Volume 1 | Number 1 | Jan 2013 | Pages 1–100

ChemComm

Chemical Communications
www.rsc.org/chemcomm

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COMMUNICATION

Synthesis and photophysical properties of platinum-acetylide copolymers with thiophene, selenophene and tellurophene

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A series of platinum-acetylide copolymers with thiophene, selenophene, and tellurophene have been synthesized and studied. Photoluminescence experiments show that polymers undergo intersystem crossing to triplet states, leading to phosphorescence. The observed phosphorescence decreases in intensity moving down the group. DFT calculations are used to further understand the optical properties.

Platinum-acetylide conjugated polymers have attracted a great deal of attention due to their potential application in molecular electronics.[1] These polymers exhibit interesting photophysical properties such as efficient intersystem crossing, high triplet yields, and long-lived phosphorescent $^3(\pi,\pi^*)$ excited states, which makes them attractive materials for fundamental studies examining triplet states and phosphorescence in metal-containing polymers.[2] A platinum-acetylide polymer incorporating an unsubstituted thiophene has been previously synthesized and examined.[3] However, there have not been reports of higher chalcogenophene platinum-acetylide polymers. Heavy group 16 substitution in conjugated polymers is a promising strategy to alter electronic and optical properties.[4,5] Thus, incorporating group 16 elements into platinum-acetylide polymers may lead to enhanced photophysical properties that would make these materials further suitable for applications in organic electronic devices.[6] Herein, we report the full series of platinum-acetylide alternating copolymers with thiophene, selenophene, and tellurophene and study the effect that group 16 heteroatom substitution has on their photophysical properties.

To synthesize platinum-acetylide chalcogenophene polymers (Scheme 1), we chose to prepare chalcogenophenes

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† Electronic Supplementary Information (ESI) available: Detailed experimental information, thermogravimetric analysis traces, solid-state absorption spectra, calculated frontier orbitals, fluorescence spectra in chloroform, NMR spectra of polymers. See DOI: 10.1039/c000000x

with a dodecyl group at the 3-position to impart the final polymers with good solubility in common organic solvents. The overall monomer synthesis requires halogenation of the 3-dodecylchalcogenophenes followed by installation of trimethylsilylethynyl group at the 2 and 5 positions. 3-Dodecylthiophene (**1a**) was purchased from Sigma-Aldrich, while 3-dodecylselenophene[7] (**1b**) and 3-dodecyltellurophene[8] (**1c**) were prepared according to literature procedures. **1a** and **1c** were iodinated to give the corresponding 2,5-diiodo-3-dodecylthiophene (**2a**) and 2,5-diiodo-3-dodecyltellurophene (**2c**). Iodination attempts on **1b** were unsuccessful and it was therefore brominated to afford 2,5-dibromo-3-dodecylselenophene (**2b**). Treatment of the halogenated chalcogenophenes with trimethylsilylacetylene under Sonogashira coupling reaction conditions gave the corresponding 2,5-bis(trimethylsilylethynyl)-3-dodecylchalcogenophene monomers **3a, 3b and 3c** in 53%, 63% and 40% yield, respectively.

The platinum-acetylide chalcogenophene polymers were prepared in a single-vessel reaction by treating monomers **3a-c** with sodium methoxide, methanol, and *trans*-bis(triethylphosphine)platinum(II) dichloride under an inert
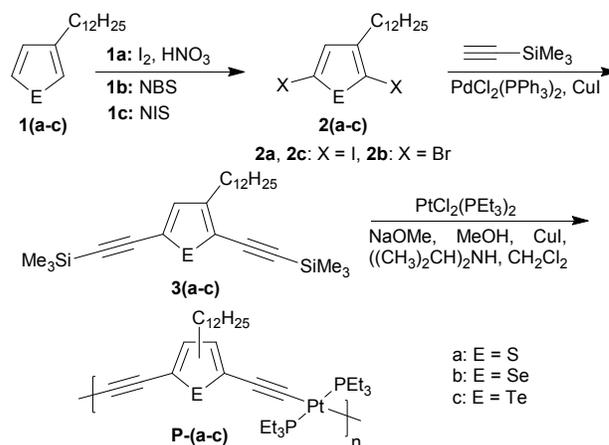
Scheme 1 Synthetic route to polymers **P-S**, **P-Se** and **P-Te**.

