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# Donor-acceptor interactions in organometallic and organic poly-ynes

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## Abstract

We compare the spectroscopic properties of donor-acceptor type poly-ynes of the type $[\text{D-C}\equiv\text{C-A-C}\equiv\text{C-}]_n$ with a fluorine-substituted phenylene or a thieno-pyrazine unit as acceptor, and platinum or alkoxy-substituted phenylene as donor.

*Keywords:* Donor-acceptor poly-ynes, Optical absorption and emission spectroscopy, Low-bandgap conjugated polymers, Charge transfer

## 1. Introduction

Organometallic poly-ynes are good model systems to study the triplet excited state because the strong spin-orbit coupling of the metal renders the spin-forbidden emission from the triplet excited state (phosphorescence) partially allowed.[1] However, these systems typically have very large optical gaps (around 3 eV). [2] To design low-gap organometallic and corresponding organic poly-ynes, we use spacers between the acetylenic units that may act as acceptors, while an electron-rich transition metal platinum or an alkoxy-substituted phenyl ring acts as a donor. This creates a donor-acceptor type system which can lower the bandgap in a fashion analogous to a pini superlattice. [3]

## 2. Experimental Methods

Excitation for the photoluminescence measurements (PL) was provided by the UV lines of an argon-ion laser (355-365 nm). The spectra were taken from spin-cast films using a spectrograph coupled to a CCD array. A continuous-flow helium cryostat was used for low temperature measurements. Absorption spectra were taken using a λ-9 Perkin Elmer spectrometer.

## 3. Materials

Some of the compounds used are shown in Fig. 1, together with the corresponding abbreviations. The synthesis and chemical characterisation of Pt-TBT and Pt-TThpT have been reported;[4,5], that of the remaining compounds will be published in separate papers. Not explicitly shown are the corresponding organometallic monomers; these are $[\text{RPt(Bu3)}_2\text{-C}\equiv\text{C-A-C}\equiv\text{C-Pt(Bu3)}_2\text{R}]$ type compounds with R = Cl or Ph. Also not shown is Pt-TB$(\text{OCH}_3)_2$T, which is Pt-TBT with an alkoxy-substituted phenyl ring.

The Pt-TBT with the phenyl ring is well studied and provides a reference system[1].The fluorine-substituted phenyl ring in Pt-TB(4F)T is expected to be electron-withdrawing. The thieno-pyrazine ring in Pt-TThpT has already a strong donor-acceptor interaction which can be enhanced by the polymer backbone.

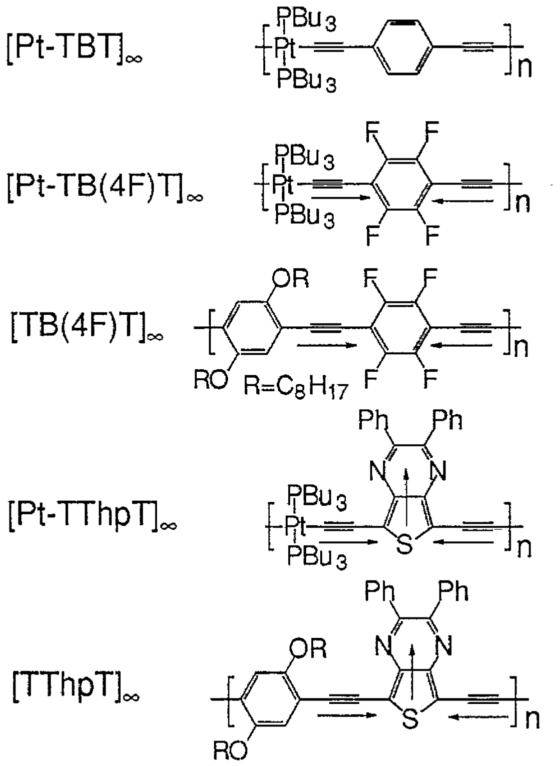

Fig. 1. The structures and abbreviations of the compounds. The arrows indicate the expected direction of electron transfer after excitation

## 4. Results

Figure 2 a-c summarises the photoluminescence and absorption spectra for the above polymers and some of their monomers. The spectra are taken at room temperature except those labelled otherwise in the figure.

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Pt-TBT (Fig. 2a) has a well-studied singlet emission (fluorescence) at 3.2 eV and a triplet emission (phosphorescence) at 2.4 eV.[1] The later shows a vibronic structure at low-temperature that is characteristic for this class of materials.[2] A redshift of about 0.4 eV in absorption from monomer to polymer indicates that the singlet extends over several repeat units, while the lack of such a shift in the triplet emission indicates a triplet state localised to less then one repeat unit.[1] Calculations show that the triplet exciton is localised between the ethynylenic units.[1]

