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Photophysics of Monodisperse Platinum-Acetylide Oligomers: Delocalization in the Singlet and Triplet Excited States

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Platinum-acetylide-based π-conjugated polymers and oligomers have attracted interest because their photophysics are dominated by long-lived and phosphorescent $^3\pi,\pi^*$ excited states.[1,2] This characteristic leads to materials that may be used to fabricate high-efficiency organic electroluminescent devices,[3] and for applications in laser protection.[4]

Considerable insight concerning excited-state structure and delocalization in organic π-conjugated systems has been acquired through the study of monodisperse oligomers.[5] Comparatively less information is available concerning the effect of delocalization on $^3\pi,\pi^*$ states in conjugated systems, because these states are spectroscopically "silent" due to the forbidden character of the $S_0 \leftrightarrow T_1$ transitions.

Herein we report the preparation and photophysical characterization of the series of linear Pt-acetylide oligomers (PAOs) shown in Scheme 1. PAOs with $n > 2$ luminesce from the $^1\pi,\pi^*$ and $^3\pi,\pi^*$ manifolds of the Pt-acetylide π-conjugated system, which allows us to probe in detail the effect of oligomer length on the spectroscopy, energetics, and dynamics of the long-lived excited states.

PAOs are synthesized by an iterative-convergent approach that relies on the use of Pt-acetylide building blocks in which terminal acetylenes are protected using the trimethylsilyl protecting group.[5] Complete details of the synthesis and spectral characterization of the PAOs are available as Supporting Information.

Absorption spectra of the PAOs (Figure 1a) exhibit three well-resolved bands. The spectra are dominated by an intense band (I) arising from the long-axis polarized π,π^* transition. The maximum of band I red-shifts with increasing PAO length (Table 1), but the difference in λ_{max} between **Pt-5** and **Pt-7** is small, indicating that the effective conjugation length as probed by the Franck−Condon absorption event is ~6 repeat units. The width of band I also increases with PAO length, possibly signaling the existence of conformers that differ with respect to the relative orientations of the chromophoric units (i.e., the phenylene rings and the plane defined by the PtP_2R_2 units) along the chain. Band broadening may occur because the number of different conformers increases with PAO length. Two other absorption bands (II and III) are resolved at shorter wavelengths. The intensity of these bands increases with PAO length, but their absorption maxima do not vary systematically. This observation is consistent with the notion that the high-energy bands arise from short-axis polarized transitions localized on the phenylene rings. Importantly, the spectra of the longer PAOs are very similar to the absorption of the analogous Pt-acetylide polymer,[1a,b] which indicates that the oligomers are effective models for the excited-state properties of the corresponding polymer.

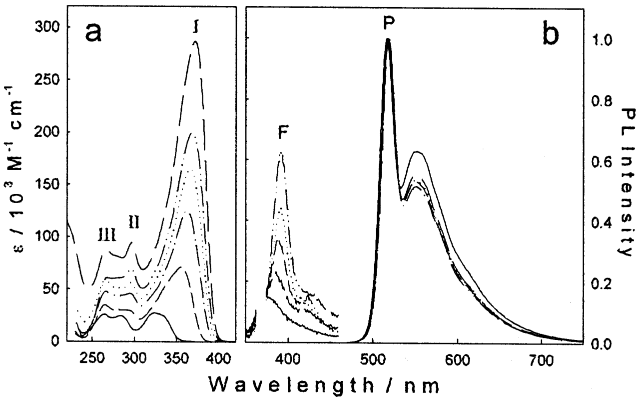
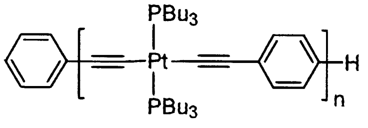


Figure 1. (a) UV−visible absorption spectra of PAOs in THF. In order of increasing intensity: **Pt-1**, **Pt-2**, **Pt-3**, **Pt-4**, **Pt-5**, **Pt-7**. (b) Photoluminescence spectra in deoxygenated THF. F is the fluorescence: in order of increasing intensity **Pt-2**, **Pt-3**, **Pt-4**, **Pt-5**, **Pt-7**. P is phosphorescence: in order of decreasing intensity in 0−1 band **Pt-2**, **Pt-3**, **Pt-4**, **Pt-5**, **Pt-7**. Note that the fluorescence intensity scale is magnified 100× as compared to phosphorescence.