Table 1 M_n, M_w, Đ and % yields of the synthesized polymers.

Polymer	M_n (kg mol^{-1})	M_w (kg mol^{-1})	Đ	% yield
P-S	25.8	48.2	1.87	68%
P-Se	30.9	64.4	2.08	54%
P-Te	13.9	51.3	3.69	47%

atmosphere. Sodium methoxide and methanol convert bis(trimethylsilylethynyl)-3-alkylchalcogenophene to the free alkyne species *in-situ*, which then undergoes a dehydrohalogenation reaction with *trans*-bis(triethylphosphine)platinum(II) dichloride to produce the desired polymer.[9] Following polymerization, the volatile compounds were removed under reduced pressure and the residual solids were suspended in methanol and filtered through a soxhlet thimble. The solids were washed with methanol and hexanes, and then extracted into chloroform to afford the target polymers **P-S**, **P-Se**, and **P-Te** in 47-68% yields (Table 1).

To confirm the polymeric nature of the materials, chain-length approximation was conducted in tetrahydrofuran (THF) at room temperature by gel permeation chromatography (GPC) relative to polystyrene standards (Table 1). While it is known that GPC references to polystyrene overestimates conjugated polymer molecular weight, in the case of heteroatom substitution it is particularly useful for relative comparisons because the identity of the heteroatom is unlikely to change the hydrodynamic radius of the polymer. Accordingly, **P-Te** has a lower M_n (13.9 kg mol^{-1}) and a broader Đ (3.69) compared to the sulfur and selenium analogues. This is likely due to lower solubility of the tellurium polymer which terminates polymerization.[8] The solid-state properties of the polymers were examined by thermogravimetric analysis (see ESI†). **P-S**, **P-Se**, and **P-Te** experience 5% mass loss at 309 °C, 290 °C, and 270 °C, respectively. This decrease in thermal stability of the heavier analogues may be due to the increased lability of chalcogen-carbon bond resulting from the larger size of the heteroatom and consequently longer C-Se and C-Te bond distances. It is however noteworthy that all three analogues are stable up to 250 °C.

The polymers were further characterized using NMR spectroscopy (see ESI†). The ^{1}H NMR spectra of the polymers have resonances from the single chalcogenophene proton in the aromatic region, six broad resonances between 2.53 and 0.87 ppm; four of which are assigned to the dodecyl chain on the basis of their integration, and the remaining two broad resonances are assigned to the phosphine ethyl groups. The ^{31}P{^{1}H} NMR spectra of the polymers have three phosphorus signals due to the different regioisomers, and each signal contains platinum satellite peaks. The $^1J_{Pt-P}$ values for the polymers are in the range of 2359-2374 Hz, which are consistent with the *trans* orientation of the triethylphosphines.[10] The lack of a terminal alkyne proton signal in the ^{1}H NMR spectra together with the presence of additional signals in the ^{31}P{^{1}H} NMR spectra indicates that the terminal group is likely a platinum centre with triethylphosphine and chlorine ligands. Unfortunately, we were unable to observe any signals in the ^{195}Pt NMR spectra of the polymers, and this is likely because the platinum signal is very broad and as a result cannot be detected. A peak is observed at 711.3 ppm in the ^{77}Se NMR for **P-Se** and at 1005.0 ppm in the ^{125}Te NMR for **P-Te**, confirming the presence of these chalcogens in the respective polymers.

