underline{C}$-Au), 105.2 (-Fl-C≡$\underline{C}$-Btz-$\underline{C}$≡C-Fl-), 97.7 (-Fl-$\underline{C}$≡C-Btz-C≡$\underline{C}$-Fl-), 85.5 (-Fl-$\underline{C}$≡C-Au), 57.1 ((Btz)N-$\underline{C}H_2$-C_5H_{11}), 55.2 (carbon at 9-position of Fl), 40.6, 31.8, 31.3, 30.2, 30.1, 29.4, 29.3, 23.8, 22.6, 22.5, 14.1, 13.9 (alkyl carbons); $^{31}P\{^{1}H\}$ ($CDCl_3$, 162 MHz): 42.7 ppm; FTIR (KBr, cm^{-1}): 2200 ($\upsilon_{C\equiv C\ stretching}$); MALDI-TOF MS (m/z): $C_{114}H_{125}Au_2N_3P_2$; Calculated 1992.875 ($[M+H]^{+}$); Experimental 1992.790 ($[M+H]^{+}$); Anal. Calc. for $C_{114}H_{125}Au_2N_3P_2$: C, 68.70; H, 6.32, N, 2.11. Found: C, 67.48, H, 6.66, N, 2.36. UV-Vis λ_{max}: 410 nm ($\varepsilon = 6.64\times10^{4}\ M^{-1}cm^{-1}$); $\lambda_{em}(\lambda_{ex})$: 462 (410) nm.

Synthesis of OM3. OM3 was synthesized analogously to **OM1** using **OH3** (157 mg, 0.16 mmol), $Au(PPh_3)Cl$ (162 mg, 0.33 mmol) and NaOMe (42 mg, 0.78 mmol in 6 mL of dry MeOH). It was purified by a short (column height 6 cm and diameter 18 mm) alumina column using degassed and distilled EtOAc/ hexanes as eluent under inert atmosphere to afford pure red solid of **OM3**. Yield: 0.275 g (91%). ^{1}H NMR ($CDCl_3$, 600 MHz): δ (ppm) 7.83 (s, 2H, H_{Btd}), 7.67-7.47 (m, 42H, $H_{Fl,\ Ph}$), 1.97-1.94 (m, 8H, octyl CH_2 attached to fluorene), 1.25-1.02 (m, 40H, H_{octyl}), 0.82-0.80 (m, 12H, H_{octyl}), 0.66-0.55 (m, 8H, H_{octyl}); $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 150 MHz): 154.6, 151.4, 151.1, 142.3, 139.4, 134.6, 132.7, 130.9, 131.8, 130.2, 129.8, 129.4, 129.3, 127.4, 126.4, 120.7, 120.0, 117.4 (aromatic carbons), 105.5 (-Fl-C≡$\underline{C}$-Au), 105.4 (-Fl-C≡$\underline{C}$-Btd-$\underline{C}$≡C-Fl-), 99.2 (-Fl-$\underline{C}$≡C-Btd-C≡$\underline{C}$-Fl-), 85.7 (-Fl-$\underline{C}$≡C-Au), 55.4 (carbon at 9-position of Fl), 40.8, 32.0, 30.3, 29.6, 24.0, 22.8, 14.3 (alkyl carbons); $^{31}P\{^{1}H\}$ ($CDCl_3$,

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162 MHz): 42.9 ppm; FTIR (KBr, cm^{-1}): 2200 ($\upsilon_{C\equiv C\ stretching}$); MALDI-TOF MS (m/z): $C_{108}H_{112}Au_2N_2P_2S$; Calculated 1925.743 ($[M+H]^+$); Experimental 1925.690 ($[M+H]^+$); Anal. Calc. for $C_{108}H_{112}Au_2N_2P_2S$: C, 67.35; H, 5.86, N, 1.45. Found: C, 67.21, H, 6.04, N, 2.13. UV-Vis λ_{max}: 453 nm (ε = 3.32×10^4 M^{-1}cm^{-1}); $\lambda_{em}(\lambda_{ex})$: 564 (453) nm.

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(47) The crystal diffracted very weakly beyond 1.3 Å resolution, and the ratio of observed/unique reflection is too low of 20%. Moreover, two molecules of **O3** are present in the asymmetric unit suffering disorder and significant thermal vibration associated with the long alkyl groups (octyl) and terminal trimethylsilyl groups. Thus relatively higher R_1 and wR_2 values are unsurprising as reported for other published structures.[28]

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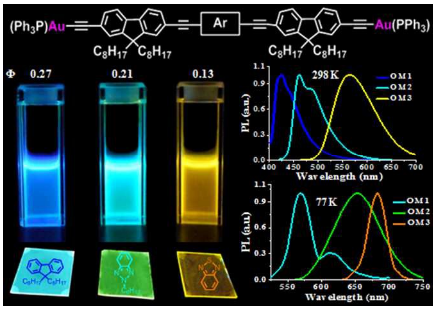
TOC



Yellow light emitting fluorenyl-alkynyl based D-π-A-π-D rod-shaped oligomer with alkynyl termini, and the corresponding binuclear Au(I) organometallic wire are achieved by fine tuning of the bandgap through systematic modulation of the π-conjugated spacers.