Scheme 1



Pt-n (n = 1 - 5, 7)

Table 1. Photophysical Data for PAOs[a]

	UV–vis λ_{max} /nm (log ϵ)	emission/nm					
		λ_{max}^F	λ_{max}^P	ϕ_P[b]/%	τ_P /μs	k_r[c] /10^3 s^{-1}	k_{nr}[c] /10^4 s^{-1}
Pt-1	324 (4.44)						
Pt-2	355 (4.85)	374.0	515.9	5.2	17.7	2.9	5.4
Pt-3	363 (5.10)	385.5	517.3	5.8	18.4	3.2	5.1
Pt-4	367 (5.22)	389.0	517.8	6.7	18.6	3.6	5.0
Pt-5	368 (5.30)	390.6	518.2	6.6	19.3	3.4	4.8
Pt-7	371.5 (5.46)	391.0	518.2	7.1	24.2	2.9	3.8

[a] All measurements carried out in vacuum-degassed THF solutions. [b] *fac*-Ir(2-phenylpyridine)$_3$ used as the actinometer ($\phi = 0.4$). [c] $k_r = \phi_P/\tau_P$; $k_{nr} = (1 - \phi_P)/\tau_P$. Decay rate computed under the assumption that the intersystem crossing efficiency is unity.

Figure 1b illustrates the photoluminescence spectra of the series of PAOs **Pt-2**−**Pt-7** obtained in degassed THF solutions. (At room temperature, **Pt-1** is a nonemissive compound.) Each of the PAOs exhibits a very weak fluorescence band that is Stokes-shifted very little from the low-energy absorption (band I), indicating that the emission emanates from the lowest singlet state (S_1). In addition, the PAOs feature a moderately intense phosphorescence band with a maximum at ~515 nm. Table 1 lists the λ_{max} values for the fluorescence and phosphorescence bands, along with the phosphorescence quantum yield (ϕ_P), the phosphorescence lifetime (τ_P), and radiative and nonradiative decay rates (k_r and k_{nr}, respectively) for the triplet excited state.

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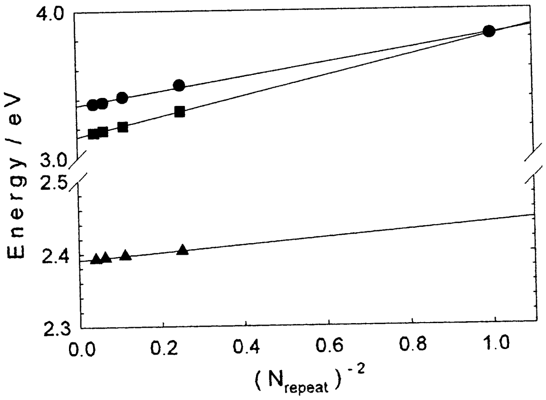

Figure 2. Plots of optical transition energies in eV versus the inverse squared number of repeat units that represents relative molecular length for each oligomer. (●) absorption; (■) fluorescence; (▲) phosphorescence. Note that the *y*-scale for the phosphorescence is expanded by a factor of 5.