^{1}H-^{31}P-CIGAR NMR experiments on the polymers show an unusual six or seven bond coupling between the phosphorus and the chalcogenophene backbone proton (see ESI†). While this is somewhat unexpected, a five bond correlation between chalcogen and phosphorus centres has been observed
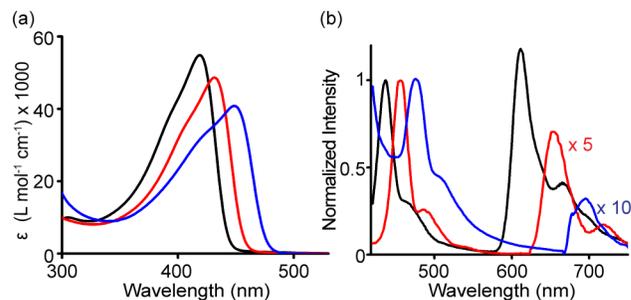

Fig. 1 (a) Absorption spectra of polymers **P-S** (black), **P-Se** (red) and **P-Te** (blue) in chloroform solution at room temperature. (b) Emission spectra of **P-S** (black), **P-Se** (red) and **P-Te** (blue) in degassed 2-MeTHF solution at 77 K normalized to the fluorescence band maxima. An excitation wavelength of 400 nm was used. The phosphorescence bands of **P-Se** and **P-Te** have been multiplied by 5 and 10, respectively, to compare the relative phosphorescence intensities. The peak shapes of **P-Se** and **P-Te** were smoothened using the Savitzky-Golay filter.

previously in related platinum-acetylide chalcogenophene small molecules, which demonstrates the ability of the platinum-acetylide framework to facilitate long range through-bond coupling.[9] We conducted ^{1}H-^{31}P-EXSIDE NMR experiments to probe the magnitude of ^{1}H-^{31}P coupling in the different chalcogenophenes; however, we could not obtain the coupling constant from these experiments due to low signal-to-noise for the phosphorus nuclei.

Optical absorption spectra of the polymers were recorded in chloroform at room temperature (Fig. 1). As expected for heavy atom substitution in conjugated materials,[4] the absorption maxima, λ_{max}, of the polymers shifts to longer wavelengths as one moves from **P-S** (418 nm) to **P-Se** (431 nm) to **P-Te** (448 nm). Furthermore, the absorption coefficient (based on the molecular weight of the repeat unit) at the absorption maxima decreases in intensity moving from **P-S** (55,000 L mol^{-1} cm^{-1}) to **P-Se** (49,000 L mol^{-1} cm^{-1}) to **P-Te** (41,000 L mol^{-1} cm^{-1}), a phenomenon that has been observed in other chalcogen-containing conjugated materials.[4] Density functional theory (DFT) and time dependent DFT (TD-DFT) calculations were performed on model oligomers to elucidate the origin of the features observed in the solution optical experiments (see ESI†). Model oligomers containing five chalcogenophene and four *trans*-bis(trimethylphosphine)platinum subunits were used as this conjugation length is generally sufficient for reproducing experimentally obtained electronic properties while minimizing computational demand.[11] TD-DFT calculations predict that the main transition in the polymers is HOMO⟶LUMO+1. The molecular orbital (MO) diagrams of the HOMO and LUMO+1 show delocalized electron density distributed across the length of the sulfur and selenium model oligomers (see ESI†), with delocalization decreasing in the tellurium model oligomers (Fig. 2). Furthermore, the MO diagrams indicate that the HOMO⟶LUMO+1 transition is a delocalized π-π* transition. The LUMO+1 is more stabilized moving from S (-0.86 eV) to Se (-0.92 eV) to Te (-1.05 eV) while the HOMO energy level is not affected by the heavy atom substitution. Thus, the red-shift in optical absorption can be attributed to lowering of the LUMO+1 energy level moving down the group. The solid-state absorption spectra (see ESI†) of the polymers are similar to the solution absorption spectra. The lack of aggregation-induced absorption features (such as additional vibronic bands and a spectral shift) suggests minimal interchain electronic coupling in the solid-state. We speculate that this is
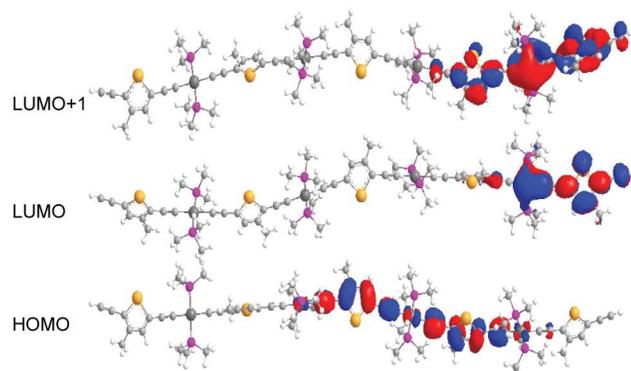
Fig. 2 Calculated HOMO, LUMO and LUMO+1 molecular orbital diagrams of the tellurophene model oligomer (B3LYP; 6-31G(d)/SDD; isocontour value 0.02).

due to the regioirregularity of the polymers.