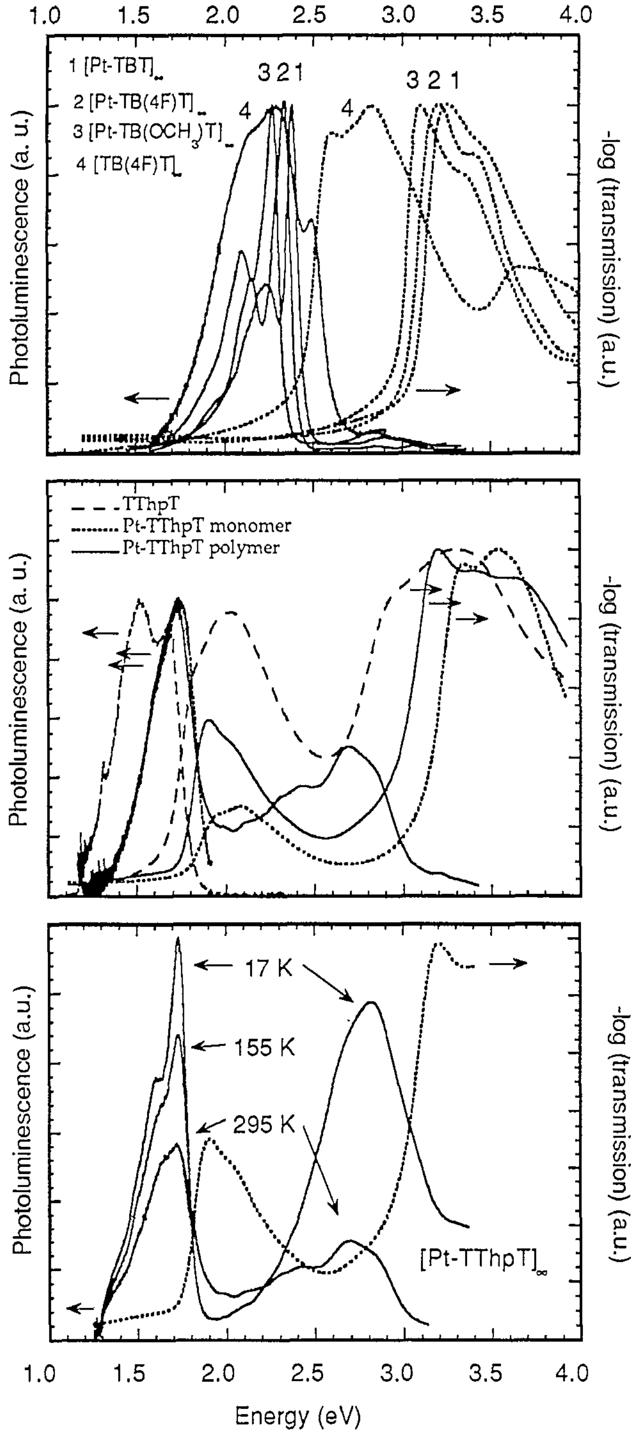

Fig. 2 a - c. Photoluminescence and absorption spectra

The effect of alkoxy or fluorine substitution of the phenyl ring on the energy of $S_0$-$S_1$ and $T_1$-$S_0$ transitions is small (Fig. 2a). Thus, there is no donor-acceptor interaction between the platinum ion and the fluorine-substituted phenyl spacer. We observed the same typical strong temperature dependence and vibronic structure[1] for Pt-TB(4F)T than for Pt-TBT, indicating an analogous localised triplet exited state as origin. Replacing the platinum ion by the alkoxy-phenylene ring lowers the optical gap by 0.5 eV (Fig. 2a).

Replacing the phenylene spacer by a thieno-pyrazine unit lowers the energy of the $S_0$-$S_1$ transition substantially from 3.2 eV to 1.7 eV compared to Pt-TBT (Fig. 2b). The lack of a energy shift in the $S_0$-$S_1$ transition between polymer and monomer indicates an singlet excited state confined to one repeat unit on the polymer, in contrast to Pt-TBT and other materials of this class [1,2]. Also unlike other Pt-poly-ynes, the low-temperature emission has no vibronic structure and only a small temperature dependence (Fig. 2c). This and the small Stokes' shift identifies the emitting state as a singlet excited state. Between 1.2 eV and 3.0 eV, we observed no emission from a triplet excited state, again in contrast to other Pt-poly-ynes. However we observe an additional high-energy emission feature centred at 2.8 eV, which we take to indicate decoupling of two emitting states. From all these results, we attribute the localised state centred at 1.9 eV to a strong donor-acceptor interaction. We consider that the donor-acceptor interaction already present in the thieno-pyrazine unit is enhanced by the polymer backbone containing the electron rich platinum ion. Replacing the platinum by alkoxy-substituted phenylene preserves this charge-transfer type transition.

When rationalising the lack of a donor-acceptor interaction obtained for the fluorine-substituted phenyl ring with the strong interaction achieved for the thieno-pyrazine unit, two points are worth considering: First, the latter is a large unit *orthogonal* to the chain so that the pyrazine ring pulls charge out of the main chain (see arrows in Fig. 1). Second, the resulting configuration in the excited state will be of a more aromatic character than the ground state. In contrast to this, the fluorine-substituted ring is *in* the chain so that charge is only redistributed along the chain. Furthermore, a charge-transfer type configuration would have to transfer the aromatic ground state into a quinoid excited state, which is less favourable.

## 5. Summary and Conclusion

The fluorine-substituted phenyl ring is too weak an acceptor to cause a donor-acceptor type interaction with the platinum ion, while the donor-acceptor interaction already present in the thieno-pyrazine unit is enhanced by the electron system in the polymer backbone. This causes a charge-transfer type transition which lowers the optical gap from 3.0 eV to 1.7 eV. The decoupling between the first and second excited state is strong enough to allow emission from the second excited state.

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