The fluorescence intensity of all of the PAOs is low ($\phi_F < 10^{-3}$). This implies that intersystem crossing is extremely rapid (e.g., $k \gg 10^9\ s^{-1}$), and we conclude that the triplet yield is approximately unity. The maximum of the fluorescence band red-shifts from $n = 2$ to 5, but it levels off between $n = 5$ and 7. This trend is consistent with the trend in the absorption spectra and implies that the effective conjugation length in the relaxed singlet state (S_1) is ~6 repeat units. Additional insight concerning the effect of delocalization on S_1 is provided by the fluorescence band shape. Specifically, the electron-vibrational coupling (which decreases with increasing excited-state delocalization)[6,7] in S_1 is proportional to the ratio of the 0−1 and 0−0 vibronic bands in the fluorescence spectrum ($I_{01}{}^F/I_{00}{}^F$).[6,7] Inspection of the fluorescence spectra in Figure 1b shows that $I_{01}{}^F/I_{00}{}^F$ decreases with increasing PAO length (see the Supporting Information for an expansion of the fluorescence spectra). Interestingly, the ratio drops sharply from 0.45 to 0.2 between $n = 4$ and 5, but it is then approximately the same for $n = 5$ and 7. This observation is consistent with the trends in the absorption and fluorescence maxima, which imply that the S_1 state is delocalized over ~6 repeat units.

In contrast to the absorption and fluorescence, the phosphorescence λ_{max} shifts by only 2 nm across the PAO series. This indicates that the energy of the triplet state (T_1) is influenced little by PAO length, and it also implies that the triplet is localized on 1 or 2 repeat units. This finding is consistent with previous work which suggests that the degree of delocalization of T_1 in Pt-acetylides is considerably less than that of S_1.[1c]

Figure 2 illustrates a plot of the energies of the Franck−Condon S_1 state (estimated from $E_{max}{}^{abs}$), the relaxed S_1 state (estimated from $E_{max}{}^{flr}$), and the relaxed T_1 state (estimated from $E_{max}{}^{phos}$) versus $(N_{repeat})^{-2}$, where N_{repeat} is the number of Pt-acetylide units in the oligomer. N_{repeat} is used here because it is proportional to PAO length, and based on an analytical Hückel model, the HOMO−LUMO gap is expected to vary as (PAO length)$^{-2}$.[8] Note that all three correlations are approximately linear. In addition, the correlation shows that the energy of the relaxed S_1 state varies the most strongly with PAO length and that the singlet−triplet (S−T) splitting varies from 0.92 eV for **Pt-2** to 0.77 eV for the polymer (where the latter parameter is obtained by extrapolation of the lines to $N = \infty$). The latter value is in excellent agreement with S−T splittings estimated from studies of analogous Pt-acetylide polymers.[1f] The relatively low S−T splitting is consistent with the notion that S_1 is delocalized, while T_1 is localized.

Despite the evidence which suggests that the triplet state is strongly localized in the PAOs, several lines of evidence indicate that the properties of the triplet exciton are influenced by PAO length. First, the ratio $I_{01}{}^P/I_{00}{}^P$ decreases systematically with increasing PAO length (where I^P is phosphorescence intensity, see Figure 1b). This clearly indicates that electron-vibrational coupling in T_1 decreases with increasing PAO length, which signals that even though the triplet energy is not affected by delocalization, the triplet wave function is sensitive to oligomer length.

More quantitative information regarding the effect of PAO length on the electron-vibrational coupling in the triplet state is provided by the dependence of the nonradiative decay rate (k_{nr}) on PAO length. Interestingly, as shown in Table 1, k_{nr} decreases by more than 20% across the series **Pt-2** → **Pt-7**. Application of nonradiative decay theory under the assumption that an average high-frequency mode with $h\omega = 1300\ cm^{-1}$ is coupled to T_1 decay indicates that the observed 20% decrease in k_{nr} can be accounted for by a 5% decrease in the Huang−Rhys constant across the series.[7] (The Huang−Rhys constant is a quantitative measure of the degree of electron-vibrational coupling.[6,7])

In conclusion, a new series of PAOs has been synthesized by an iterative-convergent approach. Absorption and photoluminescence spectroscopy of the oligomers provide considerable insight into the extent of delocalization in the singlet and triplet excited states in Pt-acetylide materials.

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Supporting Information Available: Descriptions of the synthesis and spectroscopic characterization of PAOs, and the photophysical methods, figures showing expansion of fluorescence spectra, the phosphorescence decays, and calculated fits (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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