The emission λ_{max} for **P-S**, **P-Se**, and **P-Te** in chloroform solution occurs at 438 nm, 452 nm and 460 nm, respectively (see ESI†). This red-shift in emission λ_{max} in **P-Se** and **P-Te** is consistent with a lowering of the LUMO+1 energy as predicted by the TD-DFT calculations. The fluorescence quantum yield for **P-S**, **P-Se**, and **P-Te** in chloroform solution is 0.34%, 0.32% and 0.06%, respectively. On the basis that selenium and tellurium have a large spin-orbit coupling constant, and can therefore promote intersystem crossing, we obtained emission spectra of the polymers in degassed chloroform solutions (see ESI†). Degassing is essential as it removes dissolved oxygen which can cause diffusional quenching of triplet emission, and loss of phosphorescence intensity.[12] After degassing, fluorescence was still observed in the polymers, but to our surprise we also observe new emission bands with maxima at 617 nm, 641 nm, and 671 nm for **P-S**, **P-Se**, and **P-Te**, respectively. The emergence of these new spectral features after degassing strongly suggests that the polymers are phosphorescent. Appreciable photoluminescence is not observed in the polymer thin-films.

To further investigate phosphorescence from the polymers, emission spectra were obtained in 2-methyltetrahydrofuran (2-MeTHF) solution at 77 K (Fig. 1). We observe emission bands with maxima at 435 nm (**P-S**), 457 nm (**P-Se**), and 474 nm (**P-Te**) that are similar in peak shape to the fluorescence spectra recorded in chloroform. Additional bands are observed for **P-S**, **P-Se**, and **P-Te** with maxima at 611 nm, 654 nm, and 695 nm at 77 K, respectively, which are assigned to phosphorescence. The intensity of each is increased with respect to the room temperature measurement, and is attributed to suppression of non-radiative decay pathways in the rigid, low temperature 2-MeTHF matrix.[12]

To investigate the effect that group 16 elemental substitution has on phosphorescence intensity in these polymers, we plotted the 77 K total emission spectra when the fluorescence intensity was normalized (λ_{max}) (Fig. 1). Interestingly relative to fluorescence intensity, stronger phosphorescence is observed in the sulfur analogue compared to the selenium and tellurium analogues. This is unexpected as heavy atoms such as selenium and tellurium have large spin-orbit coupling constants of 1659 cm^{-1} and 3384 cm^{-1}, respectively, and would therefore be expected to promote intersystem crossing through the well-known heavy atom effect.[13] The decreased phosphorescence intensity in the selenium and tellurium analogues could therefore be due to

increased twisting of the polymer backbone as predicted from the optimized geometries (see ESI†), which may promote non-radiative internal conversion back to the ground state and thus a lower triplet yield.[14] Another interesting feature in the low temperature emission spectra is that all the polymers display vibrationally resolved fluorescence and phosphorescence bands. This is commonly observed in low temperature experiments on conjugated polymers, and likely arises from a small subset of conformations in the low temperature environment.

In conclusion, we have synthesized a series of novel platinum-acetylide chalcogenophene polymers by an *in-situ* deprotection-dehydrohalogenation strategy and carried out a systematic study on their photophysical properties to gain insight into the effect of the heavy atom substitution in these polymers. Heavy-atom substitution causes a red-shift in optical absorbance, fluorescence, and phosphorescence. The relative phosphorescence intensity decreases in the heavier analogues. NMR experiments confirm long range coupling between the phosphorus and the chalcogenophene proton through the Pt centre, while DFT shows some differences in geometry and electronic delocalization that depends on the identity of the heteroatom. These are rare examples of main-group and transition metal-containing polymers. Their straightforward synthesis and interesting photophysical properties should motivate their continued study and application.

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